Thermal and Electrical Conductivities of Tungsten and Tantalum*

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An investigation was made of the variation with temperature of the resistance, thermal conductivity, and Wiedemann-Franz ratio of pure tungsten and tantalum wires. Measurements were made of the resistance, as a function of power input, of the wires suspended in vacuum and thermostated at 77°K, 90°K, 273°K and 373°K. The resistivity of the wires was determined from the resistance at zero power input. A method was developed for calculating the thermal conductivity from the resistance at zero power input and the slope of the resistance *versus* power input curve. Limitations were found on the method, particularly lack of available data on the emissivity of tantalum at the temperatures used. An anomaly was observed in the variation with temperature of the resistance of tantalum.

INTRODUCTION

SOME preliminary measurements made in this laboratory[1,2] on the thermal conductivity of tungsten at temperatures below room temperature, as well as the results of other workers on various metals, indicate that the Wiedemann-Franz law does not hold for low temperatures. A search of the literature reveals a need for data on electrical and thermal conductivities of pure metals at moderately low temperatures. Several values have been published for tungsten[3–16] but these show very little agreement with one another, particularly on thermal conductivity. Only two published values have been found for the thermal conductivity of tantalum[8,17] at these low temperatures. The purpose of the present work was to measure more precisely than has previously been done both the electrical and thermal conductivities of pure tungsten and tantalum at temperatures ranging from 77°K to 373°K so as to find the nature of the variation with temperature of the Wiedemann-Franz ratio, and check as far as possible modern theories of the conductivity of solids.

The method of measurement was similar to that used by Kannuluik,[18] Roberts,[14] Michels and Cox,[2] and Raines[19] in measuring thermal conductivities and accommodation coefficients. Kannuluik and Roberts developed the theory of the heat losses from an electrically heated wire with its ends and surroundings thermostated at a known temperature. Michels and Cox extended the theory for application to a wire supported by springs. Raines added a correction for the variation of resistivity along the wire. In this paper the equation for the wire is further corrected and a rigorous and explicit solution found for the thermal conductivity.

THEORY OF HEAT LOSSES FROM A WIRE

A wire of length L and radius a is supported in an evacuated tube and immersed in a constant temperature bath so that the ends of the wire and the walls of the tube are maintained at a temperature T. A current i is sent through the wire causing any point in the wire to be raised to a

* From a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Bryn Mawr College, Bryn Mawr, Pennsylvania.

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temperature t above the surroundings, t being a function of x, the distance from one end of the wire. Let ρ be the resistivity of the metal at the temperature $T+t$, e the total emissivity at that temperature, and K the thermal conductivity. Let ρ_0, e_0, and K_0 be the values of these quantities at the temperature T, α and β the temperature coefficients of electrical and thermal resistance, respectively, and σ the radiation constant. R and R_0 are the resistances of the wire at the temperatures $T+t$, and T, respectively.

If, in a section of wire of length dx the power input is dW, the heat lost by conduction dQ_K, and the heat lost by radiation dQ_R, then

$$dW=dQ_K+dQ_R, \tag{1}$$

or

$$i^2\rho_0(1+\alpha t)dx/\pi a^2=-\frac{\pi a^2K_0}{1+\beta t}\frac{d^2t}{dx^2}dx + 2\pi ae\sigma[(T+t)^4-T^4]dx. \tag{2}$$

This is a differential equation of the form

$$d^2t/dx^2+B-At-Ct^2-Dt^3-Et^4-Ft^5=0, \tag{3}$$

where

$$A=8\sigma eT^3/K_0a-i^2\rho_0(\alpha+\beta)/\pi^2a^4K_0,$$

$$B=i^2\rho_0/\pi^2a^4K_0,$$

$$C=(12\sigma eT^2+8\sigma eT^3\beta)/K_0a-i^2\rho_0\alpha\beta/\pi^2a^4K_0,$$

$$D=(8\sigma eT+12\sigma eT^2\beta)/K_0a,$$

$$E=(2\sigma e+8\sigma eT\beta)/K_0a,$$

$$F=2\sigma e\beta/K_0a.$$

In previous work it has been assumed that the terms Ct^2, Dt^3 etc. were negligible compared with the first three terms of the equation. The equation was solved by neglecting these terms, and definite experimental values of the current i and the corresponding average temperature rise $\bar{t}$ were inserted in the solution. K_0 was then calculated by successive approximations. In the case of the wires used in this experiment, the coefficient A is very small for any reasonable value of i, and may be comparable with Ct. Thus it is a very poor approximation to keep the term At and neglect the term Ct^2 if the solution is to be applied to a wire with a definite power input. In the limiting case, however, as the power input in the wire is made very small and the temperature rise t becomes correspondingly small, the ratio Ct^2/At approaches zero and the equation describing the temperature distribution along the wire does approach the form

$$d^2t/dx^2+B-At=0. \tag{4}$$

This is the differential equation which has been solved by previous workers, but it must be kept in mind that it is valid only for a wire in which the power input is very low. The method of solution shown below allows a calculation of the thermal conductivity from the limiting case of zero power input, and justifies the use of the approximate differential equation, as well as simplifies the calculations.

Integration of the equation with the boundary condition that $dt/dx=0$ at $x=L/2$ gives

$$(dt/dx)_{x=0}=B(\cosh LA^{\frac{1}{2}}-1)/A^{\frac{1}{2}}\sinh LA^{\frac{1}{2}} =BLF(LA^{\frac{1}{2}}), \tag{5}$$

where

$$F(x)=(\cosh x-1)/x\sinh x =(e^x+e^{-x}-2)/x(e^x-e^{-x}). \tag{6}$$

If the total power input in the wire is W and the heat losses from the entire wire by conduction and radiation are Q_K and Q_R,

$$Q_K=2\pi a^2K_0(dt/dx)_0=2i^2\rho_0LF(LA^{\frac{1}{2}})/\pi a^2, \tag{7}$$

$$Q_R=2\pi ae\sigma\int_0^L[(T+t)^4-T^4]dx =8\pi ae\sigma LT^3\bar{t}, \quad \text{for } t\ll T, \tag{8}$$

$$W=\int_0^L i^2\rho_0(1+\alpha t)dx/\pi a^2=i^2\rho_0L(1+\alpha\bar{t})/\pi a^2. \tag{9}$$

We may set $\bar{t}=W(dR/dW)/(dR/dt)$, since R varies linearly with both power input and temperature over ranges much larger than are assumed here. Also

$$W=Q_K+Q_R, \tag{10}$$

or

$$F(LA^{\frac{1}{2}})=1/2\{1-8\pi ae\sigma T^3L(dR/dW)/(dR/dt)\}\cdot \{1+(W/R_0)(dR/dW)\}. \tag{11}$$

But A is a continuous function of W, and $F(LA^{\frac{1}{2}})$ a continuous function of A so that

$$\lim_{W\to 0} F(LA^{\frac{1}{2}}) = F(\lim_{W\to 0} LA^{\frac{1}{2}}) = F(LA_0^{\frac{1}{2}}), \quad (12)$$

where

$$A_0 = 8\sigma e T^3/K_0 a. \quad (13)$$

Taking the limits of both sides of Eq. (11) one obtains

$$F(LA_0^{\frac{1}{2}}) = 1/2\{1 - 8\pi a e \sigma L T^3 (dR/dW)/(dR/dt)\}. \quad (14)$$

The quantity dR/dW must be evaluated at $W=0$. This is possible because, when measured values of R are plotted against the values of W used in an actual experiment, the points fall on a straight line. This constancy of dR/dW over a relatively large range of power input makes possible a precise determination of its value at zero power input. Use of the limiting equation for $W=0$ insures the validity of the approximate form of the differential equation which is used.

The value of $F(LA_0^{\frac{1}{2}})$ can be calculated from Eq. (14). $LA_0^{\frac{1}{2}}$ is then found graphically or from tables, and from this is found A_0, and therefore K_0 from Eq. (13).

At the lower temperatures, (77°K and 90°K), the term to be subtracted from 1, in Eq. (14), becomes so small and the value of $F(LA_0^{\frac{1}{2}})$ so close to $F(0)=\frac{1}{2}$ that the calculation can not be made in the same way. For this case let $LA_0^{\frac{1}{2}}=x$ and let $8\pi a e \sigma T^3 L(dR/dW)/(dR/dt)=y$. Equation (14) becomes

$$(\cosh x - 1)/x \sinh x = (1-y)/2. \quad (15)$$

Expansion of the hyperbolic functions into power series yields

$$1-y = (1+x^2/12+x^4/360+\cdots)/(1+x^2/6+x^4/120+\cdots)$$
$$= 1 - x^2/12 + x^4/120 - 17x^6/20160 + \cdots. \quad (16)$$

Neglecting terms in x^4 and higher powers of x, we find

$$x^2 = 12y. \quad (17)$$

In the case where this solution is used, x^2 is about 5×10^{-8}, so that the approximation is completely justified. In intermediate cases, where this expression is not quite correct, another term may be kept in the expansions and the resulting quadratic equation in x^2 solved, giving

$$x^2 = 12y(1+1.2y+\cdots). \quad (18)$$

Thus for very low temperatures Eq. (17) holds and K_0 is obtained from the equation

$$K_0 = L(dR/dt)/12\pi a^2 (dR/dW), \quad (19)$$

which does not depend on the emissivity of the metal. When x^6 is very small but x^4 is considerable, Eq. (18) gives

$$K_0 = L(dR/dt)/12\pi a^2 (dR/dW)(1+1.2y). \quad (20)$$

In the latter case y and therefore the emissivity comes in only as a small correction term. Equation (20) was found valid for tungsten at 273°K and was used to check the calculation there, but it is not valid for tantalum at that temperature.

EXPERIMENTAL METHOD

The metal used was in the form of drawn wires 0.010 inch in diameter and about 40 cm long. The tungsten wire was contributed by Dr. W. E. Forsythe of the General Electric Company. Dr. Forsythe sent the wire in 1939 and stated that it was the highest purity tungsten wire that had then been made. The tantalum wire was obtained from the Fansteel Corporation, and according to their report had a purity of 99.9 percent.

In order to eliminate supporting springs, which complicate the calculations and increase the uncertainty of the results, the wire was hung in a glass tube bent so that its axis was a catenary. This method of support allowed the wire to expand and contract without being strained or touching the tube, but allowed the thermostating bath to surround the wire over its entire length. The experimental tube with an ionization gauge attached was sealed off at a pressure of less than 10^{-6} mm of Hg after the glass and metal parts had been cleaned up on a vacuum system. The wire to be measured was first heated with direct current so that it could be kept away from the walls of the tube with a magnet while it was first being brought up to the temperature at which it would hang freely in the tube. After the wire had

TABLE I. Experimental values and emissivity e.

Tube	T (°K)	R_0 (ohms)	dR/dW (ohms/watt)	dR/dt (ohms/°K)	e[a,b]
Tungsten No. 2	77.4	0.05588±0.00013	5.62±0.10	0.001509	
	90.2	0.075754±0.000092	6.18±0.14	0.001629	
	193	0.2635±0.001			
	273.2	0.417613±0.000054	6.804±0.020	0.0018682	0.01579
	372.8	0.613195±0.000048	5.569±0.017	0.0020032	0.02389
Tungsten No. 8	77.36	0.049830±0.000043	5.159±0.048	0.001472	
	90.2	0.069518±0.000080	5.760±0.072	0.001590	
	273.2	0.408953±0.000011	6.7414±0.0020	0.0018672	0.01579
	373.1	0.603460±0.000033	5.6787±0.0085	0.0020175	0.02392
Tantalum No. 3	77.33	0.194403±0.000045	49.82±0.13		
	273.2	0.979331±0.000070	24.99±0.10	0.0037587	0.055±0.005*
	373.4	1.355954±0.000068	11.841±0.083	0.0037587	0.067±0.005*

[a] See reference 24 in text.
[b] See reference 20 in text.
* Extrapolated.

acquired its proper catenary form all heating was done with 60-cycle alternating current.

The wire was aged by passing through it as high a current as was possible without evaporating the metal. A slight amount of evaporation did take place during the determination of this highest safe current, but not enough to change the diameter of the wire beyond the uncertainty of the measurement of the diameter. Tungsten tube No. 2 was aged at temperatures of 2400°C and 2600°C, tungsten tube No. 8 at 2300°C and tantalum tube No. 3 at 1800°C and 2000°C. The aging was interrupted at intervals and a determination made of the resistance of the wire as a function of power input with the tube at 0°C. The resistance at zero power input was plotted as a function of time of aging. The resistance decreased rapidly at first and finally reached a stable value, at which time it was assumed that the wire had acquired a stable crystalline structure. About 370 hours of aging were necessary for tungsten and 2750 hours for tantalum, although the latter time could have been shortened as the first part of the aging was carried out at an unnecessarily low temperature.

After the wire had been aged, the tube was immersed in various baths and readings were taken of voltage across the tube, and current in it, by means of a Queen Gray potentiometer. From these readings resistance and power input could be determined, and then R_0 and dR/dW calculated. A temperature of 273.2°K was obtained by surrounding the tube with finely crushed ice packed down in water in a one-gallon Dewar flask. A second point was found by immersing the tube in briskly boiling water of which the temperature was determined, in some cases with mercury in glass thermometers later calibrated in steam at a measured atmospheric pressure, and in others directly from the barometric reading. The latter method was the more satisfactory providing the water could be kept pure for a long enough time to take the readings. Temperatures of 77.4°K and 90.2°K were obtained by using boiling liquid nitrogen and boiling liquid oxygen. The latter could not be used for the tantalum tube owing to wartime restrictions on the transportation of liquid oxygen. Attempts to thermostat the tubes at intermediate temperatures, in solid CO_2 and in melting tetrachlorethane, were not successful, probably because of the large volume of the Dewar flask used, and because of the high constancy of temperature necessary to make the experimental points lie on a straight line on the R–W graph within the uncertainty of the measurements.

From the values of R_0 at different bath temperatures, dR_0/dT and therefore dR/dt could be found. In the case of tungsten R_0 is not linear in T and the slope of the R_0–T curve is difficult to

TABLE II. Constants of the wires.

Tube	a (cm)	L (cm)	$\sigma\times10^{12}$[a] (watts/cm² deg.⁴)
Tungsten No. 2	0.01252±0.00002	40.85±0.02	5.75±0.03
Tungsten No. 8	0.01252±0.00002	40.00±0.02	5.75±0.03
Tantalum No. 3	0.01270±0.00006	40.00±0.02	5.75±0.03

[a] *International Critical Tables of Numerical Data* (1929), Vol. 5, p. 237.

estimate at low temperatures. Log R_0 was plotted against log T and the curvature was thus arranged so that it was possible, on a large graph, to estimate $dR_0/dT=(R_0/T)(d \log R_0/d \log T)$ with fairly good precision. In the case of tantalum it was impossible to determine this quantity except at the two higher temperatures.

The diameter of the tungsten wire after aging was determined by means of the screw of a dividing engine, with a dial indicator to bring two blocks together always with the same pressure. A pair of Webber blocks was used both for the calibration of the screw and for the actual measurement, in which two pieces of the wire separated the blocks. The probable error of this determination was 0.2 percent. The diameter of the tantalum wire was specified by the Fansteel Corporation with a tolerance of 0.5 percent.

Attempts to prepare a molybdenum wire for measurement have so far been unsuccessful. Because of the large difference in emissivity between the oxide and the clean surface of this metal, when the wire is first heated up for outgassing that portion of the surface which happens to get rid of its oxide first gets so extremely hot that it is impossible to get the rest of the wire hot enough without burning out that part which is clean. In cleaning up tungsten and tantalum the same phenomenon is observed to a lesser degree, one portion of the wire becoming very bright, but in those cases the bright area soon spreads over the entire wire.

RESULTS

The experimental values of R_0, dR/dW, and dR/dt, together with the values used for the total emissivity are shown in Table I, and the constants of the three wires used in Table II. Table III gives the values for the resistivity, thermal conductivity, and Wiedemann-Franz ratio calculated from the data in Tables I and II.

TABLE III. Values of resistivity and thermal conductivity and $W-F$ ratio.

Tube	T (°K)	K (watts/cm deg.)	$\rho\times10^6$ (ohm cm)	$K\rho/T\times10^8$ (volt²/deg.²)
Tungsten No. 2	77.4	1.86	0.6736	1.62
	90.2	1.82	0.9132	1.84
	193		3.18	
	273.2	1.70	5.034	3.13
	372.8	1.73	7.392	3.43
Tungsten No. 8	77.36	1.93	0.6135	1.53
	90.2	1.87	0.8558	1.77
	273.2	1.69	5.035	3.11
	373.1	1.68	7.429	3.35
Tantalum No. 3	77.33		2.46	
	273.2	0.36±0.04	12.41	1.64
	373.4	0.19±0.17	17.18	0.87

Tantalum

The high uncertainty in the thermal conductivity of tantalum, at 273°K and especially at 373°K, is due to lack of knowledge of the emissivity of tantalum at these temperatures. Malter and Langmuir's[20] data at temperatures from 1000°K to 1500°K were extrapolated to yield the highly uncertain values of e shown in Table I. The magnitude of the term $8\pi ae\sigma T^3L(dR/dW)/(dR/dt)$ is such that a 10 percent error in e, at 373°K, causes a 90 percent error in K while the percentage error in K at 273°K, due to e, is about equal to the percentage error in e.

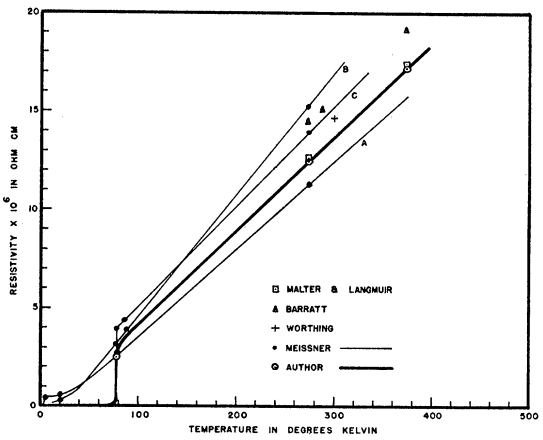

FIG. 1. The resistivity of tantalum. Of Meissner's curves, the curves marked A and B were obtained from lamps of unknown purity, which had been in use for a long time. Curve C was made from a lamp containing Fe_2O_3 and flashed at 2800°K.

At 77°K the second method of calculation is valid for both metals, but at this temperature it was impossible to evaluate dR/dt for tantalum as R does not vary in a regular manner with T throughout the range. As can be seen in Fig. 1, the value of R at 77°K is considerably below that which would be expected from the two upper values. That is, a reasonable curve drawn through

[20] L. Malter and D. B. Langmuir, Phys. Rev. 55, 743 (1939).

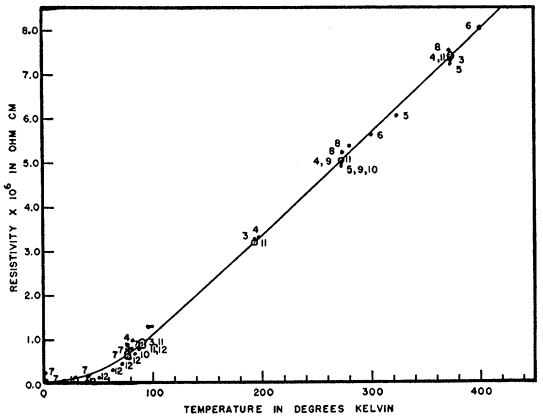

FIG. 2. The resistivity of tungsten. The curve is drawn through the circles, which represent the author's experimental points. The numbers on the other points refer to the footnotes giving the sources of the data shown.

the three points would be concave towards the axis and could not be made to go through the origin or to give a positive resistance intercept. In studying Meissner's[7] data on the resistivity of tantalum in this temperature range it was observed that some of his samples showed a peculiar sudden drop in resistance at low temperatures. Curves for three of his samples are shown in Fig. 1, with the author's points plotted on the same scale. One sample showed this sudden drop at 77°K and another at 4°K. It is unfortunate that liquid oxygen could not be obtained for data on tantalum at 90°K to check this anomalous behavior.

Although the data on tantalum are insufficient for any check on theory, the values given for ρ and the rough value of K at 273°K are thought to be reliable. The values of ρ check very well with those of Malter and Langmuir.[20]

Tungsten

The values of ρ, which are plotted in Fig. 2, show a very satisfactory check with those of other workers.[3–12] Previous measurements of K[8–13] show such wide disparity that comparison is difficult. The values of Barratt,[8] Weber,[9] and Coolidge,[13] however, are probably not reliable as pure tungsten was not available at the time at which their work was done. A good check was found with Kannuluik[11] throughout the range, particularly with one of his samples, and with Langmuir and Taylor[15] at 273°K. The author's values of K are plotted in Fig. 3, with those of other workers.

The theory of conductivity at low temperatures as worked out by Bloch[21] predicts that at temperatures very small compared with the Debye characteristic temperature the electrical conductivity should be proportional to T^{-5} and the thermal conductivity proportional to T^{-2}. Sommerfeld and Bethe[22] point out that the values of K for tungsten measured at 21.2°K and 83.2°K by Gruneisen and Goens[10] are nearly proportional to T^{-2}. But the characteristic temperature for tungsten is 310°K so that it is not to be expected that the T^{-2} law will hold in a range as high as 83°K. The author's values of K at 77°K and 90°K do not obey the T^{-2} law. The values given by de Haas and de Nobel[12] show, also, that the T^{-2} law does not hold for temperatures as high as 80°K. The use of Gruneisen's data by Sommerfeld and Bethe to show $1/K \propto T^2$ does not seem to be justified over such a large range. The good agreement between the author's values and those

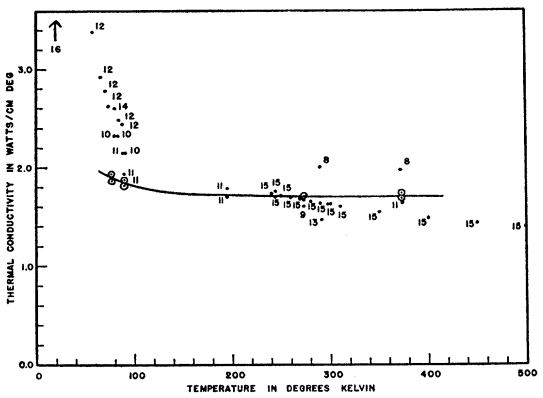

FIG. 3. The thermal conductivity of tungsten. The curve is drawn through the circles, which represent the author's experimental points. The numbers on the other points refer to the footnotes giving the sources of the data shown.

of Kannuluik indicate that the values of Gruneisen and of de Haas and de Nobel for the thermal conductivity of tungsten are probably too high.

Another comparison with theory may be made by considering the variation with temperature of the quantity $K\rho/T$. In the very low temperature range, if $\rho \propto T^5$ and $1/K \propto T^2$ we should expect

[21] F. Bloch, Zeits. f. Physik **52**, 555 (1929); **59**, 208 (1930).
[22] A. Sommerfeld and H. Bethe, *Handbuch der Physik* (1933), Vol. 24, Part 2, p. 535.

$K\rho/T \propto T^2$. The temperatures used do not extend to a sufficiently low range to test this relation. However the extrapolation in Fig. 4, based on a T^2 law, is not inconsistent with the experimental observations.

At high temperatures, $K\rho/T$ approaches a constant value, higher than the classical theoretical value. Mott and Jones[23] show that $K\rho/T$ should have the classical value for temperatures appreciably higher than the Debye characteristic temperature, except for transition metals. The approximations used involve the assumption that $kT \ll \zeta$, where ζ is the Gibbs potential per electron. This is not true for transition metals, in which ζ is very small. Thus in the case of tungsten one should not expect $K\rho/T$ to have the classical value, even at high temperatures. The theoretical calculations have not been carried sufficiently far to predict the correct high temperature value of $K\rho/T$ for a transition metal.

While the results presented are inconclusive in the case of tantalum and not numerous in the case of tungsten, it is believed that the method outlined for the measurement of thermal conductivity of metals is a practical one, especially if it were used in conjunction with measurements of emissivity according to the method of Langmuir and Taylor.[24]

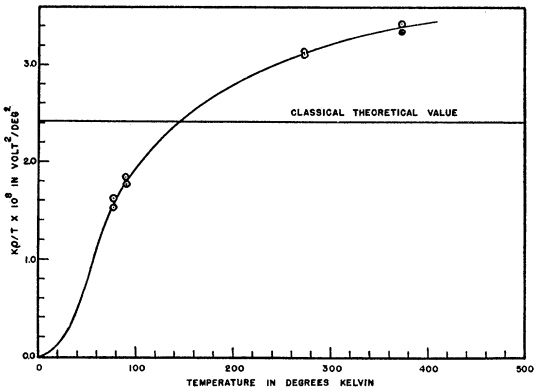

FIG. 4. The Wiedemann-Franz ratio for tungsten.

The author wishes to express sincere thanks to Dr. Walter C. Michels for suggesting the problem and for many helpful suggestions in carrying out the work.

[23] N. F. Mott and H. Jones, *The Theory of the Properties of Metals and Alloys* (Oxford University Press, 1936).

[24] I. Langmuir and J. B. Taylor, J. Opt. Soc. Am. **25**, 321 (1935).