The V^3I Relation for Vaporizing Molybdenum†

FRANCIS T. WORRELL*
University of Pittsburgh, Pittsburgh, Pennsylvania
(Received February 2, 1942)

If a cylindrical filament of circular cross section, whose radiancy and resistivity are functions of temperature only, be maintained at a constant and uniform temperature in vacuum by electrical heating alone, and it vaporizes uniformly, the product of the current by the cube of the voltage drop across the filament will be a constant. In order to test this for filaments under ordinary experimental conditions, voltage and current measurements have been made on well-aged Mo filaments which have been maintained in vacuum of the order of 2 to 5×10^{-8} mm Hg at a constant brightness temperature till they burned out. It was found that V^3I decreased rather uniformly with time of operation for each of the four filaments tested. For 500 minutes of operation at 2250°K the percentage decreases found for V^3I ranged from 0.49 percent to 0.85 percent, corresponding to temperature changes ranging from 7.5°K to 13°K. Possible changes in electrical and radiation properties of the filaments, and their effect on V^3I, are discussed.

INTRODUCTION

THE V^3I relation may be stated as follows: If a uniform cylindrical wire in vacuum be maintained at a constant and uniform temperature by electrical heating alone, then, regardless of changes in the diameter of the wire owing to uniform vaporization, the product V^3I remains constant, where I is the current in the wire and V is the voltage drop along this wire. It is assumed here that the electrical and radiation properties of the wire do not change with time. This relation has been used by Langmuir,[1] who first derived it, Langmuir and Mackay,[2] Langmuir and Malter,[3] and probably others, as a means of maintaining the temperature of a filament at a constant value.

Some data obtained by Worthing (unpublished) and by Norris[4] indicate that this relation does not hold. Norris, using molybdenum in sealed-off lamps, found that for filaments electrically heated in vacuum the temperature did not stay constant when V^3I was held constant. He found instead that roughly a constant temperature-constant current relation held.

The V^3I relation can be derived rather simply. Consider a solid filament of circular cross section of diameter $2r$, length L, and resistivity ρ. Let this filament be electrically heated in vacuum to a constant and uniform temperature. If the potential difference between the ends of the filament be V, and the current through the filament I, then

$$V/I=R=\rho L/\pi r^2. \quad (1)$$

Under the conditions specified, since there are no

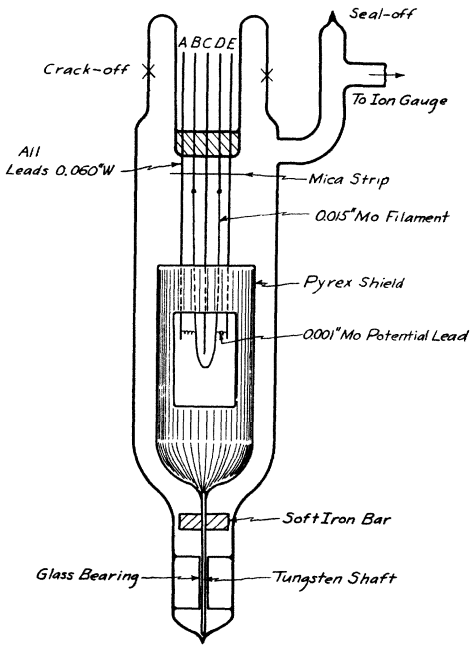

FIG. 1. Diagram of the experimental tube.

† Submitted to the Graduate School of the University of Pittsburgh in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

* Now at the Department of Physics, University of Tennessee, Knoxville, Tennessee.

[1] I. Langmuir, Phys. Rev. **2**, 329 (1913).

[2] I. Langmuir and G. M. J. Mackay, Phys. Rev. **4**, 379 (1913).

[3] D. B. Langmuir and L. Malter, Phys. Rev. **55**, 748 (1939).

[4] L. H. Norris, M. S. Thesis, University of Pittsburgh, 1933.

conduction or convection losses, all the energy supplied electrically is given off as radiation. Thus we may also say

$$VI = \mathfrak{R} 2\pi r L, \tag{2}$$

$\mathfrak{R}$ being the radiancy of the wire, expressible, for instance, in watts/cm². To be strictly correct one should add to the right side of (2) a term which represents the energy per unit time required to vaporize the molybdenum. However, at the temperature at which measurements were taken this can be neglected. If we square (2) and multiply by (1) we get

$$V^3I = 4\pi L^3 \rho \mathfrak{R}^2. \tag{3}$$

If we assume that the radiancy and resistivity are functions of the temperature alone, then, at constant temperature, the right side of (3) is constant, and, therefore V^3I is constant. Note that r does not appear in the equation. This relation, therefore, is independent of the filament diameter, and can be used as a criterion of temperature constancy for a vaporizing filament, under the above conditions.

APPARATUS

The experimental tube is shown in Fig. 1. There were five leads through the top. Leads B and D supported the filament. The lower ends of leads A and E were connected to the filament by fine wire potential leads. In operation lead C was at about -200 volts with respect to the filament. This served to stop electron emission from the filament.

The mica strip, which was anchored to leads B and C, prevented the deposition of vaporized molybdenum on the support for the leads, thus avoiding trouble from leakage currents between the various leads.

The glass shield inside the tube could be rotated by placing a U-magnet outside the tube close to the soft iron bar, and rotating it. This shield had two holes oppositely placed through which the pyrometer could be sighted on the filament in the tube. When measurements were not being taken, and the filament was at a higher temperature, the portion of the tube wall through which readings were taken was protected from vaporizing molybdenum by having the shield rotated to a position 90° away from the former one.

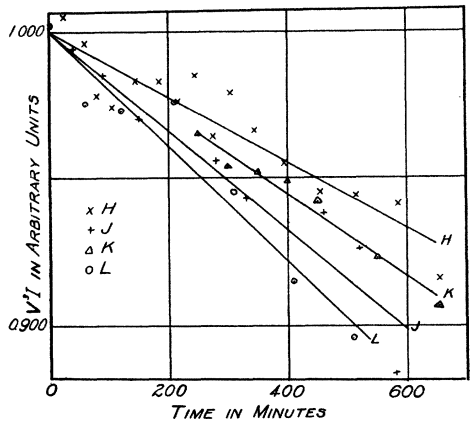

FIG. 2. Variation of V^3I with time of operation at 2250°K for four filaments. All values of V^3I are expressed as percentages of an early value.

Temperature measurements were made with a laboratory-built, disappearing-filament optical pyrometer.[5] The calibration of Stephens[6] was used.

Current and voltage measurements were made with a type K potentiometer modified[7] to a limited double potentiometer with one branch a deflection instrument. This feature allowed the rapid measurement of two quantities in succession without changing the position of the drum.

PROCEDURE

Preparation of the Tube

The 0.015″ molybdenum filament, which had previously been polished, was arc-welded to leads B and D, as shown in Fig. 1. Potential leads of 0.001″ molybdenum were tied to the lower ends of leads A and E and to selected points on the filament. The contacts where the leads were tied were improved by discharging through the potential leads a 0.02-μf condenser charged to 110 volts. Since the potential leads were small in diameter compared with the filament, the temperature drop because of conduction losses was negligible; so the section of the filament between them was essentially at a uniform temperature.

After mounting the internal structure the tube was sealed along the line marked X–X (Fig. 1), and sealed to the pump. The tube was then

[5] 1919 Report of Standards Committee on Pyrometry, J. Opt. Soc. Am. **4**, 305 (1920).
[6] R. E. Stephens, J. Opt. Soc. Am. **29**, 158 (1939).
[7] A. G. Worthing, J. Opt. Soc. Am. **10**, 599 (1925).

baked at 500°C for about 50 hours, and the filament outgassed by passing an electric current through it. No attempt was made to outgas the other metal parts. After the pressure had gone below 5×10^{-8} mm Hg the filament was aged for 5 minutes at 2450°K. Then, with the filament at a lower incandescent temperature, and after a preliminary warming of the pumping line, the tube was sealed off. The pressure in any one tube remained constant after sealing, and varied among the different tubes from 2×10^{-8} mm Hg to 5×10^{-8} mm Hg, as measured by an ion gauge.

Taking the Readings

The filament was heated to 1500°K. Readings were taken of the current I, voltage drop between the potential leads V, and voltage drop across the entire filament V', measured between two points immediately outside the tube. The temperature of the filament was then raised to a value determined by the heating current, $I'=2.20I$, where I is the previously determined current. This corresponded to a temperature of 2250°K. After the filament had been at the higher temperature for a period ranging from 60 to 100 minutes the temperature was again lowered to 1500°K, and readings were taken. This procedure was continued till the filament burned out.

A.c. was used to heat the filament to the higher temperature, since d.c. heating results in a wavy filament surface.[8]

At the beginning and ending of the run on each filament the transmission of the tube wall was measured to find what blackening may have occurred. This was done by forming inside the tube an image of the filament of an auxiliary lamp, and measuring the brightness of this image with and without the tube in position. The ratio of the first brightness to the second is the square of the transmission. If any change in the transmission of the wall occurred it was assumed to be linear with time, and a corresponding correction was applied to the values of V^3I.

RESULTS

The variation of V^3I with time of operation at 2250°K for four filaments, H, J, L, and K, is shown in Fig. 2. For comparison purposes the values of V^3I for each filament are expressed as percentages of that for an early reading. It is seen that in the first 500 minutes of operation the decrease in V^3I is 5.6 percent for filament H, 8.4 percent for J, 9.8 percent for L, and 6.9 percent for K. From some data by Worthing[9] on molybdenum we may show that, at 1500°K,

$$d(V^3I)/V^3I=11.5dT/T. \qquad (4)$$

This means that the above-mentioned changes in V^3I correspond to changes in temperature of about 0.49 percent, 0.73 percent, 0.85 percent, and 0.60 percent, respectively, or about 7.5°K, 11.0°K, 13°K, and 9.0°K, respectively, at 1500°K.

It can be seen that the data for filament K are the best; individual readings deviate on the average about 0.4°K from the curve. For filament H the deviation is about 0.6°K. The values for filament L are moderately consistent; those for J are so scattered as to be not very reliable, though they show the same trend as the others.

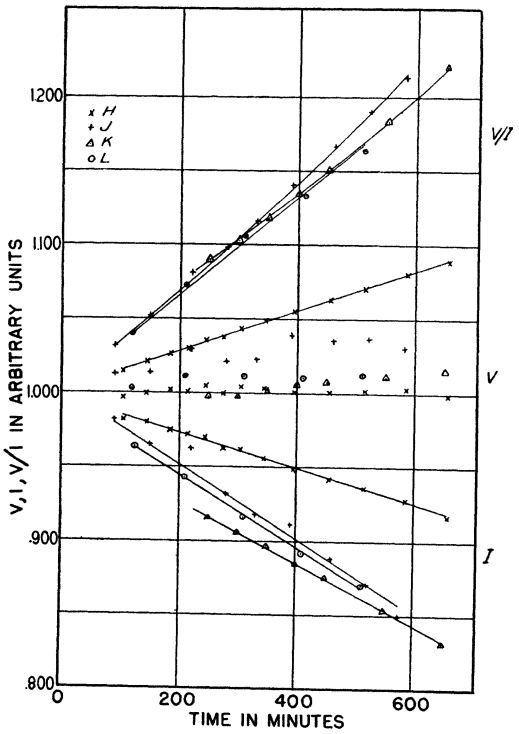

FIG. 3. Variation of V, I, and V/I with time of operation for the four filaments. V, I, and V/I are expressed as percentages of an early value.

[8] R. P. Johnson, Phys. Rev. **54**, 459 (1938).

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

The relative variations of V, I, and V/I with time for the same filaments are shown in Fig. 3. The curves for filaments J, K, and L appear to agree well with one another, but not with those for H. The values of V scatter more for J and L than for H and K.

A limit is imposed on the certainty of the values of V^3I by the fluctuations in V, for which possibly unsatisfactory potential lead contacts are to blame.

DISCUSSION

The data show definitely that V^3I does not remain constant, but decreases with time. The theoretically necessary conditions for constancy of V^3I are constancy of temperature with time, uniformity of temperature along the wire, good vacuum conditions, a wire of circular cross section, and dependence of resistivity and radiancy on temperature only. With the possible exception of the dependence of resistivity and radiancy on temperature only, these conditions were apparently satisfied. Within the range of pressures used in the tube for various filaments the change in V^3I did not appear to depend on vacuum conditions.

It is seen from Eq. (1) that a decrease in V^3I could be caused by a decrease in resistivity, a decrease in radiancy, or both. If there were a decrease in resistivity it might result from some change in the internal structure of the material. Such a decrease is known to take place during aging.[10] The initial effect of aging is to remove strains and change the wire structure from a fibrous one to a granular one. Later, the effect is probably to cause grain growth and changes in the surface. The later aging takes a much longer time than the initial aging, and during this period the resistivity decreases. After aging is completed no change in resistivity is to be expected.

The resistivity of the wire would decrease if some impurity originally present in the wire were removed by vaporization as time went on. The principal impurity in the wire was iron, amounting to 0.005 percent. It does not seem likely that 0.005 percent of iron dissolved in molybdenum would cause the resistivity change of the order of 10 percent needed to cause a 10 percent change in V^3I. The slopes at zero composition of resistivity-composition curves seem to be an order of magnitude less than this.

Radiancy is also affected by changes in internal structure,[10] and, in addition, by surface changes. All that can be said about the surface conditions is this: Each filament was polished before using, till its surface, when examined under a microscope, appeared smooth, except for a few residual die marks. The surfaces were still smooth after the filaments had burned out. It is still possible, however, for sufficient surface changes to have taken place to cause variations in radiancy large enough to account for the observed changes in V^3I.

An inspection of Figs. 2 and 3 will show that the filaments do not agree with one another. From Figs. 2 and 3 we see that, compared with J, K, and L, V^3I and I in filament H decreased less rapidly, and V and V/I increased less rapidly. Filament H was possibly operated at a lower temperature than the others, though a consideration of the operating conditions does not make this seem plausible. Since the higher temperature of operation of each filament was determined by the current, which was a constant multiple of the current corresponding to a temperature of 1500°K, and since the latter temperature was determined by a pyrometer, it would appear that filament H could have been at a lower temperature than the others only if it had a higher emissivity. It is not obvious why this should happen.

Filament H was apparently not aged to the extent that the others were. This appears to be the reason for an initial rapid decrease in V^3I with a sudden leveling off afterwards to a straight-line variation of smaller slope. This initial rapid decrease in V^3I does not appear on the graph in Fig. 2, because in plotting the data for H the time axis was moved so that time started after the change in slope of the curve. Because the higher operating temperature was determined by the current, and the aging temperature was taken too low to produce sufficient aging, it happened that the chosen operating temperature was higher than the aging temperature. Whitney,[11] while measuring the emissivity

[10] I. Langmuir and J. B. Taylor, Phys. Rev. **50**, 78 (1936), footnote.

[11] L. V. Whitney, Phys. Rev. **48**, 458 (1935).

of molybdenum, found that when molybdenum which had been heated to a certain temperature was raised to a higher temperature its emissivity immediately dropped, then gradually rose to its original value. If the emissivity of filament H were rising during this early period, and, therefore, its temperature at constant brightness were dropping, one would indeed have a rather rapid decrease in V^3I until the emissivity reached its final value. This does not explain, however, why the various curves for H should differ from the corresponding curves for the other filaments.

In conclusion, the data show that there is a definite decrease in V^3I with time, though quantitatively the results obtained from the various filaments do not agree. No explanation has been found for the differences between the various filaments on the basis of the available data. It would seem necessary, in view of the results, to reconsider previous work in which constancy of V^3I was assumed.

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. He also wishes to thank his colleagues for the help they have rendered at various times. Special thanks are due Dr. David Halliday and Dr. Charles S. Smith, for helpful discussions. The analysis of the wire used in the filaments was supplied by Mr. A. Poritsky, of the Cleveland Wire Works of the General Electric Company.

APRIL 1 AND 15, 1942 PHYSICAL REVIEW VOLUME 61

On the Calculation of the Distribution Function

C. W. UFFORD, *Allegheny College, Meadville, Pennsylvania*

AND

E. P. WIGNER, *Princeton University, Princeton, New Jersey*

(Received January 22, 1942)

The distribution function for particles confined to a large circle is found for a repulsive potential of long range. The distribution function is calculated exactly from the Boltzmann-Gibbs equation, and compared with the solution of an implicit equation of the type used by Debye and Hückel in the theory of electrolytes. The solution of the Debye-Hückel equation agrees, for our particular potential, only fairly well with the exact distribution function.

I.

ALTHOUGH the problem of classical statistical mechanics is, in principle, solved by the Boltzman-Gibbs equation

$$P(x_1, y_1, z_1, \cdots x_n, y_n, z_n)dx_1\cdots dz_n = \exp(-\beta V)dx_1\cdots dz_n \quad (1)$$

for the probability of the configuration characterized by the rectangular coordinates x_1, y_1, z_1, $\cdots$, x_n, y_n, z_n, the answering of questions of immediate physical interest meets, in most cases, serious mathematical difficulties. In (1), $\beta=1/kT$ and V is the potential energy

$$V=\sum_{i<k} v(|r_i-r_k|), \quad (1a)$$

which we shall assume to be the sum of interactions between pairs.

Many of the quantities of immediate physical importance depend on the distribution function $g(r)$, i.e., on the probability of a distance r between, say, the particles 1 and 2. This is given by

$$g(|r_1-r_2|)=\text{const.}\int\cdots\int \exp(-\beta V) \times dx_3dy_3dz_3\cdots dx_ndy_ndz_n. \quad (2)$$

However, one can evaluate (2) easily only in the case of dilute matter, i.e., gases. For condensed material, the integrations in (2) are so difficult that indirect methods had to be devised for the