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The Effect of High Electrostatic Fields upon the Vaporization of Molybdenum*

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It has been found for wires of varying diameters, (1) that, for field strengths of about 0.52×10^6 volts/cm or less at the wire surface, there was no change in the rate of change of resistance with time and hence the rate of vaporization upon application of the field; (2) that, for field strengths above approximately 0.52×10^6 volts/cm, as successively higher fields were applied, the rate of vaporization first decreased slowly, then more rapidly, and finally asymptotically toward zero at field strengths over 1.8×10^6 volts/cm; (3) that, with increasing temperatures, the same field strength applied at the surface of a wire produced progressively smaller decreases in the rate of vaporization; (4) that, when there was an effect upon the rate of vaporization, sudden increases in resistance occurred when the field was applied, and sudden decreases when it was removed. Worthing has reported similar results for tungsten except that the sudden increases and decreases were opposite to those of platinum and molybdenum.

INTRODUCTION

THE filament of a tungsten lamp operated at its normal temperature of about 2450°K is known to decrease in cross-sectional area with time. Evidence of this change may be seen by the deposition of metal upon the sides of the lamp. This change, because of vaporization of the metal, is accompanied by an increase in resistance of the wire.

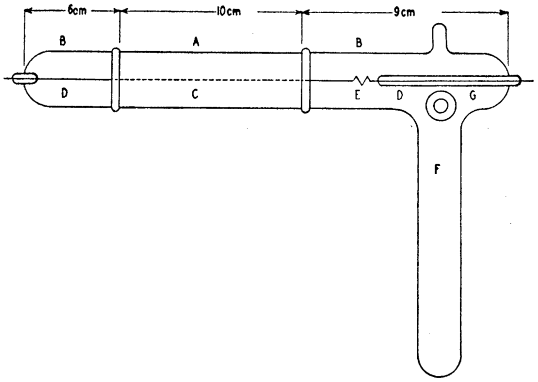

FIG. 1. Tube used for mounting molybdenum wires. *A*, copper tube, 2.8 cm I.D., walls 0.2 cm thick; *B*, Nonax glass tubing; *C*, molybdenum wire; *D*, 20-mil tungsten lead wires; *E*, small spring of 5-mil tungsten wire to provide slight tension; *F*, liquid-air tube; *G*, side tubes containing tungsten electrodes, on either side of main tube, for "cleaning up" residual gases.

In an investigation of the effects of high electrostatic fields upon the vaporization of small heated tungsten wires Worthing[1] has found that for a wire 0.020 mm in diameter, operated at 2500°K, a radial field of strength 2.7×10^6 volts per cm at the wire surface reduced the rate of increase of resistance, and hence the rate of vaporization, to 45 percent of the value without the field. He further observed that, upon applying the field, there was a sudden decrease in resistance of the wire and that, upon removing

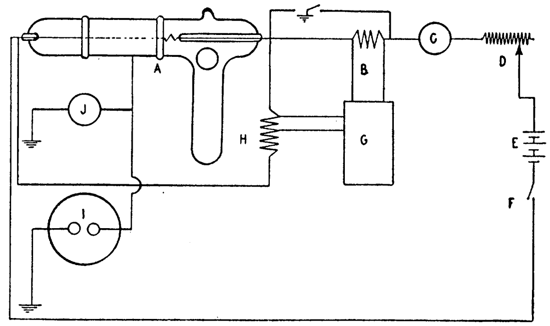

FIG. 2. Electrical arrangement for measuring the rates of vaporization of molybdenum wires. *A*, tube containing molybdenum wire; *B*, standard resistance; *C*, milliammeter; *D*, variable rheostat; *E*, storage batteries; *F*, switch; *G*, potentiometer; *H*, voltage multiplier; *I*, Wimshurst machine; *J*, electrostatic voltmeter; *K*, single pole double throw switch for grounding the circuit containing the molybdenum wire.

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* This work was carried out during the year 1931–32. Publication has been delayed because of an apparent discrepancy with data on the vaporization of molybdenum already published. Now that an explanation of this discrepancy has been found (see following paper), it is offered for publication.

** Now at the Department of Physics, University of Maryland, Baltimore, Maryland.

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

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

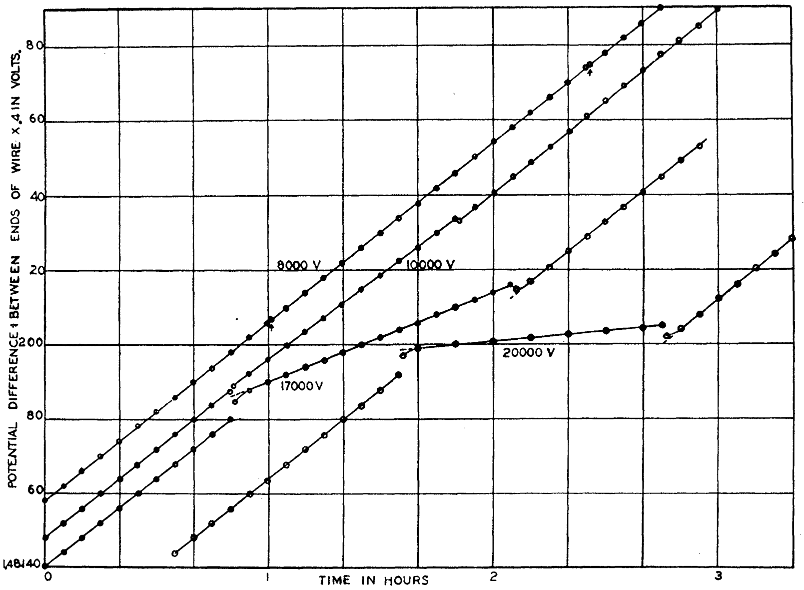

FIG. 3. Change in the rate of vaporization of a molybdenum wire ($r=0.00243$ cm, $T=1462°K$) upon application of four different electrostatic potentials. (Ordinate scales differ by a constant.)

the field, there was a sudden increase. Greibach[2] has predicted, on the basis of classical theory, that the effect of an electric field, such as used by Worthing, should be to decrease the rate of vaporization by less than one percent.

The present investigation was undertaken to obtain information on the behavior of small molybdenum wires under conditions somewhat similar to those described for tungsten. Prior to using molybdenum wires, a similar study of small platinum wires was attempted. A decrease in the rate of vaporization was observed when they were under the influence of the electric field. Contrary to the case for tungsten, a sudden increase in the resistance of the wire took place at the instant of applying the field and a decrease when the field was removed. However, the data were not consistent, probably on account of the difficulty in out-gassing the platinum; and so the work on platinum was dropped temporarily.

APPARATUS

The molybdenum used was obtained from the Cleveland Wire Works of the General Electric Company at Cleveland, Ohio, in the form of wires 0.00486 cm, 0.00684 cm, and 0.00762 cm in diameter. While no analyses of the particular samples used were available, the Cleveland Wire Works reported that analysis of powdered metal, similar to that from which the wires were made, ran 99.9 percent molybdenum. A fourth size wire used was obtained by electrolytically etching the 0.00486-cm wire to 0.00458 cm. The wires were examined under a microscope and initially found to have polished surfaces with no pits. Their diameters were determined by weighing a measured length on a microbalance. Approximately 10-cm lengths of these wires were mounted in highly evacuated tubes, as indicated in Fig. 1. During the evacuation, which took about 18 hours, the tubes were heated in a furnace at about 425°C.

Figure 2 represents the electrical arrangement for measuring the change in resistance of the wire while keeping the current constant. For convenience of measuring potential differences, a Leeds and Northrup potentiometer, modified to operate as a limited double potentiometer, as described by Worthing and Forsythe,[3] was used. The electrostatic potential difference was measured by means of an electrostatic voltmeter as described by Shrader.[4]

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[3] A. G. Worthing and W. E. Forsythe, J. Opt. Soc. Am. **10**, 599 (1925).

[4] J. E. Shrader, J. Opt. Soc. Am. **6**, 273 (1922).

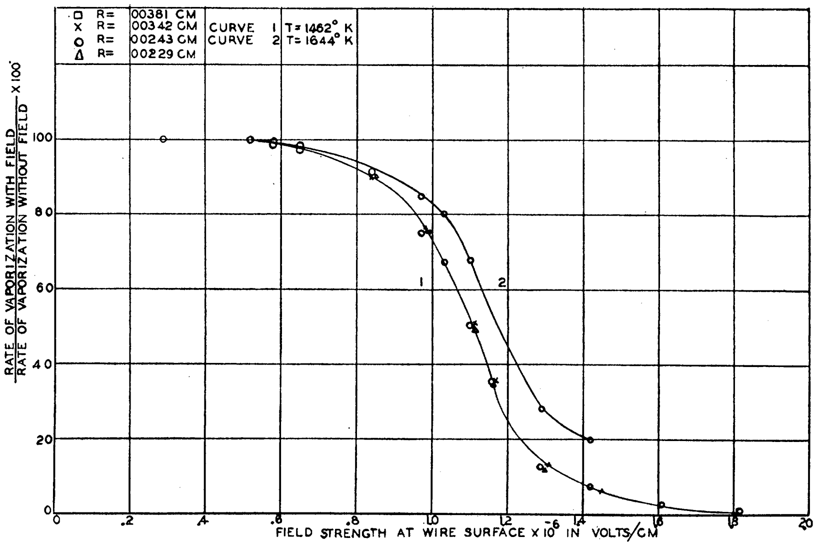

FIG. 4. Variation in the rate of vaporization of molybdenum wires with electrostatic field strength applied at the surface of the wires.

PROCEDURE AND RESULTS

Before making the initial run on any sample, the wire in the tube was first aged for a period of several hours, at a temperature above 2000°K, and then run at the desired temperature for approximately two hours, or until conditions became steady. Following this, by repeated adjustments, the current in the wire was kept constant to about one part in 200,000 and differences in potential between the ends of the wire measured every five minutes. By use of the limited double potentiometer mentioned above, it was possible, once adjustments were made, by merely throwing a single switch, to change directly from the current balance to the potential balance without disturbing the galvanometer. Thus the two measurements could be made in rapid succession, a condition essential in this work.

Figure 3 contains a typical set of curves showing the changes in the rates of increase of voltage with time, for a wire 0.00486 cm in diameter operated at an average temperature of about 1462°K, upon the application of several high potentials between the cylinder and the wire. To obtain a single curve, three steps are necessary. Consider the curve for 17,000 volts. After the preliminary heating, the wire was operated at constant current for a period of 50 min., with a potential of 45 volts only between the wire and the cylinder, to eliminate thermionic emission effects. During this time, the potential difference between the ends of the wire was found to increase regularly, so that when voltage was plotted against time, the slope of the curve, that is, the rate of increase of potential difference, was constant, and in this instance had a value 8.00

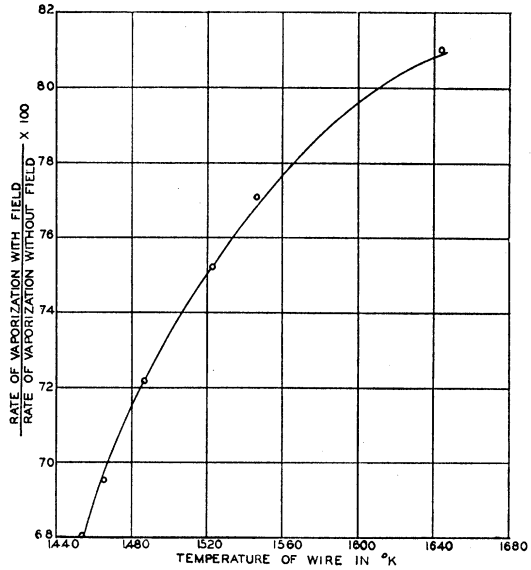

FIG. 5. Relative change of vaporization rate of a molybdenum wire ($r=0.00243$ cm) with temperature. Electrostatic field 1.03×10^6 volts/cm.

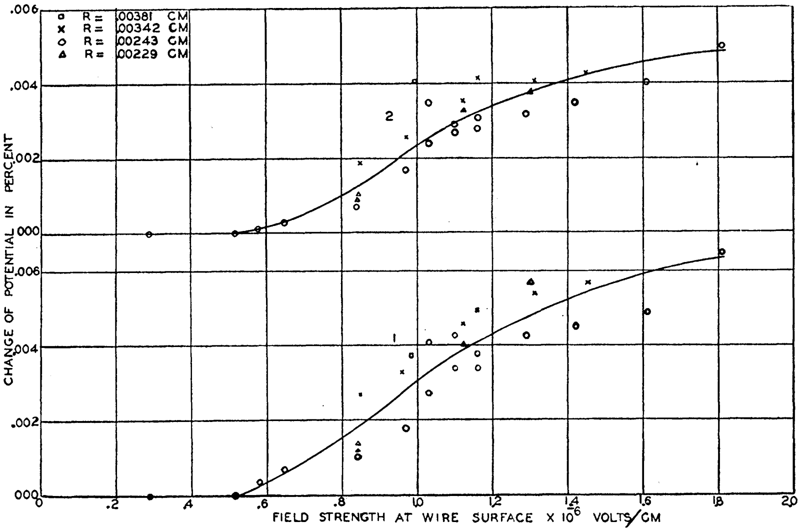

FIG. 6. Sudden changes in potential difference between the ends of molybdenum wires upon application and removal of high electrostatic fields.

$\times 10^{-6}$ volt per min. The 45-volt potential difference then was changed suddenly to 17,000 volts and the changes in potential drop along the wire followed for one hour and 15 min., the rate being 4.00×10^{-6} volt per min. Finally the high potential was removed, the 45 volts reapplied, and again changes in potential drop along the wire were followed for 50 min. The slope of the curve returned to 8.00×10^{-6} volt per min. In many cases, this procedure was continued through two more steps, making five in all. Since in each run the current was kept constant, the slope of the curve is proportional to the rate of change of resistance of the wire. Now as a wire evaporates, its cross-sectional area diminishes; and, since this varies inversely with resistance, a change in the rate of increase of resistance is interpreted as a change in the rate of vaporization. As appears later in the discussion, there is a disturbing factor in this interpretation.

The slopes of the curves before and after the application of the high potentials were always the same for any one run. For the runs graphed in Fig. 3, the application of a potential of 8000 volts resulted in no change of slope. A slight change of slope was observed for 10,000 volts, more of a change for 17,000 volts, and for 20,000 volts the curve became almost horizontal. In addition, for all potentials above 8000 volts, a sudden increase in potential difference between the ends of the wire was observed when the high potential was applied, and a decrease, though not quite so great in magnitude, when it was removed.

Similar runs to those just described were made on the same wire with other high potentials and at other temperatures, and on other wires of different diameters. Curve 1 of Fig. 4 is a composite curve showing the results obtained from four sizes of wire operated at about 1462°K. In this curve, the percentage variation in the rate of vaporization is plotted against field strength at the wire surface. For reasons appearing later under "Discussion," field strength has been chosen as abscissas rather than potentials. As is evident from the curve, for a given field strength, the change in rate of vaporization is independent of the size of the wire. No change of rate of vaporization was found for field strengths of 0.52×10^{6} volts per cm or less. However, for increasing field strengths above this value, the rates of vaporization, upon applying the field, decreased, at first slowly, then more rapidly, and finally asymptotically toward zero at field strengths above 1.8×10^{6} volts per cm. Curve 2 shows similar results for an average temperature of 1644°K. As for 1462°K, no change was found for field strengths of 0.52×10^{6} volts per cm or less. At higher field strengths, the vaporization rates are higher for the higher temperature.

Figure 5 represents the variation of the rate of vaporization for the 0.00486-cm wire with temperature, the field in all cases being the same. Again, the higher the temperature of the wire, the less the field decreases the vaporization rate.

In Fig. 6, curve 1, the sudden increase in resistance of the wire upon application of a field is plotted against field strength at the wire surface, and in curve 2, the sudden decrease upon removing the field. The values in the former case are somewhat larger than those in the latter. Both curves, however, have similar shapes. In neither case was an effect observed for field strengths of 0.52×10^6 volts per cm or less.

To determine whether or not the change in resistance could be ascribed to vaporization, approximately 20-cm lengths of the wires were mounted in tubes and operated for 50 hours or more at an average temperature of 1462°K, the average temperature used in most of the runs just described. From the weights of a measured length of wire before and after the prolonged heating, the amount of metal vaporized was calculated and compared with that expected from the resistance changes in the runs on the wire from which the data of Fig. 3 were obtained. For a 0.00486-cm wire, which had first been aged at a temperature above 2000°K for about an hour and then weighed and put in operation, the ratio of the loss in weight of the wire to its original weight was 0.0253, while for the same sized wire for which resistance variations were followed the rate of change of resistance (dR/dt) was 114.3×10^{-6} ohm per min. In this latter case, the average value of $(1/R)(dR/dt)$ was 6.16×10^{-6} min.$^{-1}$, and the value of $(1/R)(dR/dt)t$ was 0.0211, where t is the total time of operation of the wire. On the assumption of no pitting or roughening of the surface during operation, this value is subject to a correction for change in temperature. This is necessary to give the fractional change in resistance had the initial and final resistance measurements been made at the same temperature. When thus corrected, a value of 0.0147 is obtained. (See Appendix.) If one considers the uncertainties resulting from (1) the difficulty in obtaining small differences in weight with a microbalance (the difference was 0.068 mg), (2) the end losses (the vaporization rate was less at the cooled ends of the wire than at the center), (3) the slight roughening of the surface of the wire with operation (the roughening of a surface by increasing the radiating area cuts down the increase in temperature which normally follows operation of such a wire on constant current), and (4) the possible decrease in resistivity, or in radiancy, or both (this follows a decrease in V^3I, which Worrell[5] has shown to be true for a molybdenum wire mounted in a highly evacuated tube), the ratio 0.0253 seems not inconsistent with the ratio 0.0147, and it seems reasonable to attribute the change in resistance to vaporization.

It is interesting to compare the rate of vaporization which may be obtained from the above with that reported by Langmuir and Mackay.[6] They give for molybdenum the following expression:

$$\log m = 17.11 - 38600/T - 1.76 \log T,$$

where m is the rate of vaporization in g/(cm^2 sec.), and T the temperature in °K. On the scale of temperature used by Langmuir and Mackay, 1462°K becomes 1443°K. Substituting this temperature in the formula, one obtains a value of 6.31×10^{-17} g/(cm^2 sec.) for m. The value obtained from the above run is 1.36×10^{-9} g/(cm^2 sec.). This difference is discussed in the following paper by Reid.

DISCUSSION

To account for the decrease in the rate of vaporization of the various sizes of wire with the application of a strong electrostatic field, it may be assumed that the atoms which have left the surface of the wire in a high electrostatic field become dipoles and that many of them are forced back by the field to the surface of the wire where the field is strongest. Consider a dipole of length l and charge e in a radial field of strength R between two concentric cylinders, the inner cylinder having a radius a, and the outer cylinder a radius b.

$+e \quad -e$

$\cdot \leftarrow l \rightarrow \cdot$

$\leftarrow r \rightarrow$ to positively charged wire.

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[5] F. T. Worrell, Phys. Rev. **61**, 520 (1942).

[6] I. Langmuir and G. M. J. Mackay, Phys. Rev. **4**, 377 (1914).

The force on the dipole is accordingly

$$F=[R+\tfrac{1}{2}l(\partial R/\partial r)]e-[R-\tfrac{1}{2}l(\partial R/\partial r)]e$$
$$=le(\partial R/\partial r).$$

Let us assume, as is usually done, that the dipole moment le is related to the field strength R, thus

$$\alpha R=le,$$

where α is the polarizibility. Now the work done by a vaporized atom at the expense of its kinetic energy against the field in moving from the wire to the cylinder is

$$W=\int_a^b Fdr,$$

or substituting the above values, we have

$$W=\int_a^b le(\partial R/\partial r)dr=\alpha\int_a^b R(\partial R/\partial r)dr.$$

Substituting for R and $\partial R/\partial r$ the values

$$R=-V_b/r\ln(b/a)$$

and

$$\partial R/\partial r=(1/r^2)[V_b/\ln(b/a)],$$

where V_b is the potential at the outer cylinder, the inner cylinder being grounded, we obtain

$$W=\frac{-\alpha V_b^2}{\left(\ln\dfrac{b}{a}\right)^2}\int_a^b\frac{dr}{r^3}=\frac{\alpha V_b^2}{2\left(\ln\dfrac{b}{a}\right)^2}\left[\frac{1}{b^2}-\frac{1}{a^2}\right].$$

To produce equal decreases in the rates of vaporization for two wires of different radii, at the same temperature and placed concentrically in cylinders of the same size, requires the same work per dipole for the transfer from a to b. Thus, where W_1 is the work in the case of a wire of radius a_1, and W_2 the work for the same effect upon the rate of vaporization in case of a wire of radius a_2,

$$\frac{W_1}{W_2}=1=\frac{V_{b1}[\ln(b_2/a_2)][(1/a_1^2)-(1/b_1^2)]^{\frac{1}{2}}}{V_{b2}[\ln(b_1/a_1)][(1/a_2^2)-(1/b_2^2)]^{\frac{1}{2}}}.$$

Neglecting the b^2 term since b is large compared with a, it follows that

$$W_1/W_2=R_{a1}/R_{a2}=1,$$

where R_{a1} is the field strength at the surface of the wire of radius a_1, and R_{a2} that for a wire of radius a_2. Hence for equal field strengths at the surfaces of the wires, equal decreases in the rates of vaporization are expected. This is in accord with Fig. 4. It is to be noted that though the rate of vaporization is proportional to the field strengths, the existence of a dR/dr is the characteristic of the field which produces the change.

In the case of the sudden increase in resistance observed when the field was applied, or decrease when it was removed, it was first thought that this might result from a current between the wire and the surrounding cylinder due to either a positive ion current from the wire or a leakage current over the surface of the glass. To test for such a current, the effect of switching the ground connection from one terminal of the standard resistance B, Fig. 2, to the other was investigated. No indication of such a current was found. If a current had been present, due to its inclusion or exclusion from that passing through the standard resistance, it would have been detected in the potential measurements. While potential differences could be read to about one part in 200,000 and a sudden increase in resistance caused a change of as much as one part in 10,000, the change in the ground connection never produced any detectable effect. Further, since the introduction of grounded guard rings did not alter the sudden increase and decrease of resistance, the possibility of leakage currents seemed excluded. Again since a positive ion current, if present, would be expected at fields lower than that which just produced the sudden changes in resistance, the possibility of such a current being present seemed likewise excluded.

As mentioned above, there is a disturbing factor in the interpretation of the rate of increase of resistance as proportional to the rate of vaporization. It is the difference in the sudden changes of resistance when applying and removing the electric field. During a run of three steps, as described earlier, the total change in resistance is not equal to the sum of those occurring during the individual steps, the difference being that between the two sudden changes.

Increases and decreases of resistance in the same direction were observed for platinum, but for tungsten Worthing reported opposite changes.

These changes are further discussed in the following paper.

APPENDIX. CORRECTION OF OBSERVED $(1/R)(dR/dt)$ FOR CHANGE IN TEMPERATURE

Consider the resistance of an electrically heated wire in vacuum as a function of its temperature T, and its radius r, thus

$$R=f(T, r).$$

As the wire evaporates, its resistance changes with time t, and

$$dR/dt=(\partial R/\partial T)_r(dT/dt)+(\partial R/\partial r)_T(dr/dt). \tag{1}$$

Let

$$[(\partial R/R)/(\partial T/T)_r]=(T/R)(\partial R/\partial T)_r=\beta.$$

Multiplying (1) by $(1/R)$ and substituting, we obtain

$$\frac{1}{R}\frac{dR}{dt}=\frac{\beta}{T}\frac{dT}{dt}-\frac{2}{r}\frac{dr}{dt}=\frac{\beta d(\ln T)}{dt}-2\frac{d(\ln r)}{dt}. \tag{2}$$

Now the energy dissipated from a wire of length l, carrying a current I, is

$$I^2R=\rho lI^2/\pi r^2=2\pi rl\mathcal{R} \tag{3}$$

where ρ is the resistivity, and $\mathcal{R}$ the radiancy expressed in watts/cm². Then

$$\rho/\mathcal{R}=2\pi^2r^3/I^2=(\rho_0/\mathcal{R}_0)(T/T_0)^{(\beta-x)}, \tag{4}$$

where $\rho=\rho_0(T/T_0)^\beta$; $\mathcal{R}=\mathcal{R}_0(T/T_0)^x$ and ρ_0 and $\mathcal{R}_0$ are fixed values at T_0. The terms β and x are taken as constant values for the small interval of temperature considered. From (4)

$$r^3=[(I^2/2\pi^2)(\rho_0/\mathcal{R}_0)](T/T_0)^{(\beta-x)} \tag{5}$$

and

$$d(\ln r)/dt=(\beta-x/3)[d(\ln T)/dt]. \tag{6}$$

Substitution in (2) gives

$$1/R(dR/dt)=[\beta-\tfrac{2}{3}(\beta-x)](1/T)(dT/dt). \tag{7}$$

For $(T/R)(\partial R/\partial T)_r=\beta$, and for $(T/\mathcal{R})(\partial\mathcal{R}/\partial T)_r=x$, at 1466°K, Worthing[7] gives, for molybdenum, 1.145 and 5.14, respectively. Substitution in (7) and multiplication by t gives

$$(1/R)(dR/dt)t=3.80(1/T)(dT/dt)t. \tag{8}$$

Since for the region considered (dR/dt) and (dT/dt) are constant, except for minor fluctuations, we may replace $(1/R)(dR/dt)t$ and $(1/T)(dT/dt)t$ by $\Delta R/R$ and $\Delta T/T$ where ΔR and ΔT are the changes in R and T during the interval t.

For the run described in "Procedure and Results,"

$$(t/R)(dR/dt)=(\Delta R/R)_0=0.0211, \tag{9}$$

the observed value which is to be corrected for variation in temperature during the run to give the fractional changes in resistance had the initial and final resistance measurements been made at the same temperatures.

Substitution of the value 0.0211 in (8) gives $\Delta T/T=0.0056$. From this it follows that the average temperature is equal to the final observed temperature times $[1-\frac{1}{2}(\Delta T/T)]$, and in this case the final observed temperature of 1466°K yields an average temperature of 1462°K.

Upon applying this correction to $(\Delta R/R)_0$, the corrected value $(\Delta R/R)$ becomes

$$(\Delta R/R)_c=\frac{R_b(1-0.0028\beta)-R_0(1+0.0028\beta)}{\frac{1}{2}(R_b+R_0)}, \tag{10}$$

where R_b is the final resistance and R_0 the initial resistance of the wire. Substitution in (10) yields for $\Delta R/R$ (corrected for temperature variation during the run) 0.0147 in place of the uncorrected value 0.0211.

The writer wishes to express his indebtedness to Dr. A. G. Worthing, who suggested this problem, for his help and encouragement during the course of the work.

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[7] A. G. Worthing, Phys. Rev. **28**, 190 (1926).