A New Method for Determining the Thermionic Work Functions of Metals and Its Application to Nickel

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A new procedure for determining thermionic work functions of metals has been developed. The metal sample is in the form of an approximate sphere and is heated by electron bombardment from an auxiliary filament which is disconnected when measurements are made. Electron emission from the cooling sample charges a condenser which, at predetermined times, is discharged through a ballistic galvanometer. Temperatures are determined by a Pt, Pt+10 percent Rh thermocouple spot-welded to the sample. The thermionic constants are obtained from the equation: $\log_{10}(T^2/SQ)=\log_{10}(2.3/aA)+\Phi/(1.988\times10^{-4}T)$ where Q is the quantity of charge yet to flow upon cooling the sample from a given temperature to absolute zero and $-S$ is the slope of the $\log Q$ *vs.* time curve. This equation is derived from Richardson's. The values of the thermionic constants obtained by applying this method to the case of thoroughly outgassed nickel are found to be $\Phi=5.03\pm0.05$ volts and $A=1.38\times10^3$ amp./cm^2 deg.^{2}.

INTRODUCTION

THE usual method for determining the thermionic constants of a metal depends upon heating the sample by passing an electric current through it. Generally, the specimen is in wire or strip form and, since a uniform temperature of the emitting surface is essential, it is necessary that the cross section of the sample be uniform at the start and remain so throughout the experiment. It is not possible to treat many substances by this method, due, in some instances, to their rapid evaporation during the outgassing process and, in others, to the fact that they cannot conveniently be made into a wire or strip form. The method here described eliminates these difficulties by using a sample in the form of an approximate sphere which is heated by electron bombardment from an auxiliary filament. The required data are obtained as the specimen cools. This necessitates measuring the charge accumulated over a period of time rather than measuring a current so that a modification of the Richardson equation must be made. The method has been applied so far to nickel.

EXPERIMENTAL

The tube and vacuum system

The tube, Fig. 1, was connected through two liquid air traps in series to a single stage Hg diffusion pump backed by a Cenco oil pump. A General Electric Pliotron FP-62, sealed to the tube, served to measure the pressure in the system. The complete high vacuum system was of Pyrex and 702p glasses with no waxed or greased joints. All the metal parts within the tube were of molybdenum, tungsten, or nickel, spot-welded together and previously outgassed by an induction furnace. The molybdenum collector surrounding the emitter was cylindrical in shape, open at the top but closed at the bottom except for a $\frac{1}{4}$ inch hole through which the auxiliary filament leads passed.

The nickel emitter

Before machining, the emitter was cast in a vacuum tungsten resistance furnace from electrolytic nickel obtained from the International Nickel Company. It was nearly spherical in shape and weighed approximately 15 grams. The 20 mil tungsten wire supporting the emitter and the wires to the thermocouple junction, spot-welded to the upper part of the emitter, were inclosed by fine quartz tubes to prevent contamination by evaporated nickel. The evaporated nickel coat deposited on the quartz prevented the quartz from emitting.

Outgassing

Before placing the sample in the tube of Fig. 1, it was heated by electron bombardment for a preliminary period of 1000 hours in another tube.

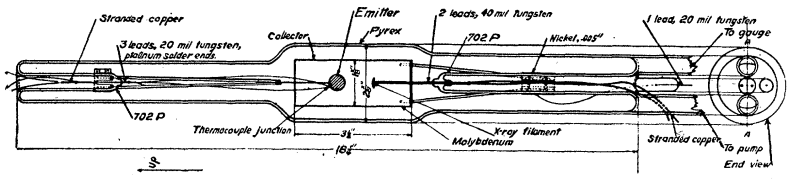

FIG. 1. Longitudinal section through and end view of thermionic emission tube.

Then it was mounted as described and its temperature maintained at 1375°K for 575 hours after which it was removed, measured, weighed, photographed, and replaced. No data used in determining the final values of the constants were taken until after a further period of heating at about 1440°K for 375 hours, followed by a 72-hour period, during which the temperature of the sample varied from 1500°K to 1650°K. After replacing the sample, the tube, ionization gauge and first air trap were baked for 10 hours at temperatures ranging from 415°C to 460°C. These glass parts had been baked previously for 53 hours.

Taking data

The method of heating and taking data can be explained by referring to the wiring diagram, Fig. 2. During the heating process, the switches

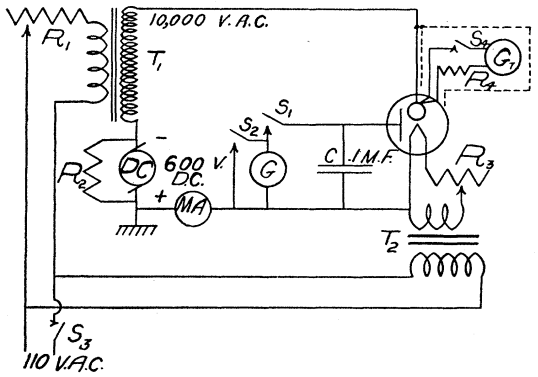

FIG. 2. Circuit diagram for thermionic emission tube.

S_1, S_2 and S_3 were closed. After maintaining the temperature of the emitter at some chosen value for five minutes, S_3 was opened simultaneously with the starting of a stopwatch. Opening this switch, shut off both the filament current and the high potential, thus allowing the voltage produced by d.c. to accelerate the thermoelectrons from the cooling emitter to the collecting cylinder. At the end of a predetermined time, S_1 was opened, thereby allowing the emission current to charge a condenser C which was discharged through the ballistic galvanometer G at the end of another time interval. This accumulation of charge and subsequent discharge was repeated several times until the nickel became too cold to emit appreciably. No charge data were taken during the first interval of about 30 seconds, to allow heat conduction to eliminate temperature gradients in the specimen. An empirical relation between time and temperature was determined in the form of a cooling curve.

Theoretical

If we denote by dq the quantity of charge emitted by the metal in a time dt, then

$$dq/dt = I = aAT^2 \exp(-\Phi e/kT) \qquad (1)$$

in which the current is given by Richardson's equation multiplied by the area of the emitter a. Although it is theoretically possible to determine various values of the current from the slopes taken at different points upon the q *vs.* t curve practically it is impossible to draw the required tangents with sufficient accuracy.

Here q is the quantity of charge which has been accumulated since the starting of the cooling process. If Q is defined as the quantity of charge yet to flow upon cooling the emitter from any variable, intermediate temperature to absolute zero, then $q+Q$ is a constant for any starting temperature and $dq = -dQ$. Also

$$dQ/dt = -aAT^2 \exp(-\Phi e/kT). \qquad (2)$$

A logarithmic curve, from which the slope may

be determined with sufficient accuracy, is obtained from (2) by dividing by $2.3Q$.

$$dQ/2.3Qdt = -(aAT^2/2.3Q)\exp(-\Phi e/kT)$$

$$d(\log_{10} Q)/dt = -S = \tag{3}$$

Here $-S$ is the slope of the log Q *vs.* t curve. This relation can be expressed in logarithmic form as follows:

$$\log_{10}(T^2/SQ) = \log_{10}(2.3/aA) + \Phi e/2.3kT$$
$$= \log_{10}(2.3/aA) + \Phi/(1.988\times10^{-4}T). \tag{4}$$

A straight line should result from plotting log (T^2/SQ) against $1/T$, from the slope of which Φ can be determined.

The theoretical shape of the log Q *vs.* t curve can be derived from the integrated form of (2) and is given by

$$S = K\Phi eT^2/2.3k.$$

The constant K contains the thermal emissivity of the emitter and its heat capacity. As the percentage variation of T in the experimental range is not great the resulting curve is nearly straight. Although at first q appears to be the more logical quantity to use in the derivation of Eq. (4), intuition shows that the shape of the log q *vs.* t curve would eliminate this method. At the initial temperature q is zero; it rises rapidly at first as time increases and then asymptotically approaches a constant value. The log q *vs.* t curve would, therefore, start at $-\infty$, rise rapidly and then asymptotically approach a constant value while S would start at ∞ and go nearly to zero within the experimental range.

Results

Curves

In all, 48 sets of charge-time data were taken, of which 24 were used in computing the final values of the thermionic constants. These data were divided into three arbitrary groups depending upon when they were taken and each group was analyzed separately. The resulting curves from one set of data as required by Eq. (4) are shown in Figs. 3 and 4.

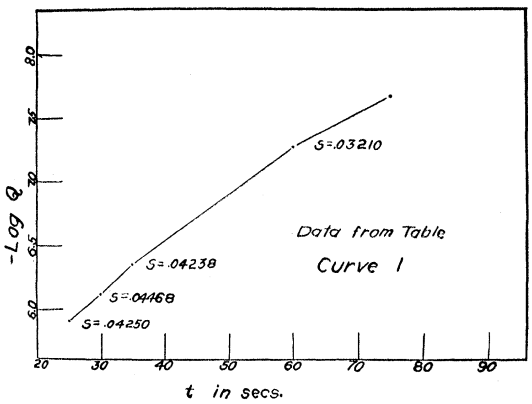

FIG. 3. Log Q *vs.* t curve for nickel.

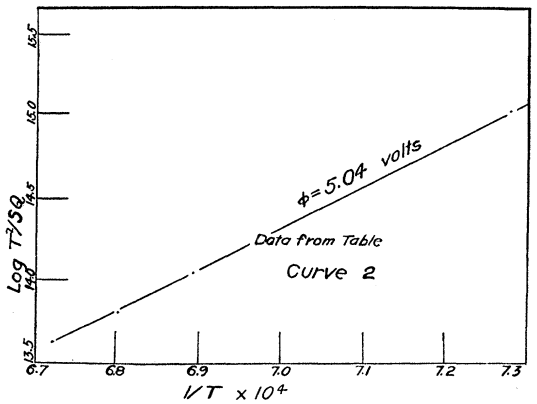

FIG. 4. Log T^2/SQ *vs.* $1/T$ curve for nickel.

Pressure in the tube

While the data used in computing the final values of the thermionic constants were being taken, the pressure as measured by the Pliotron FP-62 ranged from 1.7 to 2.9×10^{-6} mm of Hg. Upon allowing the emitter to cool nearly to room temperature, the pressure dropped to and remained at 1×10^{-7} mm of Hg as long as the emitter remained cold. It is interesting to note that the approximate vapor pressure of nickel as computed from the loss of 2.365 g during the last 475 hours of heating was about 2×10^{-5} mm of Hg, which was ten times the pressure of the residual gas in the tube.

Area of the emitter

Before it was possible to determine the constant A from Eq. (4), it was necessary to know

the area of the emitter. As the emitter was made by turning on a lathe, it was a figure of revolution, the area of which could, therefore, be computed by use of the first theorem of Pappus. The length of the generating arc was obtained from the length of a uniform copper strip bent to coincide with half of the perimeter of an enlarged photograph of the emitter. Its centroid was obtained by the use of an analytical balance and the elementary theory of moments as applied to the same copper strip. The area so obtained was for a similar enlarged solid, which, when divided by the square of the magnification, yielded the area desired (6.11 cm^2).

Values of constants

The final values of the thermionic constants for nickel were obtained by taking the weighted averages of the values from the last three groups of data analyzed and are $\Phi = 5.03 \pm 0.05$ volts and $A = 1.38 \times 10^3$ amp./$cm^2 deg.^2$. This value of Φ agrees with that of 5.01 ± 0.02 volts obtained photoelectrically by Glasoe.[1] The only other thermionic determination for nickel was made by Schlichter[2] in 1915 and yielded the anomalous value 2.77 volts. Although A does not agree with the universal value derived by Dushman,[3] this deviation might be expected from the position of nickel in the periodic table. The value for platinum in the same periodic group was found by DuBridge[4] to be 1.7×10^4 amp./$cm^2 deg.^2$.

Conclusion

The authors feel that the agreement furnished by this method with the photoelectric method in the case of nickel recommends it for use with other metals which are too hard, or, like nickel, are too volatile to be treated by the conventional method. Work on other metals is continuing in this laboratory.

[1] G. N. Glasoe, Phys. Rev. **38**, 1490 (1931).
[2] W. Schlichter, Ann. d. Physik [4] **47**, 573 (1915).
[3] S. Dushman, Phys. Rev. **21**, 623 (1923).
[4] L. A. DuBridge, Phys. Rev. **32**, 961 (1928).