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LIVERMORE

UCRL-50962

**AN AC TEMPERATURE TECHNIQUE
FOR MEASURING THE HIGH TEMPERATURE
SPECIFIC HEAT OF METALS**

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229

Contents

Abstract	1
Introduction	i
Theory	3
Experimental Apparatus and Procedures	12
Optical System	12
Bridge System	15
Sample Selection	18
Temperature Measurement	20
Experimental Results	22
Discussion	27
Summary and Conclusions	45
Acknowledgments	47
Appendix A: Solution of Eq. (11)	48
Appendix B: Assumptions Used to Derive Eq. (17)	50
Appendix C: Supplementary Data	53
References	68

AN AC TEMPERATURE TECHNIQUE FOR MEASURING THE HIGH TEMPERATURE SPECIFIC HEAT OF METALS

Abstract

An ac temperature technique for measuring the specific heat of electrical conductors has been developed. This technique can be used to measure the specific heat of small wire or foil samples in the temperature range of a few hundred degrees Kelvin to temperatures near the melting point of the sample. The accuracy of the specific heat data obtained using this technique is limited solely by the accuracy of the measurement of the sample's temperature coefficient of resistance.

This ac temperature technique has been used to measure the specific heat of tungsten in the temperature range 800°K to 3400°K. In this range the following equation was found to represent the specific heat with an estimated accuracy of $\pm 1\%$ at low temperatures to $\pm 3\%$ at high temperatures:

$$c_p(T) = (5.43) + (9.50 \times 10^{-4})T + (1.05 \times 10^{-7})T^2 \\ + (2.92 \times 10^{13}/T^2) \exp(-4.63 \times 10^4/T) \text{ cal/mole-}^\circ\text{K.}$$

A method of analyzing specific heat data to determine the contribution of lattice mono-vacancies has also been developed. This method has been used to determine the following data for tungsten:

1. The energy of formation of mono-vacancies, $\Delta E_v = 3.90 \pm 0.30$ eV.
2. The entropy of formation of mono-vacancies, $\Delta S_v/k = 8.4 \pm 1.3$.
3. The concentration of mono-vacancies at the melting point, $c_{mp} = 2.1 \pm 0.7$ mole percent.
4. The migration energy for mono-vacancies, $E_M = 2.74 \pm 0.56$ eV.
5. The anharmonic-lattice specific heat ($800^\circ\text{K} < T < 3400^\circ\text{K}$),
 $c_A = -0.48 + (0.57 \times 10^{-3})T + (0.015 \times 10^{-6})T^2 \text{ cal/mole-}^\circ\text{K.}$

Introduction

The high-temperature heat capacity is a quantity which frequently is of scientific and engineering importance. Its value as a function of temperature yields useful information about the electronic and atomic structure of materials from the point of view of the scientist while at the same time constituting vital information for engineering in the high-temperature regime. Unfortunately, the specific heat of any substance is

difficult to measure at high temperatures, i.e., temperatures above 1500°K, using conventional drop calorimeter techniques.¹ Although accurate data has been obtained in some cases (see particularly the work of V. A. Kirillin et al.^{2,3}), much of the data obtained using these methods exhibits a significant lack of agreement among different experimenters. Some progress toward reliable data has been made with the development of the pulse-heating technique.⁴⁻⁹ However, this method suffers from the fact that accurate measurements of transient voltages and temperatures are difficult.

Early in this century Corbino^{10,11} devised a method for measuring high-temperature specific heats of metals which promised to avoid most of the difficulties encountered with other techniques. He noticed that when an electrical conductor is heated by an alternating current, the temperature of the conductor is generally a periodic function of time. That is, $T(t) = \bar{T} + \Delta T(t)$, where $T(t)$ is the temperature of the conductor, $\bar{T}$ is the average temperature, and ΔT is a periodic function of time which will henceforth be called the "ac temperature." In investigating the ac temperature, Corbino discovered that its amplitude could be related to the heat capacity of the electrical conductor.

Shortly after Corbino's work, Worthing,⁴ Smith and Bigler,¹² Bockstahler,¹³ and Zwiker¹⁴ all attempted to use his method to measure the specific heat of tungsten at high temperatures. With the metal in the form of a wire, they attempted to determine the amplitude of the ac temperature from the resulting oscillations of the thermionic emission current. Their results showed considerable scatter, probably due to the fact that the thermionic emission current is very sensitive to the microscopic state of the metal surface.¹⁵

Langmuir and Malter¹⁶ used Corbino's method to measure the specific heat of tantalum in 1939. They apparently measured both the ac light output and the ac thermionic emission current. However, they did not give details about their experimental technique.

More recently, Lowenthal,¹⁷ Kraftmacher,¹⁸⁻²³ and Holland²⁴⁻²⁶ have used Corbino's method combined with modern electronic techniques to measure the specific heats of several metals. Kraftmacher and Holland, in particular, have developed the technique to a considerable level of sophistication. Filipov and Yurchak²⁷ have extended the technique to cover electron-beam heating of the sample.

The modern extensions of Corbino's method are similar to techniques for measuring the low temperature specific heats of metals developed by Sullivan and Seidel^{28,29} and Handler, Mapother, and Rayl.³⁰ These experimenters have measured the change in the heat capacity of indium between the normal and superconducting states, the quantum oscillations in the heat capacity of beryllium due to the variation of the density of electronic states at the Fermi level produced by a magnetic field, and the heat capacity of nickel near its critical point.

The first objective of the present work is to investigate the theory and practice of Corbino's method for measuring the high temperature specific heats of metals. The

first section of the text consists of a detailed discussion of the theory behind this method. The second section describes an experimental apparatus capable of accurate measurements of the specific heats of metals from several hundred degrees Kelvin to the melting point of most metals. The third section contains the results of the measurement of the specific heat of tungsten made with this apparatus. These results illustrate the capabilities of the method and of the equipment.

Near the melting point, a sharp rise in the heat capacity at constant pressure has been observed in many metals (aluminum,^{31,32} copper,³³ gold,⁵⁴ lead,³¹ molybdenum,^{2,9,20} niobium,^{21,35} platinum,²³ potassium,³⁶ rhenium,⁹ sodium,³⁷ tantalum,^{9,38} thorium,³⁹ tungsten,¹⁹ and zirconium²²). This rise in heat capacity has been used by some authors (Kraftmacher and Strelkov,⁴⁰ Wallace,³⁹ Pochapsky,³¹ Carpenter,⁴¹ and Kirillia et al.²) to calculate the energy of formation and concentration of vacancies. However, this approach has been criticized because of the calculational procedures used. Hence, the second objective of this work is to examine the possibility of developing an improved technique for obtaining the energy of formation and concentration of vacancies from high-temperature heat capacity data. The fourth section of the text presents several calculational techniques which can be used to determine the energy of formation and concentration of vacancies from specific heat data for some metals. Aluminum and copper data are used to illustrate the accuracy of these techniques, which are then applied to the tungsten data contained in the third section of this work.

Theory

Given a thin metal wire (or foil) which is heated by an electric current, the equation for the conservation of power (neglecting power loss through heat conduction out of the ends of the wire and the radial temperature gradient) is

$$I^2 R = (dT/dt)C_p + L \quad (1)$$

where

t is the time (units: seconds),

$T = T(t)$ is the temperature (degrees Kelvin),

$I = I(t)$ is the electric current (amps),

$R = R(T)$ is the resistance (ohms),

$C_p = C_p(T)$ is the heat capacity at constant pressure (joules per degree Kelvin), and

$L = L(T)$ is the rate of energy loss from the metal surface (watts).

The electric current is composed of a direct current plus an alternating current of circular frequency ω ,

$$I = i_0 + i(\sin \omega t) \quad (2)$$

where i_0 is the direct current, and $(\sqrt{2}/2)i = i_{rms}$ is the root-mean-square value of the alternating current.

Now assume the following:

$$T = \bar{T} + \Delta T \text{ with } \Delta T < \bar{T}, \quad (3)$$

$$L = \bar{L} + (dL/dT)_{\bar{T}} \Delta T, \quad (4)$$

$$R = \bar{R} + (dR/dT)_{\bar{T}} \Delta T, \quad (5)$$

and

$$C_p \approx \bar{C}_p, \quad (6)$$

where a bar over a quantity indicates the time average of the quantity. ΔT is a small alternating component of the temperature which is produced by the alternating electric current. The derivatives in Eqs. (4) and (5) are evaluated at the average temperature, $\bar{T}$. The variation of C_p with T is neglected in Eq. (6). This results in the loss of a term proportional to the amplitude of ΔT squared from Eq. (1). If we use these assumptions, Eq. (1) becomes

$$[i_0 + i(\sin \omega t)]^2 \cdot [\bar{R} + (dR/dT)_{\bar{T}} \Delta T] = (d\Delta T/dt) \bar{C}_p + \bar{L} + (dL/dT)_{\bar{T}} \Delta T. \quad (7)$$

Now the average power must be conserved, therefore

$$\bar{R}(i_0^2 + i^2/2) = \bar{L} \quad (8)$$

where a term proportional to the amplitude of the ac temperature times $(dR/dT)_{\bar{T}}$ has been neglected. With this approximation Eq. (7) reduces to

$$\begin{aligned} 2i_0 i \bar{R}(\sin \omega t) + (i_0^2 + i^2/2)(dR/dT)_{\bar{T}} \Delta T - \bar{R}(i^2/2)(\cos 2\omega t) \\ + 2i_0 i (dR/dT)_{\bar{T}} \Delta T(\sin \omega t) - (dR/dT)_{\bar{T}}(i^2/2)\Delta T(\cos 2\omega t) \\ = (d\Delta T/dt) \bar{C}_p + (dL/dT)_{\bar{T}} \Delta T. \end{aligned} \quad (9)$$

The terms proportional to $(dR/dT)_{\bar{T}} \Delta T$ are small compared to the terms proportional to $\bar{R}$. Therefore, in order to simplify the solution of Eq. (9), the last two terms on the left-hand side of Eq. (9) will be neglected. That is,

$$\frac{d\Delta T}{dt} + \left(\frac{M}{\bar{C}_p}\right) \Delta T = \left(\frac{2i_0 i \bar{R}}{\bar{C}_p}\right) (\sin \omega t) - \left(\frac{\bar{R} i^2}{2\bar{C}_p}\right) (\cos 2\omega t) \quad (10)$$

where

$$M \equiv (dL/dT)_{\bar{T}} - (i_0^2 + i^2/2)(dR/dT)_{\bar{T}}. \quad (11)$$

The solution of this equation is shown in Appendix A to be given by

$$\Delta T = \Delta T_1 \sin(\omega t - \phi) - \Delta T_2 \sin(2\omega t + \theta) \quad (12)$$

where

$$\Delta T_1 = \{(2i_0 i \bar{R})/(\omega \bar{C}_p)\} \sin \phi, \quad (13)$$

$$\tan \phi = (\omega \bar{C}_p)/M, \quad (14)$$

$$\Delta T_2 = \{(i^2 \bar{R})/(4\omega \bar{C}_p)\} \cos \theta, \quad (15)$$

and

$$\tan \theta = M/(2\omega \bar{C}_p). \quad (16)$$

Therefore, the heat capacity of the specimen is given by

$$\bar{C}_p = (2i_0 i \bar{R})/(\Delta T_1 \omega) \sin \phi \text{ or } \bar{C}_p = (i^2 \bar{R})/(\Delta T_2 4\omega) \cos \theta. \quad (17)$$

If ΔT_1 or ΔT_2 can be measured experimentally with ω sufficiently large so that $\phi = 90^\circ$ or $\theta = 0^\circ$, then Eq. (17) can be used to calculate the heat capacity of the metal wire (or foil) specimen. Alternately, if ΔT_1 or ΔT_2 can be measured at two or more frequencies, Eq. (17) is replaced by a system of equations which can be solved to give the heat capacity of the specimen without a priori knowledge of ϕ or θ .

In Appendix B the assumptions used in the derivation of Eq. (17) are examined. It is shown that these assumptions do not place any serious restrictions upon the use of this equation for the design and analysis of practical experiments.

An idea of the size of the ac temperature can be obtained from Figs. 1, 2 and 3 where ΔT_1 is plotted as a function of the frequency (these plots and the ones which follow are based on ones drawn by a Calcomp plotter using a program developed by J. R. Terrall⁴²). In the figures $P1 = 2i_0 i \bar{R}$, $P2 = \bar{C}_p$, and $P3 = M$, so that

$$\Delta T_1 = \frac{P1}{P2} \cdot \frac{1}{\omega} \sin \phi \text{ with } \tan \phi = \frac{P2}{P3} \cdot \omega. \quad (18)$$

Fig. 1. Plot of Eq. 18. $P_2 = 0.05 \text{ J/}^\circ\text{K}$, $P_3 = 0.5 \text{ W/}^\circ\text{K}$.

Fig. 2. Plot of Eq. 18. $P_1 = 5 \text{ W}$, $P_3 = 0.5 \text{ W/}^\circ\text{K}$.

Fig. 3. Plot of Eq. 18. $P_1 = 10 \text{ W}$, $P_2 = 0.05 \text{ J/}^\circ\text{K}$.

It is possible to measure ΔT_1 and ΔT_2 by purely electrical means. Toward this end, consider the potential drop, V , in the specimen corresponding to a current, I . The impedance of the specimen is equal to its resistance since the parallel capacitance and series inductance of the wire are assumed to be negligible. Therefore,

$$Z = R = \bar{R} + \Delta T(dR/dT)_{\bar{T}}, \quad (19)$$

and the potential drop is given by

$$V = IZ = [i_0 + i \sin \omega t]$$

$$[\bar{R} + \Delta T(dR/dT)_{\bar{T}}]. \quad (20)$$

The following identities are needed:

$$\begin{aligned}\sin(\omega t - \phi) &= (\sin \omega t)(\cos \phi) - (\cos \omega t)(\sin \phi), \\ \sin(2\omega t + \theta) &= (\sin 2\omega t)(\cos \theta) + (\cos 2\omega t)(\sin \theta), \\ (\sin \omega t)(\sin 2\omega t) &= 1/2(\cos \omega t - \cos 3\omega t),\end{aligned}\tag{21}$$

and

$$(\sin \omega t)(\cos 2\omega t) = 1/2(\sin 3\omega t - \sin \omega t).$$

Now using Eq. (12) and the above identities in Eq. (20), we can write

$$V = V_0 + V(\omega) + V(2\omega) + V(3\omega)\tag{22}$$

with

$$\begin{aligned}V_0 &= i_0 \bar{R} + (i/2)(\Delta T_1)(dR/dT)_{\bar{T}}(\cos \phi), \\ V(\omega) &= [(i_0 \Delta T_1)(dR/dT)_{\bar{T}}(\cos \phi)] (\sin \omega t) + (i \bar{R})(\sin \omega t) \\ &\quad - [(i/2)(\Delta T_2)(dR/dT)_{\bar{T}}(\cos \theta)] (\cos \omega t) \\ &\quad - [(i_0 \Delta T_1)(dR/dT)_{\bar{T}}(\sin \phi)] (\cos \omega t) \\ &\quad + [(i/2)(\Delta T_2)(dR/dT)_{\bar{T}}(\sin \theta)] (\sin \omega t), \\ V(2\omega) &= -[(i_0 \Delta T_2)(dR/dT)_{\bar{T}}] [(\cos \theta)(\sin 2\omega t) \\ &\quad + (\sin \theta)(\cos 2\omega t)], \\ V(3\omega) &= +[(i/2)(\Delta T_2)(dR/dT)_{\bar{T}}] [(\cos \theta)(\cos 3\omega t) \\ &\quad - (\sin \theta)(\sin 3\omega t)].\end{aligned}$$

It is convenient to rewrite $V(\omega)$ in complex form (a bar under a symbol will be used to indicate a complex number),

$$\underline{V}(\omega) = v_1(\omega) + jv_2(\omega)\tag{23}$$

where

$$j^2 = -1,$$

$$v_1(\omega) = i \bar{R} + [(dR/dT)_{\bar{T}}] [i_0 \Delta T_1 \cos \phi + (i/2)(\Delta T_2) \sin \theta],$$

and

$$v_2(\omega) = -[(dR/dT)_{\bar{T}}] \{ (i_0 \Delta T_1) \sin \phi + (i/2) (\Delta T_2) \cos \theta \}.$$

The alternating component of the current in complex form is

$$\underline{I}_{ac} = i + j0 = i. \quad (24)$$

Now the equivalent impedance of the specimen at frequency ω for the alternating component of the current in complex form is

$$\underline{Z} = \{ \underline{V}(\omega) / \underline{I}_{ac} \} = v_1(\omega) / i + j[v_2(\omega) / i]. \quad (25)$$

Therefore,

$$\text{Re}(\underline{Z}) = \bar{R} + [(dR/dT)_{\bar{T}}] \{ (i_0 / i) (\Delta T_1) \cos \phi + (1/2) (\Delta T_2) \sin \theta \} \quad (26)$$

and

$$\text{Im}(\underline{Z}) = -[(dR/dT)_{\bar{T}}] \{ i_0 / i (\Delta T_1) \sin \phi + (1/2) (\Delta T_2) \cos \theta \}. \quad (27)$$

The impedance, $\underline{Z}_A$, of a resistance, R_A , shunted by a small capacitance, C_A , has a form which is similar to Eq. (25), that is

$$\underline{Z}_A = \{ 1 / (1 + \omega^2 C_A^2 R_A^2) \} [R_A - j(\omega C_A R_A^2)] \quad (28)$$

or

$$\underline{Z}_A \approx R_A - j(\omega C_A R_A^2) \text{ when } (\omega C_A R_A)^2 \ll 1. \quad (29)$$

This suggests that $\underline{Z}$ might be measured with an impedance bridge of the type shown in Fig. 4. When this bridge is balanced,

$$\underline{Z} = (\underline{Z}_A / \underline{Z}_B) \underline{Z}_C. \quad (30)$$

Now let

$$\underline{Z}_I = R_I + jX_I \quad (I = A, B, C) \quad (31)$$

so that using Eq. (30), the balance condition, we have

Fig. 4. Impedance bridge for specific heat measurement.

$$[\text{Im}(\underline{Z})/\text{Re}(\underline{Z})] = (X_A R_C) - (\text{Re}(\underline{Z})X_B)$$

$$+ (R_A X_C) / [R_A R_C + \text{Im}(\underline{Z})X_B - X_A X_C]. \quad (32)$$

In general, the bridge impedances $\underline{Z}_I$ will have the form

$$\underline{Z}_I = \{R_I + j[L_I(1 - \omega^2 C_I L_I) - C_I R_I^2]\} / [1 - \omega^2 C_I L_I^2 + \omega^2 C_I^2 R_I^2], \quad (33)$$

which is the impedance of a resistance, R_I , and a series inductance, L_I , shunted by a capacitance, C_I . We will assume that $\omega^2 C_A L_A \ll 1$; then

$$\underline{Z}_A = [R_A + j(L_A - C_A R_A^2)] / [1 + \omega^2 C_A^2 R_A^2]. \quad (34)$$

Therefore

$$X_A = X'_A + X''_A \quad (35)$$

with

$$X'_A = -(\omega C_A R_A^2) / (1 + \omega^2 C_A^2 R_A^2)$$

and

$$X''_A = (\omega L_A) / (1 + \omega^2 C_A^2 R_A^2). \quad (36)$$

Using Eqs. (36) in Eq. (32), we find

$$\text{Im}(\underline{Z})/\text{Re}(\underline{Z}) = (R_C X'_A + R_X) / (R_A R_C + X_X) \quad (37)$$

where

$$R_X = R_C X_A'' - \operatorname{Re}(\underline{Z}) X_B + R_A X_C$$

and

$$X_X = \operatorname{Im}(\underline{Z}) X_B - X_A X_C.$$

Now we assume that the bridge is constructed so that $X_X \ll R_A R_C$, so Eq. (37) becomes

$$\operatorname{Im}(\underline{Z})/\operatorname{Re}(\underline{Z}) = X_A'/R_A + (R_X/R_A R_C). \quad (38)$$

Using Eq. (26) with

$$\bar{R} \gg [(dR/dT)_{\bar{T}}] [(i_0/i)(\Delta T_1) \cos \phi + (1/2)(\Delta T_2) \sin \theta],$$

we find

$$\operatorname{Re}(\underline{Z}) = \bar{R}. \quad (39)$$

Therefore with Eqs. (27) and (39) we have

$$\operatorname{Im}(\underline{Z})/\operatorname{Re}(\underline{Z}) = -[(1/\bar{R})(dR/dT)_{\bar{T}}] [(i_0/i)(\Delta T_1) \sin \phi + (1/2)(\Delta T_2) \cos \theta]. \quad (40)$$

Recalling Eqs. (13) to (16) and some trigonometry, we find:

$$\Delta T_1 \sin \phi = [(2i_0 i \bar{R})/(\omega \bar{C}_p)] [(\omega \bar{C}_p)^2/(M^2 + \omega^2 \bar{C}_p^2)] \quad (41)$$

and

$$\Delta T_2 \cos \theta = [(i^2 \bar{R})/(4\omega \bar{C}_p)] [(2\omega \bar{C}_p)^2/(M^2 + 4\omega^2 \bar{C}_p^2)]. \quad (42)$$

Therefore Eq. (40) becomes

$$\operatorname{Im}(\underline{Z})/\operatorname{Re}(\underline{Z}) = -[(\omega \bar{C}_p)(dR/dT)_{\bar{T}}] [(2i_0^2)/(M^2 + \omega^2 \bar{C}_p^2) + (i_{rms}^2)/(M^2 + 4\omega^2 \bar{C}_p^2)]. \quad (43)$$

Now Eqs. (36), (38), and (43) can be combined to give

$$\begin{aligned} [(R_A C_A)/(1 + \omega^2 C_A^2 R_A^2)] &= [(dR/dT)_{\bar{T}}] [(2i_0^2 \bar{C}_p)/(M^2 + \omega^2 \bar{C}_p^2) + (i_{rms}^2 \bar{C}_p)/(M^2 + 4\omega^2 \bar{C}_p^2)] \\ &\quad + (1/\omega)(R_X/R_A R_C). \end{aligned} \quad (44)$$

Now let

$$P_1' = (dR/dT)_{\overline{T}}, \quad P_2 = \overline{C}_p, \quad P_3 = M, \quad P_4 = i_0, \quad P_5 = i_{rms}, \quad P_6 = \frac{R_X}{R_A R_C};$$

then

$$\begin{aligned} [(R_A C_A)/(1 + \omega^2 C_A^2 R_A^2)] = [P_1'] [(2P_4^2 \cdot P_2)/(P_3^2 + \omega^2 P_2^2) \\ + (P_5^2 \cdot P_2)/(P_3^2 + 4\omega^2 P_2^2)] + P_6/\omega. \end{aligned} \quad (45)$$

This equation is plotted in Figs. 5 and 6 for the indicated values of P_1' through P_6 .

Fig. 5. Plot of Eq. 45. $P_1' = 0.001 \Omega/^{\circ}\text{K}$, $P_2 = 0.05 \text{ J}/^{\circ}\text{K}$, $P_3 = 0.5 \text{ W}/^{\circ}\text{K}$, $P_5 = (P_4/10) \text{ A}$, $P_6 = 2.0 \mu\text{sec}$.

Fig. 6. Plot of Eq. 45. $P_1' = 0.001 \Omega/^{\circ}\text{K}$, $P_2 = 0.05 \text{ J}/^{\circ}\text{K}$, $P_3 = 5.5 \text{ W}/^{\circ}\text{K}$, $P_5 = (P_4/10) \text{ A}$, $P_6 = 2.0 \mu\text{sec}$.

Equation (44) can be written in a more convenient form if we let

$$P_1 = \overline{C}_p/M,$$

$$P_2 = (2/M)(dR/dT)_{\overline{T}},$$

and

$$P_3 = (1/\omega)(R_X/R_A R_C).$$

Then

$$[(R_A C_A)/(1 + \omega^2 C_A^2 R_A^2)] = [P_2] [(i_0^2 P_1)/(1 + \omega^2 P_1^2) + (i_{rms}^2 \cdot P_1/2)/(1 + 4\omega^2 P_1^2)] + P_3 \quad (46)$$

with

$$\bar{C}_p = 2(P_1/P_2) \cdot (dR/dT)_T \quad (47)$$

Equation (46) is an equation in three unknowns, P_1 , P_2 , and P_3 , which are independent of frequency (P_3 is independent of frequency since R_X is approximately proportional to the frequency, $R_X \propto \omega$). Therefore, if the bridge is balanced at three or more different frequencies, the system of equations of type (46) can be solved for P_1 , P_2 , and P_3 . Then Eq. (47) may be used to solve for the heat capacity of the specimen.

Experimental Apparatus and Procedures

Two different experimental techniques were tested. The first system, similar to Lowenthal's system,¹⁷ was designed to measure the ac temperature of a metal foil sample using optical techniques. The second system, similar to Kraftmacher's system,¹⁸ was an ac bridge designed to measure the impedance of a metal wire or foil sample.

OPTICAL SYSTEM

It was shown above in Eq. (17) that the heat capacity of a metal specimen is given by

$$\bar{C}_p = (2i_0 i \bar{R})/(\Delta T_1 \omega) \sin \phi \text{ or } \bar{C}_p = (i^2 \bar{R})/(\Delta T_2 4\omega) \cos \theta.$$

If an optical system is used to measure the ac temperature, then

$$\Delta T_i = (\sqrt{2}/2) (dT/d\bar{V}) \Delta V_i \text{ for } i = 1, 2 \quad (48)$$

where ΔV_i is the rms ac voltage out of the detector (e.g., photomultiplier tube, photo resistor or photo diode), $\bar{V}$ is the dc voltage out of the detector, and $(dT/d\bar{V})$ is the slope of temperature-versus-dc-voltage curve for the detector.

Therefore, in order to measure the heat capacity, it is necessary to measure the ac and dc currents supplied to the sample, the average resistance of the sample, the frequency of the ac current, the ac and dc voltages out of the detector, the response of the detector (i. e., $d\bar{V}/dT$), and the temperature of the sample. A schematic diagram of an optical system designed to make these measurements is shown in Fig. 7.

Fig. 7. Optical system for specific heat measurement.

The ac current was provided by an ac power supply (General Radio Type 1308-A) with a transformer-coupled output which would pass up to five amps direct current while providing up to five amps ac current. The oscillator in the power supply was used to provide the reference channel voltage to the lock-in amplifier.

The frequency of the ac current was measured with an electronic counter (Hewlett Packard). The dc current was supplied by a regulated dc power supply (Tygon Electronics Model M60-10A).

A resistor (National Bureau of Standards, calibrated, one-tenth ohm) was placed in series with the sample. The voltage across the resistor was measured and the current computed by Ohm's law.

The various voltages in the system were measured with a digital voltmeter (Dana Model 5603) which could be switched into the circuit at the desired point by using a selection switch.

The average resistance of the sample was found by measuring the voltage drop across the sample with potential leads. The resistance was obtained by dividing the voltage across the sample by the current through the sample.

An infrared microscope (Barnes Engineering Company, Infrared Radiometric Microscope Model RM-2A) was used to measure $\bar{V}$ and ΔV_i . The microscope contained an indium antimonide detector (InSb) operating at 77°K, with a spectral range of 1.8 to 5.5 microns. The optics gave a resolution of 0.00356 cm.

It was found that the electronics provided with the microscope were not suited to measuring ΔV_i . Therefore, the microscope was modified by taking the voltage directly from the indium antimonide detector to an external preamplifier thus bypassing all the original electronics.

A linear preamplifier (dc to 50kc) with a gain of one hundred was used as the external preamplifier. It had two outputs: one for ΔV_i ($\bar{V}$ was excluded by capacitive coupling), and a second for $\bar{V}$ (ΔV_i was filtered out with a RC filter).

The V_i voltage was supplied to the input channel of the lock-in amplifier (Princeton Applied Research Corporation Lock-in Amplifier Model HR-8). The meter on the lock-in amplifier was sometimes used to read the voltage ΔV_i , but usually the output was taken from the lock-in amplifier and measured with the digital voltmeter.

The samples for this system were made by cutting thin strips from a piece of platinum foil (0.5-1.0 mills by 1/8 in. by 3 in.). They were clamped at the ends with copper clamps, the top part of the clamp being connected to the current leads and the bottom part to the potential leads. The sample, supported only at its ends by the clamps, was placed in a chamber which could be evacuated or filled with argon, the chamber was fitted with a CaF_2 window through which the sample could be observed with the microscope.

Two major difficulties were encountered with this system. It was found that ΔV_2 could not be measured with sufficient accuracy, and that $d\bar{V}/dT$ was difficult to measure.

The sample was subject to mechanical vibration, a problem noted also by other authors.^{13,17} The sample vibrated in response to an interaction between the ac current and the stray magnetic fields in the neighborhood of the sample. This could be

demonstrated by placing a small permanent magnet near the sample chamber and observing the resulting change in ΔV_2 . A magnetic shield was constructed out of alternate layers of Mu metal and copper (three layers of Mu metal with two interspersed layers of copper). Since it was impossible to completely enclose the sample by the shield, the vibration was reduced, but not eliminated.

Although the vibration of the filament could not be directly observed, it was believed to be a rocking motion of the foil driven at the same frequency as the ac current. This gave rise to an ac light flux at the detector, since the detector was observing a varying amount of foil surface. The amount of area viewed by the detector passed through a maximum twice for each period of the mechanical vibration. Therefore, the frequency of the mechanically induced light flux was twice the period of the ac current, i.e., the same frequency as ΔV_2 .

Since ΔV_2 could not be measured accurately, and since we thought that the mechanical vibration should not contribute a light-flux oscillation at the frequency of the ac current, it was decided that ΔV_1 should be the quantity measured. It was found that this could be done without any effect due to the mechanical vibration of the sample being observed. It is the author's opinion that this is the preferred mode of operation for the optical method, although it does not appear to have been used before.

The response of the detector, $d\bar{V}/dT$, was measured by recording $\bar{V}$ as a function of temperature and determining the slope graphically. The temperature was measured with a calibrated pyrometer, and the true temperature calculated using an emissivity of 0.3. No window correction was necessary for the CaF₂ window. $\bar{V}$ was taken as the difference between the output ($\bar{V}_T$) of the detector when viewing the sample at temperature T, and the output of the detector ($\bar{V}_0$) when viewing a room-temperature piece of cardboard. That is, $\bar{V} = \bar{V}_T - \bar{V}_0$. This tended to minimize the effect of drift in the detector. Even so, there was considerable scatter in the data, and it was found that an accuracy of only five percent was possible for $d\bar{V}/dT$.

Because of the inaccuracy of the $d\bar{V}/dT$ measurements, the overall accuracy of the specific heat measurements was limited to plus or minus five percent with the optical system. For this reason work on the optical system was terminated, and a bridge system was constructed.

BRIDGE SYSTEM

A schematic diagram of the bridge system is shown in Fig. 8. This system measures the ac and dc currents supplied to the sample, the ac and dc voltage across the sample, the frequency of the ac current, the voltage across Z_C , and the impedance Z_A necessary to balance the bridge. With these quantities measured, Eq. (44) can be used to determine the heat capacity of the sample.

The ac and dc current were supplied by the same equipment that was used in the optical system. Again, the ground point is located between the ac and dc power

Fig. 8. Impedance bridge for specific heat measurement.

supplies. If the ground point is located inside the bridge, an ac ground loop can result because there is some capacitance to ground through the output transistors of the dc power supply. To make matters worse, this capacitance depends on the supply voltage. These problems are avoided by positioning the ground point as indicated.

The bridge components are made up of the sample, Z , the other high-current arm, Z_C , and the ratio arms, Z_A and Z_B . The sample in this case may be a wire or a foil connected as a four-terminal resistor with both current and potential leads.

The Z_C arm is made up of the 0.1-ohm standard resistor used in the optical system in series with a 1.0-ohm low-inductance resistor. This arm is capable of carrying ten amps. Initially Z_C was used with only the 0.1-ohm resistor. However,

it was determined that this gave rise to a rather large P_3 , leading to errors in the high frequency operation of the bridge. A one-ohm resistor which would carry ten amps without changes in its resistance was difficult to obtain, so the voltage across Z_C was measured at each current setting and the resistance was calculated by dividing the voltage by the current.

Two ac resistance boxes (J. G. Biddle AC-DC Decade Resistors) were used for the ratio arms. These boxes had five decades each (100-ohm, 10-ohm, 1-ohm, 0.1-ohm, and 0.01-ohm), and were normally operated so that each box had a resistance of at least one hundred ohms. The Z_A arm has a decade capacitor (General Radio Company Polystyrene Decade Capacitor Type 1419-B or 1412-BC) in parallel with the decade resistor. Two different capacitors were used; both had a maximum capacitance of 1 microfarad, but one was a five-decade box while the other had four decades. The two boxes were found to give identical results.

The lock-in amplifier was used in this case as an ac null detector. As before, the reference-channel voltage was taken from the oscillator of the ac power supply. An isolation transformer (Triad Geoformer G-10) was used to isolate the lock-in amplifier from the bridge. The lock-in amplifier could have been operated with a differential input, but it was found that there was less noise pickup with the transformer.

As in the optical case, the digital voltmeter was used to measure the various voltages. It was discovered that the best null could be obtained if the digital voltmeter was disconnected from the bridge during the balancing procedure.

It was found that great care had to be exercised in shielding and wiring the bridge to minimize the ground loops and noise pickup. The shields were constructed according to the principles discussed by Hague.⁴³ The bridge components were arranged so as to minimize the lead length between components while keeping the values of inductive and capacitive coupling small.

The bridge was balanced by an iterative process. First, a rough balance was achieved by adjusting R_A until the dc voltage was ten microvolts or less, then the sample resistance and C_A were adjusted to minimize the ac voltage across the bridge. The phase adjustment on the lock-in amplifier was adjusted so that the amplifier was locked in to the component of the bridge voltage which was in phase with the current, then the dc current was adjusted to give a minimum ac voltage. Next, the phase control was shifted by ninety degrees, and C_A was adjusted to give a minimum ac voltage across the bridge. This process was repeated with increasing sensitivity until the noise limit was reached. The noise which was encountered at low voltage levels seemed to be due to thermal fluctuations in the bridge resistance, particularly in the sample.

The bridge sensitivity was very high; changes in resistance of one part in 10^6 could be readily detected and changes in C_A of ten picofarads were normally detectable. In general, the sensitivity of the balance exceeded the absolute accuracy of the components (0.1% for the resistors and 0.5% for the capacitor).

As in the optical system, the dc and ac currents through the sample were computed by Ohm's law from the dc and ac voltages across the one-tenth-ohm calibrated resistor. The voltages were measured with high accuracy (better than 0.1%) by the digital voltmeter.

The resistance of the sample was measured in two ways: from the bridge balance with $\bar{R} = R_C(R_A/R_B)$ and from the voltage across the sample, v_0 , and the current through the sample, i_0 , with $\bar{R} = v_0/i_0$. In all cases these measurements agreed to better than 0.5%, and they usually agreed to better than 0.1%. However, the measurements were not independent since the resistance R_C was obtained by measuring the voltage across the resistor, v_C , and the current through it, i_C , with $R_C = v_C/i_C$. However, the digital voltmeter was calibrated before and after the experiment and found to be accurate to better than 0.1% in all the ranges used in the data acquisition.

As in the optical case, an electronic counter was used to measure the frequency. By measuring the period rather than the frequency, an accuracy of 0.01% could be achieved.

The zero-degree resistance of each sample was measured in an ice bath with a precision Kelvin bridge.

SAMPLE SELECTION

Tungsten was chosen as the metallic element for study for the following reasons:

- (1) Samples suitable for use in the bridge system were easily obtainable.
- (2) The high-temperature performance of the bridge could be demonstrated with tungsten.
- (3) The literature values for the specific heat of tungsten, which are in good agreement below 1200°K, differ by more than 50% in some cases at temperatures above 3000°K.
- (4) The vacancy contribution to the specific heat has been reported¹⁹ to be large.

The samples were made from a commercially available tungsten light bulb, General Electric Model 6.6A/T4Q/1CL-200-W quartz-iodine lamp. Therefore, the samples consisted of a tungsten filament in series with some lead wires of tungsten and molybdenum.

As in the optical system, the sample was fastened at the ends with the top part of the clamp being connected to the current leads and the bottom part connected to the potential leads of the bridge. In this way the lamp was supported by its leads. The leads were molybdenum wires which were spot-welded to molybdenum foil feedthroughs that passed through the quartz envelope of the lamp. Inside the quartz envelope, the molybdenum foil feedthroughs were spot-welded to tungsten leads which connected to and supported the filament.

During the normal operation of a conventional incandescent lamp, tungsten is transferred from the filament to the wall of the lamp by evaporation from the filament to the wall of the lamp by evaporation and diffusion, or in some cases through the operation of the water cycle.⁴⁴ This effect limited the operation of Lowenthal's¹⁷ equipment to temperatures below 2400°K. In the quartz-iodine lamp, these problems are avoided by the use of the iodine cycle.⁴⁵ When the iodine cycle is operating, iodine atoms produced by the pyrolysis of molecular iodine in the vicinity of the filament diffuse to the wall of the lamp and under the proper conditions react with the adsorbed tungsten, forming a volatile tungsten di-iodide which diffuses to the filament. The tungsten di-iodide is decomposed on the filament, resulting in the deposition of tungsten on the filament and the production of iodine atoms which then diffuse to the wall to repeat the cycle. Pure iodine gas is not used in these lamps, but rather argon is mixed with it to decrease the rate of evaporation of tungsten. In fact, the lamp is supplied with a mixture of argon and iodine which minimizes the rate of transfer of tungsten (approximately 600 mm of argon and 4.5 mm iodine pressure at room temperature).

Argon alone can significantly reduce the rate of evaporation of the tungsten filament. Kraftmacher and Strel'kov¹⁹ were able to obtain specific heat data up to 3600°K using a pure argon atmosphere.

Since it was thought that the action of the iodine cycle might contribute to the measured specific heat, the quartz envelope of one of the lamps was opened, evacuated, and back-filled with xenon (approximately 1/2 atmosphere pressure at room temperature). A second bulb was opened and evacuated to a pressure of less than 10^{-6} Torr and then resealed. Specific heat data was taken on the same samples before and after the gas environment had been changed so that any effect due to the iodine gas could be discovered.

The zero-degree resistance of the lamps was measured before and after the gas environment had been changed. It was discovered that the resistance of the lamp increased slightly after the quartz envelope had been opened by the glass blower. This was attributed to a slight oxidation of the filament.

The masses of all the filaments were measured at the end of the experiment on a precision balance. Care was taken in removing the filament from the leads so that the mass of the entire filament could be measured. In those cases where the gas atmosphere had been changed, the original mass of the filament was calculated from the mass of the filament at the end of the experiment and the zero-degree resistance before and after the gas had been changed. That is, $m = (R'_0/R_0)m'$, where m is the mass of the filament before the envelope was opened to change the gas, m' is the mass of the filament at the end of the experiment, R_0 is the resistance of the filament at zero degrees centigrade before the envelope was opened, and R'_0 is the resistance of the filament at the end of the experiment. The zero degree resistance of the lamps was also measured before and after the lamps were run at high temperature to see if

the possible loss of tungsten through evaporation could be detected. No loss of tungsten was observed in any of the gas-filled lamps.

In order to find the zero-degree resistance of the lamp filaments, it was necessary to measure the zero-degree resistance of the leads to the filament. This was done by attaching leads to the filament after it had been removed from the quartz envelope (at the end of the experiment) and measuring the zero-degree-centigrade resistance of the filament alone. The lead resistance was then calculated by subtracting the filament resistance from the resistance of the lamp (i. e., the filament-plus-lead resistance) which was measured at zero degrees centigrade just before the quartz envelope was broken.

TEMPERATURE MEASUREMENT

Two different methods of temperature measurement were used. The first method was the standard optical pyrometry technique. When this technique was found to be unsatisfactory, a resistance technique was employed.

A recently-calibrated optical pyrometer was used to measure the monochromatic brightness temperature of the filament at a wavelength of 0.65 microns. The true temperature was then calculated using emissivity data in the review by Thorn and Winslow.⁴⁶ Accurate results could not be obtained using this method because the brightness temperature of the filament was very nonuniform. The nonuniform brightness temperature probably was caused by the radiation conditions associated with the filament being wound in the form of a double helix. An attempt was made to measure the brightness temperature on selected portions of the filament, but this proved to be impractical.

The resistance technique used was the same one that Kraftmacher and Streikov¹⁹ used in their measurement of the specific heat of tungsten. As discussed previously, the resistance of the sample was measured during the experiment. Therefore, it was possible to calculate the relative resistance of the tungsten filament, R_T/R_{273} where R_T is the resistance of the filament at the temperature $T^\circ\text{K}$ and R_{273} is the resistance of the filament at 273°K . The procedure which was used to measure R_{273} has been discussed above. The resistance of the filament at elevated temperature, R_T , was found by subtracting the lead resistance from the total sample resistance. The lead resistance was taken to be the lead resistance as measured at 273°K as previously described. This procedure neglected the change in lead resistance with temperature, but the error introduced was one percent or less.

Literature values⁴⁷ of the relative resistance of tungsten versus temperature were fit by the method of least squares to the piecewise quadratic function

$$(R_T/R_{273})_i = a_i + b_i T + c_i T^2 \text{ with } i = 1, 2, 3$$

where $i = 1$ was used in the region 273°K to 1500°K, $i = 2$ was used in the region 1300°K to 2500°K, and $i = 3$ was used in the region 2300°K to 3600°K. The three equations were then solved to give the temperature as a function of the relative resistance. Using these equations and the measured values of the relative resistance, the temperature of the filament was calculated.

The functions $(R_T/R_{273})_i$ were also used to calculate $(dR/dT)_T$. That is,

$$(dR/dT)_T = R_{273}(b_i + 2c_i T) \text{ with } i = 1, 2, 3$$

where i indicates the same set of ranges as above. These data are given in Table 1.

Table 1. The functions $(R_T/R_{273})_i$ and $(dR/dT)_T$.

273°K $\leq T \leq 1500$ °K

$$(R_T/R_{273})_1 = (-0.253) + (4.335 \times 10^{-3})T + (0.687 \times 10^{-6})T^2$$

$$(dR/dT)_T = (R_{273})[(4.335 \times 10^{-3}) + (1.375 \times 10^{-6})T]$$

1300°K $\leq T \leq 2500$ °K

$$(R_T/R_{273})_2 = (-0.796) + (5.190 \times 10^{-3})T + (0.353 \times 10^{-6})T^2$$

$$(dR/dT)_T = (R_{273})[(5.190 \times 10^{-3}) + (0.705 \times 10^{-6})T]$$

2300°K $\leq T \leq 3600$ °K

$$(R_T/R_{273})_3 = (-1.278) + (5.613 \times 10^{-3})T + (0.260 \times 10^{-6})T^2$$

$$(dR/dT)_T = (R_{273})[(5.613 \times 10^{-3}) + (0.521 \times 10^{-6})T]$$

Langmuir⁴⁸ has criticized the use of the relative resistance technique. He claims that

"the method proves to be one of the least accurate methods of estimating temperatures for the following reasons: (1) The resistance increases relatively slowly with the temperature as compared with most other properties used for temperature estimation. (2) The resistance and its temperature coefficient are very sensitive to traces of impurities (carbon). (3) At room temperature the resistance of the filament is often so low that uncertainties in the lead and contact resistance are apt to play a large part."

With the greater accuracy of modern experimental apparatus and the use of digital computers to aid in fitting data to empirical relations, Langmuir's first point is not as important as it was when he wrote it. This can also be said of the third point since the effects due to lead and contact resistance can be adequately accounted for. The second point is still a valid objection. The literature values of the relative resistance

cited above may or may not be for pure tungsten; no analysis of the tungsten used is given by the authors. However, Kraftmacher and Strelkov¹⁹ checked the data at selected temperatures and found reasonable agreement between their data and the literature values cited above.

Experimental Results

The resistances at zero degrees centigrade, the masses and the gas environments of the tungsten filaments used in the experiment are listed in Table 2.

Table 2. Tungsten filaments and gas environments in the experiments.

Sample No.	Resistance @ 0°C	Mass	Gas
1a	0.2461 Ω	0.1662 g ^a	Ar + I ₂
1b	0.2474 Ω	0.1653 g	Vacuum
2a	0.2502 Ω	0.1714 g ^a	Ar + I ₂
2b	0.2515 Ω	0.1705 g	Xenon
3	0.2507 Ω	0.1746 g	Ar + I ₂
4	0.2408 Ω	0.1643 g	Ar + I ₂

^aValue calculated from the equation

$$m_a = (m_b \times R_{0b}) / (R_{0a})$$

where m_a is the mass of sample number 1a or 2a, m_b is the mass of sample number 1b or 2b, R_{0b} is the resistance at 0°C of sample number 1b or 2b, and R_{0a} is the resistance at 0°C of sample number 1a or 2a.

Measurements of R_A , C_A , i_0 , and i_{rms} were generally made at 20 Hz, 25 Hz, 35 Hz, 45 Hz, 55 Hz, 65 Hz, 75 Hz, 85 Hz, and 95 Hz for each value of the temperature, $\bar{T}$. However, some of the data were taken at 20 Hz, 25 Hz, 35 Hz, 55 Hz, 75 Hz, and 95 Hz. These data are tabulated in Appendix C. The system of equations of the form

$$\frac{(R_{Ak} C_{Ak})}{(1 + \omega_k^2 C_{Ak}^2 R_{Ak}^2)} = [P_2] \times \left[\frac{\left(\frac{i_{0k}^2 P_1}{(1 + \omega_k^2 P_1^2)} \right) + \frac{\left(\frac{i_{rms,k}^2 P_1}{2(1 + 4\omega_k^2 P_1^2)} \right)}{2} \right] + P_3 \quad (49)$$

(where there is one equation for each value of k , with $\omega_1 = 20$ Hz, $\omega_2 = 25$ Hz, etc., and R_{Ak} , C_{Ak} , i_{0k} , and $i_{rms,k}$ are the measured values of R_A , C_A , i_0 , and i_{rms} at frequency ω_k) was solved for P_1 , P_2 , and P_3 . Then Eq. (47), along with the value of $(dR/dT)_{\bar{T}}$ (calculated from the computer fit of the literature values of the relative resistance versus temperature) was used to calculate the heat capacity of the filament. Finally, the specific heat was calculated by dividing the heat capacity of the filament by its mass, that is,

$$\bar{c}_p = \bar{C}_p/m = (2/m)(P_1/P_2) \times (dR/dT)_{\bar{T}}. \quad (50)$$

These results are listed in Table 3.

The system of equations (49) with either six or nine equations is an overdetermined system which is nonlinear in P_1 , but linear in P_2 and P_3 . The solution of this system for P_1 , P_2 , and P_3 was based upon a modified least-squares procedure which was programmed to run on a Control Data Corporation 6600 digital computer.

An initial value of P_1 was chosen (i. e., $P_1 = P_{11}$) and then values of P_2 and P_3 were calculated to give initial values of $P_2 = P_{21}$ and $P_3 = P_{31}$. This calculation was done using a program called MLR, developed by R. E. von Holdt.⁴⁹ In this case the program determined the values $P_2 = P_{21}$ and $P_3 = P_{31}$ such that the sum of the squares of the residuals was minimized, that is,

$$sq_1 \equiv \sum_k (R_{1k})^2 = \sum_k [Y_k - YC_k(P_1, P_2, P_3)]^2 \text{ is minimized for } P_1 = P_{11}$$

when

$$P_2 = P_{21} \text{ and } P_3 = P_{31}.$$

where sq_1 is the sum of the squares of the residuals, R_{1k} ,

$$Y_k \equiv (R_{Ak} C_{Ak}) / (1 + \omega_k^2 C_{Ak}^2 R_{Ak}^2),$$

and

$$YC_k(P_1, P_2, P_3) \equiv [P_2] \times \left[\frac{(i_{0k}^2 P_1)}{(1 + \omega_k^2 P_1^2)} + \frac{(i_{rms,k}^2 P_1)}{2(1 + 4\omega_k^2 P_1^2)} \right] + P_3.$$

Table 3. Measured and calculated experimental parameters.

T (°K)	R_T/R_0 (Ω/Ω)	$(dR/dT)_T$ ($\Omega/^\circ\text{C}$)	P_1 (sec)	P_2 ($\text{\AA}^{-2}$)	P_3 (sec)	sq (sec^2)	No. data points	$\bar{c}_p$ (cal/mole-°K)
Sample No. 1a (Ar + I ₂)								
726	3.258	0.001324	2.0937	3449.5	0.06206	0.000154	9	6.30
934	4.398	0.001393	2.0883	7528.8	0.13244	0.008843	9	6.48
935	4.399	0.001393	2.0887	5059.5	0.08847	0.000290	9	6.44
1134	5.545	0.001447	2.0952	4555.2	0.07887	0.001529	9	6.62
1325	6.702	0.001496	2.0781	5355.8	0.09315	0.000391	9	6.88
1513	7.866	0.001540	2.0487	4826.0	0.08444	0.000953	9	7.12
1699	9.041	0.001572	1.9823	4161.8	0.07317	0.015496	9	7.31
1885	10.241	0.001605	1.9796	5060.1	0.09045	0.004160	9	7.59
2068	11.449	0.001637	1.9896	7531.3	0.13711	0.002941	9	7.88
2251	12.675	0.001668	1.9364	5499.4	0.10114	0.000758	9	8.11
2419	13.827	0.001692	1.9237	5437.6	0.10160	0.001137	9	8.36
2562	14.816	0.001711	1.8901	5012.3	0.09532	0.001020	9	8.60
2705	15.814	0.001728	1.8658	4751.6	0.09267	0.001018	9	8.91
2847	16.818	0.001746	1.8389	4431.3	0.08939	0.001907	9	9.31
2990	17.838	0.001764	1.8083	4200.3	0.08872	0.000844	9	9.85
3134	18.870	0.001783	1.7633	4283.5	0.09631	0.003918	9	10.60
3206	19.399	0.001792	1.4691	5440.8	0.12737	0.007869	9	11.09
3279	19.927	0.001801	1.3972	4540.1	0.11100	0.060390	9	11.64
Sample No. 1b (Vacuum)								
831	3.824	0.001368	2.1338	3524.9	0.06074	0.000068	9	6.26
1032	4.956	0.001425	2.1163	4789.4	0.08194	0.000228	9	6.48
1226	6.095	0.001477	2.1157	6805.1	0.11675	0.000088	9	6.73
1413	7.242	0.001526	2.0975	8275.6	0.14298	0.000099	9	7.01
1597	8.397	0.001563	2.0728	6150.1	0.10724	0.000148	9	7.24
1779	9.559	0.001594	2.0409	6966.9	0.12304	0.000318	9	7.48
Sample No. 2a (Ar + I ₂)								
922	4.331	0.001412	2.0881	3750.2	0.06677	0.000070	9	6.44
3166	19.108	0.001817	1.5029	4653.6	0.10870	0.005504	9	10.86
Sample No. 2b (Xenon)								
815	3.735	0.001386	2.1272	2668.8	0.04697	0.000914	9	6.29
917	4.299	0.001419	2.1131	4235.2	0.07414	0.000215	9	6.40
1016	4.860	0.001449	2.1197	6118.8	0.10655	0.000288	9	6.50
1112	5.419	0.001472	2.1226	7281.5	0.12684	0.000207	9	6.61
1207	5.981	0.001499	2.1196	8092.3	0.14086	0.000342	9	6.72

Table 3. (Continued)

T (°K)	R_T/R_0 (Ω/Ω)	$(dR/dT)_T$ ($\Omega/^\circ K$)	P_1 (sec)	P_2 (A^{-2})	P_3 (sec)	Sq (sec^2)	No. data points	$\bar{c}_p$ (cal/mole-°K)
Sample No. 2b (Xenon)(Continued)								
1299	6.541	0.001524	2.1045	5777.8	0.10161	0.000432	9	6.84
1390	7.107	0.001544	2.1018	6541.2	0.11417	0.000017	6	6.95
1482	7.676	0.001568	2.0920	6328.8	0.11106	0.000089	6	7.09
1574	8.249	0.001584	2.0777	7043.3	0.12430	0.000127	6	7.21
1664	8.820	0.001600	2.0507	6148.1	0.10912	0.000019	6	7.32
1754	9.393	0.001616	2.0319	5177.8	0.09225	0.000463	6	7.42
1843	9.973	0.001632	2.0191	5666.8	0.10168	0.000609	6	7.55
1933	10.555	0.001648	2.0090	5881.5	0.10624	0.000087	6	7.67
2022	11.142	0.001664	1.9849	5429.2	0.09843	0.000414	6	7.77
2111	11.732	0.001680	1.9842	6639.9	0.12134	0.002769	6	7.91
2199	12.324	0.001695	1.9936	7422.9	0.13667	0.004392	6	8.04
2287	12.922	0.001711	1.9831	7926.3	0.14703	0.003998	6	8.18
2375	13.520	0.001726	1.9633	7916.2	0.14805	0.005138	6	8.32
2462	14.125	0.001738	1.9256	5639.3	0.10629	0.001247	6	8.44
2550	14.730	0.001746	1.9176	5810.0	0.11078	0.001720	6	8.58
2638	15.342	0.001757	1.9052	5896.0	0.11409	0.002669	6	8.76
2654	15.458	0.001759	1.8790	5170.4	0.10019	0.001543	9	8.78
2725	15.953	0.001768	1.8547	4677.9	0.09178	0.000150	6	8.95
2813	16.571	0.001780	1.8560	4091.3	0.09227	0.000572	6	9.20
2900	17.191	0.001791	1.8346	4403.5	0.09054	0.000276	6	9.49
2987	17.816	0.001803	1.7908	7398.5	0.08030	0.005420	6	9.82
3076	18.452	0.001814	1.5425	5401.0	0.11879	0.011427	9	10.28
3146	18.962	0.001824	1.5527	8873.0	0.20205	0.003389	9	10.70
Sample No. 3 (Ar + I ₂)								
1117	5.446	0.001470	2.1077	5020.1	0.08973	0.000878	9	6.61
1490	7.725	0.001565	2.0488	3581.4	0.06393	0.004062	9	7.02
1854	10.039	0.001630	2.0309	6306.6	0.11625	0.004159	9	7.56
Sample No. 4 (Ar + I ₂)								
953	4.504	0.001368	2.1174	5372.9	0.09443	0.000379	9	6.42
953	4.504	0.001368	2.1356	6230.9	0.11024	0.000524	9	6.46
3200	19.353	0.001753	1.5582	5439.6	0.12847	0.004549	9	11.07
3202	19.364	0.001754	1.5536	5542.1	0.13080	0.004459	9	11.06
3346	20.425	0.001771	1.5000	7453.9	0.19462	0.002896	6	12.36
3383	20.691	0.001776	1.4987	6024.4	0.16219	0.004354	6	12.78
3418	20.954	0.001780	1.4927	9443.3	0.26324	0.006638	6	13.27

^aData taken after the highest temperature data.

The next step was to choose a new value of P_1 such that $sq_2 < sq_1$, then $P_1 = P_{12}$, $P_2 = P_{22}$, and $P_3 = P_{32}$. This process was repeated until $sq_{k+1} = sq_k$ (normally sixty iterations). The computer time for the total process was usually about 0.1 minute.

The above procedure gave values of P_1 , P_2 , and P_3 which gave a value of sq which was very close to the actual minimum. These values along with the final value of sq are given in Table 3.

Errors in P_1 , P_2 , and P_3 could have been introduced in the measurement of R_A , C_A , i_0 , i_{rms} , and ω , and in the use of Eq. (46) which is not an exact expression. The errors introduced in the measurement process were a few tenths of a percent at most because the bridge could be balanced with great precision (normally better than 0.1%) and the absolute accuracy of the bridge resistors and capacitors and the absolute accuracy of the current measurements were all better than half a percent. The random errors in the measurements had a minimal effect on the calculated values of P_1 , P_2 , and P_3 due to the least-squares procedure used in the calculation. The approximations involved in deriving Eq. (46) were checked and found to introduce negligible errors. This is also verified by the fact that the sum of the squares of the residuals for the calculated values of P_1 , P_2 , and P_3 is very small, indicating that the form of Eq. (46) is correct.

The above considerations indicate that the errors in P_1 , P_2 , and P_3 are certainly less than one percent. However, the error in the temperature is unknown since the temperature measurement depends upon the values of the relative resistance versus temperature, which are of unknown accuracy. The temperature measurement is certainly no better than one percent and an error of five percent would not be surprising in the high temperature region. The errors introduced in the temperature measurement are reflected in the specific heat as calculated by using Eq. (50) through the $(dR/dT)_{\bar{T}}$ term. Therefore, there is an unknown error in the value of the specific heat and in the temperature at which it was measured. As an overall estimate, the specific heat data probably is accurate to plus or minus one percent at the low temperatures with decreasing accuracy as the temperature is increased, until near the melting point an accuracy of plus or minus three percent might be expected.

The data discussed above were taken with the dc current, i_0 , much larger than the ac current, i_{rms} . An experiment was performed with i_{rms} only slightly smaller than i_0 to determine if the calculated specific heat was independent of the relative size of i_{rms} . Changing the size of i_{rms} with respect to i_0 changes the amplitudes of the ac temperatures, ΔT_1 and ΔT_2 , while keeping the frequency and the average temperature the same. The results of this experiment are shown in Table 4. Only a small effect was observed, less than one percent change in the specific heat resulted from doubling the size of the ac current. This experiment suggests that by changing the ratio of ac current to dc current when the frequency is changed, the amplitude of

Table 4. Data from $i_{rms} \leq i_0$ experiment.

T (°K)	R_T/R_0 (Ω/Ω)	$(dR/dT)_T$ ($\Omega/^\circ K$)	P_1 (sec)	P_2 (A^{-2})	P_3 (sec)	s_q (sec^2)	No. data points	i_0 (A)	i_{rms} (A)	$\bar{c}_p$ (cal/mole-°K)
2063	11.415	0.001635	2.0040	7283.8	0.13285	0.002529	9	3.526	0.500	7.88 ^a
2063	11.414	0.001635	1.9968	4621.9	0.08476	0.000362	8	3.422	1.000	7.93 ^a
953	4.504	0.001368	2.1174	5372.9	0.09443	0.000379	9	1.575	0.100	6.42 ^b
953	4.504	0.001368	2.1356	6230.9	0.11024	0.000524	9	1.552	0.300	6.46 ^b
3200	19.353	0.001753	1.5582	5439.6	0.12847	0.004549	9	6.668	0.500	11.07 ^b
3202	19.364	0.001754	1.5536	5542.1	0.13080	0.004459	9	6.679	0.250	11.06 ^b

^aData taken on Sample No. 1 (Ar + I₂).^bData taken on Sample No. 4 (Ar + I₂).

the ac temperature could be held fixed. Therefore, frequency dependent phenomena could be investigated at a constant ac temperature amplitude.

Some experimenters⁵⁰⁻⁵³ have observed time-dependent specific heats near the melting point in certain metals and semi-metals; an experiment was performed to find out if such an effect occurred in tungsten. The data at 3279°K was analyzed in the standard way and then divided into two groups, low-frequency data (20 Hz, 25 Hz, 35 Hz, and 45 Hz) and high-frequency data (55 Hz, 65 Hz, 75 Hz, 85 Hz, and 95 Hz), which were then analyzed separately. The results are presented in Table 5. The specific heat calculated from the high-frequency data is slightly larger (approximately one percent larger) than the specific heat calculated from the low-frequency data. This effect, which appears to be slightly larger than the experimental errors, is the same kind of effect that Smith⁵² observed in germanium.

Table 5^a. Data from frequency dependence analysis.

T (°K)	R_T/R_0 (Ω/Ω)	$(dR/dT)_T$ ($\Omega/^\circ K$)	P_1 (sec)	P_2 (A^{-2})	P_3 (sec)	s_q (sec^2)	No. data points	Frequencies used (Hz)	$\bar{c}_p$ (cal/mole-°K)
3279	19.927	0.001801	1.3972	4540.1	0.11100	0.060390	3	20 to 95	11.64
3279	19.927	0.001801	1.1736	3645.0	0.08879	0.036250	4	20 to 50	11.60
3279	19.927	0.001801	1.5378	239976	5.91000	0.001218	5	55 to 95	11.73

^aData taken on Sample No. 1 (Ar + I₂).

Discussion

The specific heat data from Table 2 is plotted in Fig. 9. A large increase (or excess) in the specific heat of tungsten at constant pressure can be observed at temperatures higher than 2750°K. As was pointed out in the introduction, this is a rather

Fig. 9. Heat capacity of tungsten at constant pressure.

common phenomena in metals. It is generally believed that there are three effects which can contribute to the high temperature excess specific heat in metals: the dilation term (i. e., the difference between the specific heat at constant pressure, c_p , and the specific heat at constant volume, c_v), the effects due to anharmonic lattice vibrations, and the contribution of lattice defects to the specific heat.

The dilation term is given by the standard thermodynamic formula,

$$c_p - c_v = (V\alpha^2/\kappa)T \quad (51)$$

where V is the specific volume, α is the coefficient of volume expansion, κ is the isothermal compressibility, and T is the absolute temperature. If data were available for V , α , and κ at sufficiently high temperatures, then it would be possible to calculate the dilation term and thus convert the specific heat data at constant pressure to its constant-volume value. Unfortunately, reliable data are only available for a few metals. Therefore, approximations for the dilation term are normally used.

Two approximations for the dilation term are in common use: the Grueneisen relation,

$$(V\alpha^2/\kappa) = \alpha G c_V \quad (52)$$

where G is Grueneisen's constant which is assumed to be independent of temperature, and the Nerst-Lindemann relation,

$$(V\alpha^2/\kappa) = A' c_p^2 \quad (53)$$

where A' is the Nerst-Lindemann constant which is also assumed to be independent of temperature. In general, both of these approximations have been found to be rather poor, but in most cases^{32,54,55} where they have both been compared with an experimental determination of the dilation term based upon Eq. (51), the Nerst-Lindemann relation proved to be a better approximation than the Grueneisen relation. Another way to approximate the dilation term is to expand it in a power series in T ,

$$(V\alpha^2/\kappa)T = d_0 + d_1 T + d_2 T^2, \quad (54)$$

over the temperature range of interest.

Once a suitable approximation for the dilation term has been chosen, the heat capacity at constant pressure may be reduced to its constant-volume value. Then the specific heat at constant volume can be subdivided into two components, the specific heat of the lattice at constant volume, c_L , and the specific heat of the electrons at constant volume, c_E . The lattice specific heat may be decomposed into three terms: the harmonic specific heat at constant volume, c_H , the anharmonic specific heat at constant volume, c_A , and the specific heat due to lattice defects at constant volume, c_V . Therefore, the specific heat at constant pressure becomes

$$c_p = c_D + c_E + c_H + c_A + c_V \quad (55)$$

where c_D is the dilation term.

The electronic specific heat at constant volume can be approximated by⁵⁶

$$c_E = \gamma T \left[1 - \frac{3\pi^2}{10} (T/T_F)^2 \right] \quad (56)$$

where γ is the electronic specific heat coefficient and T_F is the Fermi temperature. In most cases, the second term in Eq. (56) is less than one percent of the first term and may be neglected. That is,

$$c_E = \gamma T. \quad (57)$$

Most derivations of the lattice specific heat start with an expansion of the potential energy of the lattice in a power series in the displacements of the atoms from their equilibrium positions. If this series is terminated at the quadratic terms, the potential energy appears as a homogeneous quadratic form, the linear terms being zero because of the equilibrium conditions. The specific heat derived from this harmonic approximation of the potential energy is called the harmonic lattice specific heat. The difference between the harmonic lattice specific heat and the total lattice specific heat is called the anharmonic lattice specific heat. It should be noted that the dilation term is an anharmonic specific heat since it is not included in a harmonic lattice approximation. However, it is more convenient to analyze the lattice specific heat at constant volume where the dilation term can be treated separately.

Unfortunately, an exact expression for the harmonic lattice specific heat is not available. Therefore an approximation must be used. The Debye theory, in which the specific heat is given by⁵⁷

$$c_H = c_{\text{Debye}} = 9R(T/\theta)^3 \int_0^{(\theta/T)} \frac{x^4 e^x}{(e^x - 1)^2} dx \quad (58)$$

where R is the gas constant and θ is the so-called Debye temperature. This is one of the most useful approximations of the harmonic lattice specific heat. Tables of c_{Debye} versus (θ/T) are available⁵⁸; however, at high temperature ($T \gg \theta$) c_{Debye} can be approximated by the following expression:

$$c_{\text{Debye}} \approx 3R - \frac{3R}{20} \left(\frac{\theta}{T} \right)^2. \quad (59)$$

A theoretical expression for the anharmonic specific heat is not available. Generally, calculations⁵⁹⁻⁶³ have suggested that the anharmonic lattice specific heat is small and perhaps negative in some cases. However, these calculations can only be regarded as crude approximations. An analysis of the experimental specific heat data of aluminum³² and copper⁵⁴ indicates that for these metals the anharmonic specific heat is not small and is positive. Until more accurate theoretical work becomes available, it appears that a power series expansion in the temperature is the

most suitable way of representing the anharmonic lattice specific heat. That is,

$$c_A = a_0 + a_1 T + a_2 T^2 \quad (60)$$

over the temperature range of interest.

Lattice defects are usually divided into two groups, line defects and point defects. Line defects will be considered to include dislocations, substructure (polygonization), and grain boundaries. Although dislocation climb and polygonization do produce thermal effects, the concentration will be small in a well-annealed sample. The presence of line defects will alter the phonon spectrum in an unknown manner, and therefore, the possibility of some detectable effect on the specific heat cannot be ruled out. However, there is no experimental or theoretical evidence presently available to indicate that such effects would be large.

In a well-annealed sample, the concentration of point defects will be in thermal equilibrium. The equilibrium mole fraction of point defects, X_V , of one type (e. g., vacancies, di-vacancies, or interstitials) is given by⁶⁴

$$X_V = A[\exp(-\Delta E_V^0/RT)] \quad (61)$$

where ΔE_V^0 is the standard energy of formation at constant volume of one mole of vacancies, R is the gas constant, and A is usually referred to as the pre-exponential factor and contains all entropy terms other than the configurational entropy. In particular, A is usually given as⁶⁴

$$A = \exp(\Delta S_V^0/R) \quad (62)$$

where ΔS_V^0 is the standard entropy of formation of the defect. Now the energy absorption due to the defect formation at a given temperature is given by

$$\Delta E_V = (\Delta E_V^0)(X_V) = A(\Delta E_V^0)[\exp(-\Delta E_V^0/RT)]. \quad (63)$$

Therefore, the excess specific heat due to the point defect is

$$\Delta c_V = (d\Delta E_V/dT)_V = (A/R)(\Delta E_V^0/T)^2 [\exp(-\Delta E_V^0/RT)]. \quad (64)$$

In most metals, monovacancy point defects can be expected to make the principal contribution to the specific heat. Interstitials, di-vacancies, and other

point defect clusters may exist in the lattice, but their concentrations under conditions of thermal equilibrium should be small. Borelius^{65,66} has attempted to show that more than one defect must be considered in attempting to interpret high temperature specific heat data. However, the work of Brooks⁵⁴ and Brooks and Bingham³² on copper and aluminum tends to refute Borelius.

From an experimental point of view, it does not appear that specific heat data of sufficient accuracy can be obtained to allow for the separation of specific heat contributions from more than one lattice defect if anharmonic effects are included. Therefore, it will be assumed that the specific heat due to lattice defects at constant pressure can be approximated by the specific heat due to monovacancies. That is,

$$c_V = \Delta c_V \quad (65)$$

where ΔE_V^0 is now the energy of formation at constant volume of monovacancies, and A is given by Eq. (62) with ΔS_V^0 the entropy of formation of monovacancies.

The above approximations can be used to give an equation for the high-temperature specific heat of metals. That is, combining Eq. (55) with Eqs. (54), (57), (56), (60), (64), and (65), we find

$$c_p - c_{\text{Debye}} = p_1 + p_2 T + p_3 T^2 + (p_4/T^2) \{\exp(p_5/T)\} \quad (66)$$

with

$$\begin{aligned} p_1 &= d_0 + a_0, \\ p_2 &= d_1 + a_1 + \gamma, \\ p_3 &= d_2 + a_2, \end{aligned} \quad (67)$$

and

$$p_4 = \frac{A}{R} (\Delta E_V^0)^2,$$

and

$$p_5 = (-\Delta E_V^0/R). \quad (68)$$

Alternately, if Eq. (53) is used rather than Eq. (54), we have

$$c_p - c_{\text{Debye}} - A'Tc_p^2 = p_1' + p_2'T + p_3'T^2 + (p_4/T^2) [\exp(p_5/T)] \quad (69)$$

where

$$p_1' = a_0, \quad p_2' = a_1 + \gamma, \quad p_3' = a_2. \quad (70)$$

Both Eq. (66) and Eq. (69) contain at least five unknown parameters, p_1 through p_5 . If the Debye temperature, θ , is treated as an unknown, then there are six unknowns which must be determined from the experimental data. This is possible because of the special form of Eqs. (66) and (69) where each term has a temperature dependence which is quite different from the temperature dependence of each of the other terms. It would appear that A' in Eq. (69) could be treated as an unknown; however, the temperature dependence of this term is not sufficiently different from the other terms in the equation to allow reliable evaluation of all seven unknowns. Therefore, when Eq. (69) is used, a value of A' from other experiments must be used.

A computer program was written to fit experimental specific heat data with Eq. (66) or (69). In form it was very similar to the program which was used to calculate the specific heat from the bridge data; that is, a modified least-squares procedure was used. An initial value of p_5 and θ were chosen, then values of p_1 , p_2 , p_3 , and p_4 (or p_1' , etc.) were calculated using the MLR program. A new value of p_5 was then found, holding θ fixed, which would give a smaller value of the sum of the squares of the residuals when the new values of p_1 , p_2 , p_3 , and p_4 (or p_1' , etc.) were calculated. This process was repeated enough times so that an accurate approximation to the true minimum value of the sum of the squares of the residuals could be achieved. If the initial value of θ was chosen as a literature value of the Debye temperature, then the above process would give the best fit to the data in the least-square sense for that value. If the Debye temperature were treated as an unknown, then upon completion of the above process θ was varied while holding p_5 fixed to further reduce the sum of the squares of the residuals. The last step was to again hold the Debye temperature, θ , fixed (at its new value) and vary p_5 to reduce the sum of the squares of the residuals still further. In this way an accurate approximation of the best fit to the experimental data (in the least-square sense) by Eq. (66) or (69) could be found.

A second computer program was written which determined the best fit to experimental specific heat data (in the least-square sense) with the Debye temperature chosen so that p_1 would be approximately equal to zero. This program was almost identical to the one described above. However, in this program θ was varied while holding p_5 fixed so that the absolute value of p_1 was reduced to a value near zero.

If specific heat data were to be fit over the entire temperature range of a solid (zero degrees Kelvin to the melting temperature), then d_0 in Eq. (54) and a_0 in Eq. (60) must be zero since the dilation term and the anharmonic lattice specific heat must be zero at zero degrees Kelvin. That is, p_1 and p_1' would have to be zero if specific heat data were fit at low temperatures. Similarly, if high temperature specific heat data was to be extrapolated to very low temperatures, p_1 and p_1' should be zero. In this case, the second program should be used.

In general, the two programs will give different values for the Debye temperature, θ . The first program will give a Debye temperature which is an average of the Debye temperature over the range of the experimental data. The second program will give a Debye temperature which should be comparable to the Debye temperature determined by low-temperature specific heat data. Of course, neither of the Debye temperatures will have any meaning if the approximations involved in deriving Eq. (66) or (69) are not valid. Furthermore, the second program should not be expected to give a good approximation to the low-temperature Debye temperature for high-melting-point solids where the high-temperature specific heat data is obtained at temperatures very much higher than the Debye temperature.

In order to compare the accuracy of the various methods used to fit the specific heat data, the average root-mean-square (RMS) error, $\bar{\epsilon}_{\text{RMS}}$, of each fit can be calculated. This is just the square root of the sum of the squares of the residuals. Unfortunately, the average RMS error is not very useful when comparing fits with different numbers of unknowns. Clearly, the larger the number of unknowns calculated in the least-squares fitting procedure, the smaller will be the value of the average RMS error.

If it is postulated that the only reason that the root-mean-square error is not zero is that there are independent random errors in the experimental data points, then it is possible to obtain additional information about the accuracy of the least-squares fit. This point is thoroughly discussed by Hildebrand.⁶⁷ In particular, an estimate for the RMS deviation between the observed function and its calculated approximation over the $N + 1$ data points may be calculated. That is,

$$E_{\text{RMS}} = [(N + 1)/(N - n)]^{1/2} \times \epsilon_{\text{RMS}} \quad (71)$$

where $N + 1$ is the number of unknown parameters in the fitting function. This equation is meaningless when $N = n$, since all the data are then needed to determine the unknown parameters, and no data remain for the estimation of the error.

Unfortunately, it is not possible to assume that the only reason that the average RMS error is not zero is that there are independent random errors in the experimental data points, when fitting specific heat data. Since the fitting functions are known to be approximations rather than exact expressions, the experimental data cannot be expected

to deviate from these functions in a random way. Under these circumstances, a calculated value of E_{RMS} from Eq. (71) is meaningless.

The above programs were used to analyze the data of Brooks and Bingham³² on aluminum, and Brooks et al.³³ on copper. These authors estimate that their data has an absolute error of ± 0.7 percent. The data were used in three different fitting procedures. The first fit used the Debye temperatures given in the papers of Brooks and Bingham³² and Brooks.⁵⁴ The second fit was done with the Debye temperature treated as an unknown and a value determined which minimized the sum of the squares of the residuals. The third fit again treated the Debye temperature as an unknown, but in this case, the second program was used to find a value of θ which minimized the absolute value of p_1 . The three values of the Debye temperature will be denoted by θ_L , θ_M , and θ_0 , respectively.

The results are shown in Table 6 and in Figures 10 and 11. The curves in the figures were made using the results of the second fit. Table 6 includes data on the

Table 6. Three fits of data on aluminum³² and copper.³³

Metal	θ (°K)	P_1	P_2	P_3	P_4	$-P_5$	$\bar{\epsilon}_{RMS}$	ΔE_V^0 (eV)	$\Delta S_V^0/R$	$c_{mp}(\%)$
Aluminum	$\theta_L = 405$	0.1373	0.03234	2.106	3851	85.21	0.00761	0.735	3.28	0.29
Aluminum	$\theta_M = 453$	0.4764	-0.969	2.936	10410	96.78	0.00705	0.834	4.02	0.18
Aluminum	$\theta_0 = 380$	-0.0352	0.5551	1.660	2738	80.90	0.00765	0.698	3.05	0.37
Copper	$\theta_L = 314$	-0.157	1.149	-0.00985	5638	11.00	0.00372	0.950	3.15	0.70
Copper	$\theta_M = 287$	-0.21	1.437	-0.210	4295	10.54	0.00330	0.909	2.97	0.83
Copper	$\theta_0 = 353$	0.01881	0.7149	0.2829	9240	11.82	0.00491	1.019	3.50	0.55

Note: The values give for p_1 through p_5 have units corresponding to the specific heat in units of cal/mole-°K and the temperature in units of kilo-degrees Kelvin. In this set of units $\Delta E_V^0 = -R \times p_5$ is given in kilo-cal/mole, which can then be converted to electron volts by multiplying by 0.434 (i.e., $\Delta E_V^0 = -0.434 \times R \times p_5$ eV with $R = 1.99$ cal/mole-°K).

energy of formation of vacancies, ΔE_V^0 , the entropy of formation of vacancies, $\Delta S_V^0/R$, and the mole percent of vacancies at the melting temperature of the metal, c_{mp} . ΔE_V^0 was calculated using Eq. (68),

$$\Delta E_V^0 = -R \times p_5. \quad (72)$$

A was calculated using Eq. (68), note also,

$$A = (p_4)/(R \times p_5^2), \quad (73)$$

so that $\Delta S_V^0/R$ could be calculated using Eq. (62),

$$\Delta S_V^0/R = \ln(A). \quad (74)$$

c_{mp} was calculated using Eq. (61),

$$c_{mp} = 100 \times A[\exp(-\Delta E_V/RT_{mp})] \quad (75)$$

where T_{mp} is the temperature at the melting point of the metal.

In Table 7, the two values for the Debye temperature, θ_M , and θ_0 , obtained using the second and third fitting procedures are compared with various values of the

Table 7. Various calculations of the Debye temperature.

Metal	θ_M	θ_0	θ_0^S	θ_{298}^S	θ^M	θ_0^E	θ_{298}^E	θ_m^R	θ_m^D	θ_{298}^I
Aluminum	453	380	423	390	378	428	403	422	390	383
Copper	287	353	342	310	333	345	332	336	320	308

Note: All temperatures are given in degrees Kelvin.

Debye temperature taken from Gschneider's compilation.⁶⁸ The Debye temperature as determined from specific heat measurements is designated as θ^S , and any subscript which may be given indicates the particular temperature (absolute) at which θ^S was evaluated. θ^M refers to the Debye temperature calculated from the Lindemann equation,

$$\theta^M = K(T_{mp}/M)^{1/2} \times (1/V)^{1/3}$$

where $K = 138.5$, M is the atomic mass, and V is the atomic volume. θ^E refers to the Debye temperature as determined from elastic constants; again, the subscript indicates the particular temperature (absolute) at which θ^E was evaluated. θ_m^R is the Debye temperature determined from the electrical resistivity data. These Debye temperatures usually correspond to an average value for a wide range of temperatures, thus a subscript m is used. θ_m^D is the Debye temperature determined from thermal expansion data. θ_{298}^I is the Debye temperature at 298°K as determined from x-ray intensity data.

The fitting procedure was not very sensitive to the Debye temperature since the average error, ϵ_{RMS} , shown in Table 5 does not change very rapidly with θ . Even so, the Debye temperatures, θ_0 and θ_M are only slightly outside of the range of the Debye temperatures found from other experiments. Considering the approximations used in the fitting procedures and the fact that most of the data were taken at temperatures above the Debye temperature, the values of θ_0 and θ_M are perhaps better than one might expect.

The values of ΔE_V^0 , $\Delta S_V^0/R$, and c_{mp} given in Table 6 are compared with values obtained by other methods in Table 8. The spread in the data from the different methods of fitting shown in Table 6 may be taken as a crude approximation to the accuracy of the data. In particular, the values for ΔE_V^0 , $\Delta S_V^0/R$, and c_{mp} given in

Fig. 10. Heat capacity of aluminum at constant pressure.

Fig. 11. Heat capacity of copper at constant pressure.

Table 8. Comparison of values of ΔE_V^0 , $\Delta S_V^0/R$, c_{mp} found by various methods.

Metal	Method	ΔE_V^0 (eV)	$\Delta S_V^0/R$	c_{mp} (%)	Reference
Aluminum	a	0.76 ± 0.13	3.5 ± 1.0	0.3 ± 0.2	Table 5
Aluminum	b	$0.74 - 0.86$	$2.0 - 3.6$	$0.1 - 0.3$	(69)
Aluminum	b	0.71	1.76	0.04	(73)
Aluminum	b	0.77	1.5	0.03	(71)
Aluminum	b	0.64	1.1	0.11	(72)
Aluminum	a	1.17	8.3	0.2	(31)
Copper	a	0.96 ± 0.11	3.2 ± 0.5	0.7 ± 0.2	Table 5
Copper	b	1.17 ± 0.11	1.5 ± 0.5	0.02	(70)
Copper	c	0.7	-0.2	0.2	(74)

(a) Specific heat at high temperatures.

(b) Thermal expansion (x-ray diffraction determination of the lattice parameter).

(c) Thermal expansion (extrapolation of low-temperature data).

Table 8 are the average values of the data in Table 6 plus or minus the spread in the data. Of the data given in Table 8, that of Simmons and Balluffi^{69,70} is generally regarded as more accurate than that of the others.⁷¹⁻⁷⁴ Their data for ΔE_V^0 are in good agreement with the values obtained from the least-square fitting procedure. However, the values given by Simmons and Balluffi for $\Delta S_V^0/R$ are not in good agreement.^{69,70} This is also reflected in the c_{mp} data. The lack of agreement between Simmons and Balluffi's values for the entropy of formation of vacancies and the values obtained from the least-squares fitting procedure may be due to experimental error, either in their work or in the specific heat data or in the fitting procedure. However, theoretical studies⁷⁵ seem to indicate that the values obtained from the least-squares fit are too large. On the other hand, these high values for $\Delta S_0/R$ are consistent with the estimates of Holder and Granato.⁷⁶

The application of the least-square fitting programs to the specific heat data of copper and aluminum illustrated the value of the method in obtaining the energy of formation of vacancies. The next step was to apply the same procedures to the analysis of the specific heat data of tungsten.

In addition to the three methods of fit used above, several other fitting procedures were used to analyze the tungsten data. Two fits based on Eq. (69) were computed using Gschneidner's⁶⁸ value of the Nernst-Lindemann constant for tungsten ($A' = 0.412 \times 10^{-5}$ mole/cal). The first of these fits used a constant value for the Debye temperature, $\theta_L^N = 380^\circ\text{K}$. In the second fit, the Debye temperature was considered as an unknown and a value was calculated which minimized the sum of the squares of the residuals. This value will be denoted by θ_M^N .

Finally, two fits were calculated using the approximation $c_{\text{Debye}} = 3R$ ($R = 1.99$ cal/mole-°K). This approximation when used in Eq. (66) gives

$$c_p = p_1'' + p_2 T + p_3 T^2 + (p_4/T^2)[\exp(p_5/T)] \quad (76)$$

with

$$p_1'' = 3R + d_0 + a_0. \quad (77)$$

The first fit used Eq. (76) directly while the second fit was based upon the further assumption that $p_3 = 0$, that is,

$$c_p = p_1 + p_2 T + (p_4/T^2)[\exp(p_5/T)]. \quad (78)$$

Equation (78) is equivalent to the linear extrapolation procedure used by Kraftmacher and others¹⁸⁻²³ to analyze specific heat data. This method is based on more assumptions than any of the other methods described above.

The results of the computer calculations for the various fitting procedures are shown in Table 9. The third fit shown in Table 9 is based upon Eq. (66) with the Debye

Table 9. Results of various fitting procedures applied to the tungsten data.

Equation	θ (°K)	p_1	p_2	p_3	p_4	$-p_5$	$\bar{c}_{\text{RMS}}$	ΔE_V^0 (eV)	$\Delta S_V^0/R$	$c_{\text{imp}}(\%)$
(66)	$\theta_L = 380$	-0.396	0.8385	0.1300	3.238×10^7	46.64	0.02313	4.03	8.92	2.34
(66)	$\theta_M = 371$	-0.402	0.8438	0.1288	3.225×10^7	46.63	0.02310	4.02	8.92	2.34
(66)	$\theta_0 = 803$	0.24310	0.4653	0.2140	4.578×10^7	47.96	0.02561	4.14	9.21	2.19
(69)	$\theta_L^N = 380$	-0.467	0.8471	0.01854	8.003×10^6	43.28	0.02044	3.74	7.67	1.68
(69)	$\theta_M^N = 354$	-0.463	0.8612	0.01533	7.888×10^6	43.22	0.02041	3.73	7.66	1.68
(76)	---	5.434	0.9502	0.1046	2.924×10^7	46.25	0.02280	3.99	8.83	2.39
(78)	---	5.181	1.293	0.000	1.135×10^7	42.75	0.03077	3.69	8.05	2.81

Note: The values given for p_1 through p_5 have units corresponding to the specific heat in units of cal/mole-°K and the temperature in units of kilo-degrees Kelvin. In this set of units $\Delta E_V^0 = -R \times p_5$ is given in kilo-cal/mole, which can then be converted to electron volts by multiplying by 0.434 (i.e., $\Delta E_V^0 = -0.434 \times R \times p_5$ eV with $R = 1.99$ cal/mole-°K).

temperature calculated to minimize the absolute value of p_1 . As discussed above, this method of fitting specific heat data should not be used in cases where the data are at temperatures higher than the Debye temperature. Therefore, this is not a valid fitting procedure for the high-temperature specific heat data of tungsten. Indeed, the average

error, $\bar{\epsilon}_{\text{RMS}}$, is larger for this fit than for any of the other fits except the last one, and the Debye temperature is much too large. The third fit was included to illustrate that the procedure does give poor results and to show how little the energy and entropy of formation of vacancies as calculated by these least-squares fitting methods depends on the Debye temperature.

As mentioned above, the fourth and fifth fits are based on Eq. (69) which uses the Nernst-Lindemann relation (Eq. (53)) for the dilation term. Since the specific heat data rise exponentially with temperature as the melting point of tungsten is approached, the Nernst-Lindemann relation gives an approximation to the dilation term which increases very rapidly at high temperatures compared to the power-series approximation used in the first three fits. The fact that the average error, $\bar{\epsilon}_{\text{RMS}}$, is smaller for these fits than for any of the others suggests that for tungsten the Nernst-Lindemann relation gives a better approximation of the dilation term than a power series expansion which is terminated at the quadratic term.

The sixth and seventh fit are based on Eqs. (76) and (78), respectively, as described above. The sixth fit gave values for the energy and entropy of formation of vacancies which are very similar to the values obtained from the first and second fits. This is to be expected since the specific heat data were taken at temperatures well above the Debye temperature. The seventh fit had the largest average error, $\bar{\epsilon}_{\text{RMS}}$. However, since it is a four-parameter fit rather than a five-parameter fit, it is not possible to compare directly the average error of the seventh fit with the average errors of the other fits. Even so, since there are more assumptions involved in the seventh fit, one would expect the results of this fit to be of questionable value. Therefore, the values of the energy and entropy of formation of vacancies obtained from the last fit will be discarded from further analysis.

Figure 12(a) is a plot of the second fit from Table 9 and Fig. 12(b) is a plot of the last fit from Table 9. The difference between the two fits is plotted in Fig. 12(c). Although this difference is small, it probably is slightly larger than the experimental error in the data at low temperatures.

The calculated values of the Debye temperature are shown in Table 10 along with the values given by Gschneidner⁶⁸ for tungsten. θ_M and θ_M^N are in surprisingly good agreement with the other values considering the weak dependence of the fits on the Debye temperature. As noted above, θ_0 was not expected to be in agreement with the other values.

In Table 11, the values for the energy and entropy of formation of vacancies and the mole percent of vacancies at the melting point ($T_{\text{mp}} = 3680^\circ\text{K}$) are given along with the values obtained by other experimenters. The entries in Table 11 were calculated by averaging the five values obtained from Table 9 after discarding the third and seventh entries. An estimate for the error was taken to be the maximum spread in the five values.

Table 10. Values for the Debye temperature of tungsten, calculated and taken from Ref. (68).

θ_M	θ_M^N	θ_0	θ_0^S	θ_{298}^S	θ^M	θ_0^E	θ_{298}^E	θ_m^R	θ_m^D	θ_{298}^I
371	354	803	388	312	291	384	370	359	310	---

Note: All temperatures are given in degrees Kelvin.

Table 11. Comparison of values of ΔE_V^0 , $\Delta S_V^0/R$, and c_{mp} found in this work and in earlier work.

Method	ΔE_V^0 (eV)	$\Delta S_V^0/R$	c_{mp} (%)	Reference
a	3.20 ± 0.30	8.4 ± 1.3	2.1 ± 0.7	Table 8
a	3.14	6.5	3.4	(19)
b	3.30 ± 0.1	1.4	0.011	(77)
b	3.6 ± 0.2	—	—	(78)

^aSpecific heat at high temperatures.

^bQuenching in superfluid liquid helium II.

Fig. 12. Heat capacity of tungsten at constant pressure (a) using the second fit from Table 9, (b) using the last fit from Table 9. (c) Difference between the curves (a) and (b).

Our values obtained from the least-squares fitting method are higher than the other values given in Table 11 (except for the value of c_{mp} which lies between the other two values). However, the other values are probably not very reliable. The data from Ref. (19) suffers from two deficiencies: the specific heat data are of questionable accuracy, and the linear extrapolation procedure used in fitting the specific heat data (the equivalent of the seventh method used above) is based on unsupported assumptions. The quenching experiments of Schultz⁷⁷ and Griphover et al.,⁷⁸ are very sensitive to small quantities of absorbed oxygen, nitrogen, or carbon in interstitial solid solution. It is possible that their data reflect the solubility of interstitial impurity atoms.

The questionable accuracy of Kraftmacher and Strelkov's data is illustrated in Fig. 13 where data is plotted from various experiments in which the specific

Fig. 13. Heat capacity of tungsten at constant pressure. Solid curve—this work, dashed curve—Kraftmacher and Strelkov.

heat of tungsten was measured. The dashed curve is the data of Kraftmacher and Strelkov. The solid curve corresponds to the second fit given in Table 8, that is, the curve from Fig. 12(b). Data from Lowenthal,¹⁷ Leibowitz et al.,⁷⁹ Hultgren et al.,⁸⁰ and Kirillin et al.³ are also plotted. The data from Fig. 12(b) are in excellent agreement with the data of Kirillin et al. up to 2000°K. From 2000°K to 2800°K, the data from Fig. 12(b) are in excellent agreement with the recent calorimetric data of Leibowitz et al. Over this same temperature range (800°K to 2800°K), the data of Kraftmacher and Strelkov are about 4% low, comparing more favorably with data of Lowenthal and Hultgren et al. At temperatures above 2800°K, the contribution of vacancies to the specific heat becomes important and the specific heat starts to rise exponentially. This effect is not present in the calorimetric data. This may be due to the fact that the vacancy contribution to the enthalpy is small compared to the vacancy contribution to the specific heat. In any event, both sets of data from the ac temperature method increase exponentially above 2800°K with the data from Fig. 12(b) continuing to be higher than Kraftmacher and Strelkov's data. It appears that there is a systematic error in Kraftmacher and Strelkov's data which resulted in a low value for the specific heat over the entire temperature range.

The data in Table 9 can be used to gain some understanding of the anharmonic specific heat of tungsten. The second fit which is based upon Eq. (66) can be used to find the specific heat due to the dilation term, c_D , plus the anharmonic lattice specific heat, c_A . That is,

$$c_D + c_A \approx (d_0 + a_0) + (d_1 + a_1)T + (d_2 + a_2)T^2$$

from Eqs. (54) and (60). Therefore, using Eq. (67)

$$c_D + c_A \approx p_1 + (p_2 - \gamma)T + p_3T^2. \quad (79)$$

The electronic specific heat constant, γ , is given by Gschneidner⁶⁸ ($\gamma = 2.92 \cdot 10^{-4}$ cal/mole $\times$ deg²). Using this value and the values for p_1 through p_3 given in the second row of Table 9, Eq. (79) becomes

$$c_D + c_A \approx -0.402 + 0.552T + 0.129T^2. \quad (80)$$

This estimate of the excess specific heat due to the dilation term and the anharmonic-lattice term is the solid curve shown in Fig. 14. The Nernst-Lindemann approximation of the specific heat due to the dilation term is the dashed curve shown in Fig. 14. The

Fig. 14. Anharmonic heat capacity of tungsten. Solid curve: excess heat capacity, Eq. (80); dashed curve: Nernst-Lindemann term; dot-and-dash curve: excess heat capacity, Eq. (82).

difference between these two curves would be an estimate of the anharmonic-lattice specific heat. However, a more consistent method for estimating the anharmonic term can be obtained based on Eq. (69).

Using Eqs. (69) and (70),

$$c_A = p_1' + (p_2' - \gamma)T + p_3'T^2. \quad (81)$$

Then, using the values for p_1' through p_3' given in the fifth row of Table 9 and the value of the electronic specific heat constant given above,

$$c_A = -0.493 + 0.569T + 0.0153T^2. \quad (82)$$

This estimate of the excess specific heat due to the anharmonic lattice is the dot-and-dash curve plotted in Fig. 14. Equation (64) implies that c_A is negative below about 850°K. While this is possible, it must be remembered that all of the above expansions are valid only in the temperature range in which the data were taken (800°K to 3418°K). Moreover, Eq. (68) is only as good as the Nernst-Lindemann approximation which itself is of unknown accuracy. Therefore, Eq. (68) can only be regarded as a rough estimate of the anharmonic-lattice specific heat.

If it is assumed that self-diffusion in tungsten occurs by a vacancy mechanism, the migration energy for vacancies, E_M , may be estimated from the energy of activation for self-diffusion, E_{SD} , and the energy of formation ΔE_V^0 . That is,

$$E_M = E_{SD} - \Delta E_V^0. \quad (83)$$

The energy of activation for self-diffusion has been measured by Andelin et al.⁸¹ and by Danneberg.⁸² Andelin et al. obtained a value ($E_{SD} = 6.64 \pm 0.26$ eV), considerably larger than the value given by Danneberg ($E_{SD} = 5.23 \pm 0.2$ eV). The value given by Danneberg is thought to be incorrect.⁸¹ The calculated value of the migration energy for vacancies is given in Table 12. The first row value is calculated from the formation energy calculated from the least-squares fits. The second was calculated using Schultz's⁷⁷ value for the formation energy of vacancies. The third row contains the data given by Gripshover et al.⁷⁸

The value for the migration energy reported by Schultz⁷⁷ ($E_M = 1.93 \pm 0.3$ eV) was said to be consistent with the observations of the recovery of cold-worked tungsten. The corrected value for the migration energy based on the activation energy found by Andelin et al. ($E_M = 3.34 \pm 0.36$ eV) is too large. The values obtained from the least-squares fit ($E_M = 2.74 \pm 0.56$) and the quenching experiment of Gripshover et al.⁷⁸ ($E_M = 2.5 \pm 0.5$) are more reasonable. These values are not much larger than the theoretical estimate of Johnson ($E_M = 2.0$ eV).⁸³

Table 12. Migration energy calculated by several methods.

Formation energy ΔE	Activation energy E_{SD}	Migration energy E_M	Reference
3.90 ± 0.30	6.64 ± 0.26	2.74 ± 0.56	This work
3.30 ± 0.1	6.64 ± 0.26	3.34 ± 0.36	(77)
3.6 ± 0.2	6.1 ± 0.3	2.5 ± 0.5	(78)

Note: All energies are given in eV.

Summary and Conclusions

An accurate method for measuring the high-temperature specific heat of electrical conductors has been presented. This method was based on the fact that an electrical conductor which is heated by the combination of an ac and dc electric current has an impedance at the frequency of the ac current that is approximately equivalent to the impedance of a resistance shunted by a small capacitance.

An ac bridge using a phase-sensitive null detector was described which was capable of accurately measuring the impedance of a sample of an electrical conductor for various frequencies of the ac current and different values of the temperature of the sample. After balancing the bridge for several different frequencies of the ac current at a constant sample temperature, the bridge-balance equations were used to calculate the heat capacity of the sample at that temperature. This was accomplished through the use of a computer code which determined the values of the unknowns in the bridge-balance equations so that these equations fit the experimental data as accurately as possible in the least-squares sense.

The accuracy of this method was limited only by the accuracy of the measurement of the temperature. In particular, the accuracy of the specific heat data depended on the accuracy of the measurement of the derivative of the resistance of the sample with respect to the temperature, evaluated at the temperature of the sample, $(dR/dT)_T$. That is, the accuracy of the specific heat measurement depended on the accuracy of the measurement of the temperature coefficient of resistance,

$$\alpha = (1/R_0)(dR/dT)_T$$

where R_0 is the resistance of the sample at zero degrees centigrade.

The temperature coefficient of resistance of tungsten was calculated from literature values of the resistance as a function of temperature. Using these values, the specific heat of tungsten from 800°K to 3414°K was found to be given by

$$c_p(T) = 5.43 + 9.50 \times 10^{-4} \times T + 1.05 \times 10^{-7} \times T^2 \\ + (2.92 \times 10^{13}/T^2) \times \exp(-4.63 \times 10^4/T) \text{ cal/mole} \cdot ^\circ\text{K}$$

with an estimated accuracy of plus or minus 1% at the low-temperature end to plus or minus 3% at the high-temperature end. These results were compared with literature values of the specific heat of tungsten and were found to be in good agreement with the most reliable values in the low- to intermediate-temperature range. At high temperature, the values were slightly larger than any of the literature values and considerably larger than the calorimetric data.

A method of analyzing specific heat data to determine the contribution of lattice mono-vacancies was presented. The result of this analysis was shown to give reliable values for the energy of formation of vacancies and reasonable values for the entropy and concentration of vacancies. Under certain conditions, the method was also shown to give a reasonable value for the Debye temperature and an estimate for the anharmonic-lattice specific heat. In particular, for tungsten the following results were found:

- (1) The energy of formation of vacancies, $\Delta E_V = 3.90 \pm 0.30$ eV,
- (2) The entropy of formation of vacancies, $\Delta S_V/R = 8.4 \pm 1.3$,
- (3) The concentration of vacancies at the melting point, $c_{mp} = 2.1 \pm 0.7$ mole percent,
- (4) The migration energy for vacancies, $E_M = 2.74 \pm 0.56$ eV, and
- (5) The anharmonic-lattice specific heat ($800^\circ\text{K} < T < 3400^\circ\text{K}$), $c_A = -0.48 + 0.57 \times 10^{-3} \times T + 0.015 \times 10^{-6} \times T^2$ cal/mole- $^\circ\text{K}$.

The two primary objectives of this work, the development of an accurate method for measuring the high-temperature specific heat of metals and an improved technique for obtaining the energy of formation and concentration of vacancies from accurate high-temperature specific heat data, have been met. However, there are several possibilities for additional research:

- (1) modification of the experimental equipment to facilitate the simultaneous measurement of the specific heat and the temperature coefficient of resistance;
- (2) the extension of the ac temperature technique to electrical insulators (through the use of a thin metallic coating over the surface of the insulator);
- (3) study of time-dependent specific heat effects by varying the frequency of the ac current over a wider range than is normally done in measuring time-independent specific heats.

An accurate and fast method of measuring specific heats at high temperatures has been demonstrated. It is hoped that accurate high-temperature specific heat data for many metals and alloys will soon be available.

Acknowledgments

The author wishes to express his appreciation to Prof. Richard J. Borg for the encouragement and advice given throughout the course of this work, to Prof. Benjamin Naylor, Dr. Michael Guinan, Dr. Lawrence Himmel, Mr. David Lai, Mr. Aki Kuramoto, Dr. Edmund Hsieh, and Mr. Robert Parker for their invaluable assistance, to the personnel of the Precision Electrical Measurements Laboratory at the Lawrence Radiation Laboratory for electronics support, and to the author's wife for her great patience and understanding. The research was performed under the auspices of the United States Atomic Energy Commission at the Lawrence Radiation Laboratory, Livermore, California, in the Inorganic Materials Division of the Chemistry Department.

Appendix A: Solution of Eq. (11)

The steady state solution of the differential equation

$$d\Delta T/dt + (M/\bar{C}_p)\Delta T = (2i_0 i\bar{R}/\bar{C}_p)\sin\omega t - (i^2 \bar{R}/2\bar{C}_p)(\cos 2\omega t) \quad (A1)$$

can be found using the method of Laplace transforms. Let

$$\xi = \omega t, \quad \mu = M/\bar{C}_p, \quad \alpha = (2i_0 i\bar{R})/\bar{C}_p, \quad \beta = (i^2 \bar{R})/2\bar{C}_p.$$

Then Eq. (A1) becomes

$$d\Delta T/d\xi = -(\mu/\omega)\Delta T + (\alpha/\omega)\sin\xi - (\beta/\omega)\cos 2\xi. \quad (A2)$$

Taking the Laplace transform of Eq. (A2), we find

$$s\Delta\tau - \Delta T(+0) = -(\mu/\omega)\Delta\tau + (\alpha/\omega)(1/s^2 + 1) - (\beta/\omega)(s/s^2 + 4)$$

where $\Delta\tau$ is the Laplace transform of ΔT . The $\Delta T(+0)$ term corresponds to a transient term in the general solution and may be neglected in the steady state solution. Therefore

$$\Delta\tau = (\alpha/\omega) [1/(s + \mu/\omega)(s^2 + 1)] - (\beta/\omega) [s/(s + \mu/\omega)(s^2 + 4)]$$

but

$$[(s + \mu/\omega)(s^2 + 1)]^{-1} = (\omega^2)/(\mu^2 + \omega^2)(s + \mu/\omega)^{-1}$$

$$+ \{-(\omega^2 s)/(\mu^2 + \omega^2)\}$$

$$+ (\mu\omega)/(\mu^2 + \omega^2) [s^2 + 1]^{-1}$$

and

$$s[(s + \mu/\omega)(s^2 + 4)]^{-1} = -(\mu\omega)/(\mu^2 + 4\omega^2)(s + \mu/\omega)^{-1}$$

$$+ \{(\mu\omega s)/(\mu^2 + 4\omega^2)\}$$

$$+ (4\omega^2)/(\mu^2 + 4\omega^2) [s^2 + 4]^{-1}.$$

Now neglecting the transient terms (the ones which have the factor $(s + \mu/\omega)^{-1}$), we have

$$\Delta\tau = [(\alpha)/(\mu^2 + \omega^2)]\{(\mu - \omega s)/(s + 1)\} \\ - [(\beta)/(\mu^2 + 4\omega^2)]\{(\mu s + 4\omega)/(s^2 + 4)\}.$$

Therefore taking the inverse Laplace transform, the solution to Eq. (A2) is

$$\Delta T = [(\alpha)/(\mu^2 + \omega^2)] [-\omega \cos \xi + \mu \sin \xi] \\ - [(\beta)/(\mu^2 + 4\omega^2)] [\mu \cos 2\xi + 2\omega \sin 2\xi]. \quad (A3)$$

Let $\tan \phi = (\omega/\mu)$ and $\tan \theta = (\mu/2\omega)$, then Eq. (A3) becomes

$$\Delta T = [(\alpha\omega)/(\mu^2 + \omega^2)] [\sin(\xi - \phi)/\sin\phi] \\ - [(2\beta\omega)/(\mu^2 + 4\omega^2)] [\sin(2\xi + \theta)/\cos\theta].$$

Now

$$1 + (\mu^2/4\omega^2) = (\cos\theta)^{-2} \text{ and } 1 + (\mu^2/\omega^2) = (\sin\phi)^{-2},$$

so that

$$\Delta T = (\alpha/\omega)(\sin\phi)\sin(\xi - \phi) - (\beta/2\omega)(\cos\theta)\sin(2\xi + \theta). \quad (A4)$$

Let

$$\Delta T_1 = (\alpha/\omega)(\sin\phi) = [(2i_0 \bar{R})/(\omega \bar{C}_p)] \sin\phi$$

and

$$\Delta T_2 = (\beta/2\omega)(\cos\theta) = [(i^2 \bar{R})/(4\omega \bar{C}_p)] \cos\theta,$$

then

$$\Delta T = \Delta T_1 \sin(\omega t - \phi) - \Delta T_2 \sin(2\omega t + \theta), \quad (A5)$$

which is Eq. (12).

Appendix B:

Assumptions Used to Derive Eq. (17)

The effects of heat conduction were neglected in Eq. (1). These effects have been analyzed by Holland and Smith²⁵ using the frequency dependent diffusion length,

$$\lambda = \sqrt{\kappa/\omega} , \quad (B1)$$

where κ is the thermal diffusivity (units: cm^2/sec).

They have shown that the effect of heat conduction in the axial direction along the sample is the generation of a damped temperature wave traveling away from the end supports. The wave is sufficiently damped at distances greater than a few diffusion lengths from the end supports so as to have a negligible effect upon the ac temperature. Therefore, Eq. (1) may be used for samples which are very long compared to the diffusion length.

Holland and Smith²⁵ have also shown that the effect of heat conduction in the radial direction from the center of the sample is the generation of a temperature wave at the surface which decays as it travels into the material, shifting its phase relative to the ac temperature given by Eq. (12). The wave has a negligible effect for samples with a radius less than the diffusion length.

Since the diffusion length depends upon the frequency, the errors introduced in using Eq. (1) are frequency-dependent. Therefore, if the specific heat is determined from experiments which are analyzed with equations derived from Eq. (1), the specific heat measured will be frequency-dependent if the effects due to heat conduction are not negligible. Conversely, if the measured specific heat is independent of frequency, the use of Eq. (1) is justified.

The diffusion length for a material may be estimated from Eq. (B1). For example, the thermal diffusivity of tungsten is approximately one (i. e., $0.5 < \kappa < 1.5$) so the diffusion length ranges from 0.04 cm to 0.13 cm for $\omega = 100$ Hz to 10 Hz. Therefore, heat conduction effects may be neglected for samples with a diameter (or thickness in the case of a foil) of less than three mils and a length greater than five inches. If samples are made with a larger diameter or a shorter length, the frequency dependence of the measured specific heat should be examined.

The approximate Eqs. (2)-(6) are quite accurate if the amplitude of the ac temperature is less than 10°C . These equations will be very accurate at high frequencies where the ac temperature is less than 1°C .

The effects of assuming Eq. (8) to be a valid approximation and neglecting the last two terms on the left-hand side of Eq. (9) can be shown by substituting Eq. (12) into the neglected terms from Eq. (9). That is, letting

$$\text{Term}_1 = 2i_0 i (dR/dT) \bar{T} \Delta T (\sin \omega t)$$

and

$$\text{Term}_2 = -(i^2/2)(dR/dT) \bar{T} \Delta T (\cos 2\omega t)$$

we have

$$\begin{aligned} \text{Term}_1 + \text{Term}_2 = & i(dR/dT) \bar{T} [i_0 \Delta T_1 (\cos \phi) + (i/4) \Delta T_2 (\sin \theta) \\ & + (i/4) \Delta T_1 \sin(\omega t + \phi) - i_0 \Delta T_2 \cos(\omega t + \theta) \\ & - i_0 \Delta T_1 \cos(2\omega t - \phi) \\ & - (i/4) \Delta T_1 \sin(3\omega t - \phi) + i_0 \Delta T_2 \cos(3\omega t + \theta) \\ & + (i/4) \Delta T_2 \sin(4\omega t + \theta)] \end{aligned} \quad (\text{B2})$$

The first two terms in this equation which do not depend upon the time were neglected in Eq. (8). A more accurate equation for the conservation of average power can now be written:

$$\bar{R}(i_0^2 + i^2/2) + i(dR/dT) \bar{T} [i_0 \Delta T_1 (\cos \phi) + (i/4) \Delta T_2 (\sin \theta)] = L.$$

The last terms in Eq. (B2) show that we have neglected high-frequency components in the ac temperature by neglecting Term_1 and Term_2 in Eq. (9). For applications, the component of the ac temperature at the frequency ω is most useful. Therefore, a closer examination of the terms in ω from Eq. (B2) is in order. Let

$$E(\omega) = i(dR/dT) \bar{T} [Ci/4) \Delta T_1 \sin(\omega t + \phi) - i_0 \Delta T_2 \cos(\omega t + \theta)].$$

Now using Eqs. (13)-(16) with some trigonometry, we find

$$\begin{aligned} E(\omega) = & [(i_0 i^3 \bar{R}) / (2\omega \bar{C}_p)] [dR/dT] \bar{T} \\ & \times \{ [1 + (M/\omega \bar{C}_p)^2]^{-1} [(M/\omega \bar{C}_p) \sin(\omega t) + \cos(\omega t)] \\ & + [1 + (M/2\omega \bar{C}_p)^2]^{-1} [(M/4\omega \bar{C}_p) \sin(\omega t) - \cos(\omega t)] \}. \end{aligned} \quad (\text{B3})$$

Now at sufficiently high frequencies

$$[1 + (M/\omega \bar{C}_p)^2]^{-1} \approx [1 + (M/2\omega \bar{C}_p)^2]^{-1} \approx 1$$

so that

$$E(\omega) \approx [(5i_0^3 M \bar{R}) / (8\omega^2 \bar{C}_p^2)] [(dR/dT)_{\bar{T}}] [\sin(\omega t)]. \quad (B4)$$

Therefore, $E(\omega)$ is proportional to ω^{-2} where as the terms included in Eq. (9) are proportional to ω^0 and ω^{-1} , and Eq. (10) is an accurate approximation at sufficiently high frequencies.

Appendix C: Supplementary Data

Sample No. 1a (Ar + I₂)

$\bar{T}$ (°K)	R_A (Ω)	$\omega/2\pi$ (Hz)	$R_A C_A$ (Ω - μ F)	i_0 (A)	i (rms A)
726	75.00	20.000	13.251	1.268	0.091
		25.000	9.269	1.268	0.090
		35.002	5.781	1.269	0.090
		45.000	4.334	1.268	0.090
		54.990	3.591	1.268	0.090
		65.003	3.164	1.269	0.090
		74.996	2.901	1.269	0.090
		84.998	2.721	1.269	0.090
		95.021	2.591	1.269	0.090
934	100.00	20.001	18.008	1.489	0.090
		24.995	12.298	1.489	0.090
		35.003	7.308	1.488	0.090
		45.002	5.208	1.489	0.090
		54.993	4.138	1.488	0.090
		64.998	3.638	1.489	0.090
		75.013	3.268	1.488	0.090
		84.998	2.968	1.489	0.090
		95.021	2.785	1.489	0.090
935	100.00	20.000	18.008	1.488	0.090
		25.001	12.298	1.488	0.090
		35.001	7.308	1.487	0.090
		45.002	5.258	1.487	0.090
		55.012	4.197	1.487	0.090
		64.990	3.618	1.488	0.090
		75.013	3.232	1.489	0.090
		85.012	2.975	1.488	0.090
		95.012	2.793	1.487	0.090
1134	125.00	20.000	24.010	1.739	0.100
		24.999	16.160	1.740	0.100
		35.001	9.310	1.738	0.100
		45.002	6.473	1.739	0.100
		55.006	5.010	1.738	0.100
		64.994	4.198	1.738	0.100

Sample No. 1a (Ar + I₂) (Continued)

$\bar{T}$ (°K)	R_A (Ω)	$\omega/2\pi$ (Hz)	R_{AC} ($\Omega-\mu F$)	i_0 (A)	i (rms A)
1325	150.00	75.008	3.664	1.739	0.100
		85.005	3.313	1.738	0.100
		95.012	3.063	1.738	0.100
		20.000	31.977	2.033	0.100
		24.999	21.240	2.032	0.100
		35.003	11.879	2.032	0.100
		45.002	8.025	2.032	0.100
		54.996	6.053	2.032	0.100
		65.003	4.926	2.032	0.100
		75.002	4.220	2.033	0.100
		84.983	3.740	2.032	0.100
		95.003	3.402	2.031	0.100
		19.999	42.277	2.367	0.110
		25.000	27.874	2.367	0.110
1513	175.00	35.003	15.248	2.368	0.110
		45.000	10.068	2.368	0.110
		54.999	7.410	2.368	0.110
		64.994	5.896	2.367	0.110
		75.008	4.935	2.366	0.110
		85.005	4.295	2.365	0.110
		94.994	3.824	2.365	0.110
		20.002	55.416	2.740	0.140
		25.004	36.416	2.739	0.140
		35.005	19.498	2.740	0.140
		45.009	12.606	2.739	0.140
		54.999	9.116	2.739	0.140
		65.007	7.098	2.739	0.140
		75.008	5.838	2.738	0.140
1699	200.00	85.005	4.982	2.736	0.140
		95.021	4.386	2.734	0.140
		20.002	71.566	3.145	0.150
		24.999	46.595	3.145	0.150
		35.001	24.853	3.144	0.150
		44.998	15.788	3.145	0.150
		54.993	11.246	3.145	0.150
		64.986	8.613	3.145	0.150
		75.002	6.966	3.145	0.150
		84.998	5.852	3.145	0.150
1885	225.00				

Sample No. 1a (Ar + I₂) (Continued)

$\bar{T}$ (°K)	R_A (Ω)	$\omega/2\pi$ (Hz)	$R_A C_A$ ($\Omega \cdot \mu F$)	i_0 (A)	i (rms A)
2068	250.00	95.012	5.083	3.145	0.150
		20.000	90.770	3.577	0.150
		25.000	58.853	3.578	0.150
		34.998	31.080	3.578	0.150
		45.005	19.583	3.578	0.150
		54.993	13.788	3.577	0.150
		64.994	10.420	3.578	0.150
		74.991	8.320	3.577	0.150
		85.005	6.908	3.577	0.150
2063	250.00	95.003	5.913	3.575	0.150
		20.001	88.470	3.526	0.500
		25.002	57.370	3.526	0.500
		35.002	30.320	3.526	0.500
		45.002	19.133	3.526	0.500
		54.996	13.503	3.526	0.500
		64.990	10.213	3.527	0.500
		75.002	8.165	3.525	0.500
		84.998	6.800	3.526	0.500
2063	250.00	94.985	5.835	3.525	0.500
		24.999	54.520	3.420	1.000
		35.001	28.870	3.421	1.000
		45.002	18.250	3.420	1.000
		55.002	12.900	3.419	1.000
		64.986	9.808	3.420	1.000
		75.002	7.853	3.420	1.000
		84.998	6.568	3.420	0.999
		95.012	5.643	3.419	1.000
2111	275.00	20.000	113.040	4.028	0.199
		24.999	73.205	4.028	0.200
		34.999	38.401	4.029	0.200
		45.002	23.997	4.029	0.200
		54.999	16.737	4.030	0.200
		64.998	12.515	4.030	0.200
		75.002	9.884	4.029	0.200
		84.999	8.121	4.028	0.200
		94.985	6.886	4.027	0.200
2419	300.00	20.000	136.100	4.461	0.220
		25.000	88.014	4.463	0.220

Sample No. 1a (Ar + I₂) (Continued)

$\bar{T}$ (°K)	R_A (Ω)	$\omega/2\pi$ (Hz)	$R_A C_A$ (Ω - μ F)	i_0 (A)	i (rms A)
2562	320.00	35.002	45.984	4.464	0.221
		44.998	28.578	4.464	0.220
		54.999	13.794	4.464	0.220
		65.007	14.706	4.465	0.220
		75.002	11.532	4.465	0.220
		85.012	9.405	4.465	0.220
		95.021	7.911	4.465	0.220
		19.999	156.830	4.838	0.240
		24.999	101.350	4.840	0.240
		35.001	52.790	4.843	0.240
		45.002	32.739	4.843	0.240
		54.999	22.528	4.843	0.240
		64.998	16.698	4.843	0.240
		74.991	12.992	4.844	0.240
		84.991	10.538	4.843	0.240
		95.030	8.810	4.843	0.240
2847	360.00	20.000	198.680	5.619	0.280
		25.001	128.310	5.624	0.280
		34.996	66.665	5.627	0.280
		45.002	41.105	5.629	0.280
		55.002	28.127	5.629	0.280
		65.003	20.678	5.630	0.280
		75.008	15.980	5.630	0.280
		84.969	12.863	5.631	0.280
		95.012	10.652	5.630	0.280
		20.000	218.350	6.032	0.300
2990	380.00	25.000	141.010	6.037	0.300
		34.999	73.101	6.040	0.300
		45.007	44.988	6.042	0.300
		54.999	30.750	6.044	0.300
		64.998	22.557	6.045	0.300
		75.008	17.366	6.045	0.300
		85.005	13.931	6.046	0.300
		95.012	11.518	6.044	0.300
		20.001	235.720	6.465	0.320
		25.000	152.190	6.471	0.320
3134	400.00	35.002	78.760	6.477	0.320
		45.000	48.464	6.479	0.320

Sample No. 1a(Ar + I₂)(Continued)

$\bar{T}$ (°K)	R_A (Ω)	$\omega/2\pi$ (Hz)	$R_A C_A$ (Ω - μ F)	i_0 (A)	i (rms A)
3134	800.00	54.993	33.040	6.482	0.320
		64.986	24.200	6.483	0.320
		75.019	18.584	6.487	0.320
		85.020	14.868	6.481	0.320
		95.012	12.264	6.481	0.320
		20.000	235.670	6.469	0.321
		25.000	151.930	6.475	0.320
		34.878	79.016	6.480	0.320
		45.000	48.160	6.483	0.320
		54.999	32.696	6.482	0.320
		64.998	23.864	6.484	0.320
		75.002	18.296	6.485	0.320
		85.005	14.616	6.486	0.320
		95.021	12.008	6.485	0.320
		19.992	243.770	6.701	0.300
		25.005	156.891	6.707	0.300
3206	820.00	35.005	80.942	6.712	0.300
		45.007	49.626	6.714	0.300
		54.981	33.710	6.716	0.300
		65.007	24.543	6.714	0.300
		75.019	18.819	6.717	0.300
		85.027	14.998	6.714	0.300
		95.012	12.308	6.714	0.300
		19.996	249.421	6.935	0.330
		25.001	160.835	6.941	0.330
		35.012	82.807	6.950	0.330
3279	840.00	44.994	50.887	6.954	0.330
		54.972	34.524	6.958	0.330
		64.994	25.108	6.959	0.331
		74.996	19.253	6.960	0.330
		84.969	15.355	6.960	0.330
		94.967	12.592	6.956	0.330

Sample No. 1b (Vacuum)

831	88.00	19.999	6.220	.750	0.101
		24.999	4.761	.750	0.100
		35.002	3.483	.750	0.101
		45.002	2.952	.750	0.100

Sample No. 1b (Vacuum)(Continued)

$\bar{T}$ (°K)	R_A (Ω)	$\omega/2\pi$ (Hz)	$R_A C_A$ ($\Omega \cdot \mu F$)	i_0 (A)	i (rms A)
1032	113.00	55.002	2.683	.750	0.100
		65.007	2.530	.750	0.100
		75.008	2.430	.750	0.100
		85.005	2.360	.750	0.100
		95.021	2.313	.750	0.100
		19.998	9.942	1.032	0.100
		24.999	7.134	1.032	0.100
		35.001	4.687	1.031	0.100
		45.000	3.682	1.032	0.100
		54.999	3.162	1.031	0.100
		64.994	2.868	1.032	0.100
		74.991	2.676	1.032	0.100
		85.005	2.550	1.032	0.100
		95.012	2.459	1.031	0.100
1226	138.00	19.999	15.536	1.350	0.100
		24.998	10.710	1.350	0.100
		34.999	6.511	1.350	0.100
		44.998	4.780	1.351	0.100
		54.996	3.900	1.351	0.100
		65.028	3.396	1.351	0.100
		75.002	3.075	1.351	0.100
		84.998	2.857	1.351	0.100
		95.003	2.710	1.351	0.100
		20.000	23.192	1.698	0.110
		25.001	15.611	1.698	0.110
		34.996	9.011	1.699	0.110
		45.000	6.276	1.699	0.110
		54.999	4.901	1.698	0.110
1413	163.00	64.994	4.103	1.699	0.110
		74.996	3.599	1.699	0.110
		84.991	3.271	1.699	0.110
		95.003	3.035	1.700	0.110
		20.000	33.366	2.080	0.130
		24.998	22.135	2.080	0.130
		34.996	12.348	2.081	0.130
		45.000	8.278	2.081	0.130
		54.984	6.238	2.082	0.130
		64.994	5.052	2.082	0.130
		20.000	33.366	2.080	0.130
		24.998	22.135	2.080	0.130
		34.996	12.348	2.081	0.130
		45.000	8.278	2.081	0.130
		54.984	6.238	2.082	0.130
1597	188.00	64.994	5.052	2.082	0.130
		20.000	33.366	2.080	0.130
		24.998	22.135	2.080	0.130
		34.996	12.348	2.081	0.130

Sample No. 1b (Vacuum)(Continued)

$\bar{T}$ (°K)	R_A (Ω)	$\omega/2\pi$ (Hz)	$R_A C_A$ (Ω - μ F)	i_0 (A)	i (rms A)
1779	213.00	75.002	4.311	2.082	0.130
		84.998	3.816	2.081	0.130
		95.012	3.470	2.082	0.130
		20.001	46.004	2.480	0.140
		25.000	30.242	2.482	0.140
		35.005	16.461	2.432	0.140
		45.000	10.786	2.483	0.140
		55.002	7.898	2.484	0.140
		65.020	6.230	2.485	0.140
		74.996	5.189	2.485	0.140
		84.983	4.490	2.486	0.140
		94.994	4.011	2.488	0.140

Sample No. 2a (Ar + I₂)

922	100.00	19.999	20.018	1.598	0.100
		24.997	13.618	1.597	0.100
		35.002	7.988	1.597	0.100
		45.005	5.668	1.597	0.100
		55.009	4.488	1.598	0.100
		64.986	3.808	1.597	0.100
		75.008	3.380	1.598	0.100
		84.998	3.095	1.599	0.100
		95.002	2.893	1.601	0.100
3166	820.00	20.003	243.300	6.699	0.319
		25.000	157.180	6.707	0.320
		35.009	81.082	6.711	0.320
		45.005	49.766	6.714	0.319
		54.996	33.800	6.715	0.320
		64.990	24.649	6.715	0.320
		75.008	18.876	6.714	0.320
		84.991	15.063	6.715	0.320
		94.994	12.366	6.719	0.320
		95.084	12.349	6.715	0.320

Sample No. 2b (Xenon)

$\bar{T}$ (°K)	R_A (Ω)	$\omega/2\pi$ (Hz)	$R_A C_A$ ($\Omega \cdot \mu F$)	i_0 (A)	i (rms A)
815	87.50	20.000	8.250	.934	0.112
		25.001	6.071	.931	0.112
		35.001	4.146	.935	0.112
		45.002	3.358	.927	0.112
		55.002	2.947	.928	0.112
		65.028	2.720	.928	0.112
		75.008	2.571	.928	0.112
		84.976	2.472	.929	0.112
		95.003	2.396	.928	0.112
917	100.00	19.999	10.078	1.053	0.120
		25.000	7.218	1.053	0.120
		35.003	4.733	1.053	0.120
		44.992	3.708	1.053	0.120
		55.002	3.178	1.053	0.120
		65.028	2.874	1.053	0.120
		75.002	2.684	1.053	0.120
		85.027	2.556	1.053	0.120
		95.003	2.464	1.054	0.120
1016	112.50	20.000	12.373	1.189	0.120
		25.004	8.677	1.188	0.120
		34.998	5.477	1.189	0.120
		44.998	4.163	1.189	0.120
		55.002	3.485	1.189	0.120
		65.003	3.102	1.189	0.120
		74.996	2.853	1.189	0.120
		84.969	2.687	1.189	0.120
		94.984	2.566	1.189	0.120
1112	125.00	20.002	15.073	1.336	0.120
		25.003	10.410	1.336	0.120
		34.998	6.364	1.336	0.120
		45.007	4.691	1.336	0.120
		55.006	3.848	1.336	0.120
		65.011	3.356	1.336	0.120
		74.996	3.046	1.336	0.120
		85.012	2.839	1.336	0.120
		94.994	2.691	1.335	0.120
1207	137.50	19.999	18.285	1.492	0.120
		25.001	12.460	1.491	0.120

Sample No. 2b (Xenon, continued)

$\bar{T}$ (°K)	R_A (Ω)	$\omega/2\pi$ (Hz)	R_{AC} ($\Omega-\mu F$)	i_0 (A)	i (rms A)
1299	150.00	34.997	7.415	1.491	0.120
		44.994	5.323	1.492	0.120
		55.002	4.265	1.942	0.120
		64.990	3.663	1.492	0.120
		75.002	3.273	1.492	0.120
		85.005	2.14	1.492	0.120
		94.991	2.830	1.492	0.120
		19.997	21.935	1.654	0.150
		25.003	14.817	1.655	0.150
		35.002	8.622	1.655	0.150
		45.002	6.036	1.654	0.150
		55.006	4.740	1.654	0.150
		65.011	3.993	1.655	0.150
		74.996	3.522	1.656	0.150
		85.005	3.206	1.657	0.150
		94.985	2.990	1.654	0.150
		20.001	26.241	1.827	0.150
		25.002	17.576	1.827	0.150
		35.001	10.004	1.826	0.150
		54.999	5.302	1.826	0.150
1390	162.50	75.008	3.822	1.825	0.150
		95.030	2.174	1.823	0.150
		20.000	31.136	2.010	0.160
		25.003	20.703	2.010	0.160
		35.005	11.615	2.010	0.160
		54.996	5.948	2.009	0.160
		75.002	4.165	2.009	0.160
1482	175.00	95.012	3.385	2.010	0.160
		20.000	36.737	2.201	0.160
		24.999	24.278	2.200	0.160
		34.997	13.431	2.200	0.160
		54.999	6.679	2.200	0.160
		75.002	4.549	2.200	0.160
		95.003	3.615	2.201	0.160
1574	187.50	20.001	42.916	2.398	0.160
		25.001	28.256	2.398	0.159
		34.997	15.448	2.398	0.160
		55.006	7.478	2.399	0.160
1664	200.00				

Sample No. 2b (Xenon)(Continued)

$\bar{T}$ (°K)	R_A (Ω)	$\omega/2\pi$ (Hz)	$R_A C_A$ ($\Omega \cdot \mu F$)	i_0 (A)	i (times A)
1754	212.50	75.003	4.974	2.399	0.160
		95.003	3.874	2.398	0.160
		20.000	49.865	2.602	0.170
		24.996	32.755	2.603	0.170
		34.999	17.714	2.602	0.170
		54.996	8.398	2.603	0.170
		74.996	5.461	2.602	0.170
1843	225.00	94.994	4.169	2.601	0.170
		19.999	57.611	2.814	0.170
		25.000	37.701	2.814	0.170
		35.001	20.223	2.813	0.170
		55.006	9.405	2.814	0.170
		74.991	5.996	2.814	0.170
		95.012	4.507	2.814	0.170
1933	237.50	20.001	66.077	3.030	0.180
		25.000	43.078	3.029	0.180
		35.002	23.000	3.030	0.180
		55.006	10.524	3.030	0.180
		74.991	6.591	3.030	0.180
		94.994	4.864	3.031	0.180
2022	250.00	20.001	75.370	3.251	0.180
		25.000	49.095	3.252	0.180
		35.001	26.088	3.252	0.180
		54.999	11.738	3.251	0.180
		75.002	7.243	3.252	0.180
		95.012	5.260	3.252	0.180
2111	262.50	20.003	85.465	3.477	0.190
		25.002	55.469	3.477	0.190
		35.004	29.363	3.478	0.190
		55.006	13.075	3.478	0.190
		74.996	7.951	3.478	0.190
		95.921	5.681	3.478	0.190
2199	275.00	20.000	96.289	3.707	0.190
		24.998	62.431	3.709	0.190
		35.004	32.896	3.708	0.190
		54.999	14.512	3.707	0.190
		74.996	8.712	3.708	0.190
		95.012	6.163	3.705	0.190

Sample No. 2b (Xenon)(Continued)

$\bar{T}$ (°K)	R_A (Ω)	$\omega/2\pi$ (Hz)	$R_A C_A$ (Ω - μF)	i_g (A)	i (rms A)
2287	287.50	20.001	107.750	3.940	0.200
		25.001	69.756	3.942	0.200
		34.998	36.653	3.942	0.200
		55.002	16.040	3.942	0.200
		75.002	9.519	3.942	0.200
		95.021	6.664	3.942	0.200
2375	300.00	20.001	119.870	4.177	0.200
		24.999	77.424	4.176	0.200
		34.999	40.581	4.178	0.200
		55.002	17.631	4.179	0.200
		75.002	10.356	4.178	0.200
		95.003	7.182	4.178	0.200
2462	312.50	20.000	132.370	4.417	0.210
		25.000	85.588	4.416	0.210
		35.002	44.713	4.418	0.210
		54.999	19.303	4.420	0.211
		75.002	11.250	4.419	0.210
		95.012	7.731	4.420	0.210
2550	325.00	20.000	145.500	4.660	0.220
		25.001	93.935	4.660	0.220
		35.001	49.017	4.662	0.220
		55.006	21.021	4.663	0.221
		74.991	12.171	4.661	0.220
		95.012	8.301	4.661	0.220
2638	337.50	20.000	158.650	4.904	0.240
		24.999	102.460	4.906	0.240
		35.002	53.318	4.907	0.240
		55.006	22.788	4.908	0.240
		75.008	13.115	4.909	0.240
		95.003	8.870	4.908	0.240
2654	340.00	20.001	161.190	4.951	0.260
		25.003	104.200	4.955	0.259
		35.002	54.257	4.957	0.260
		45.000	33.551	4.957	0.260
		54.999	23.137	4.959	0.260
		65.007	17.105	4.958	0.260
		74.996	13.304	4.958	0.260
		84.998	10.768	4.956	0.260

Sample No. 2b (Xenon)(Continued)

$\bar{T}$ (°K)	R_A (Ω)	$\omega/2\pi$ (Hz)	$R_A C_A$ ($\Omega \cdot \mu F$)	i_0 (A)	i (rms A)
2725	350.00	95.012	8.879	4.953	0.259
		20.000	172.120	5.153	0.259
		25.000	111.120	5.154	0.260
		35.002	57.813	5.157	0.260
		55.006	24.539	5.157	0.260
		75.008	14.042	5.154	0.260
2813	362.50	95.003	9.454	5.152	0.260
		20.002	185.120	5.405	0.270
		25.002	119.620	5.409	0.270
		35.003	62.143	5.411	0.270
		55.009	26.296	5.412	0.270
		75.013	15.000	5.412	0.270
2900	375.00	95.030	10.045	5.409	0.270
		20.003	198.380	5.669	0.280
		25.003	128.040	5.671	0.280
		34.999	66.488	5.675	0.280
		55.006	28.058	5.675	0.280
		75.013	15.926	5.675	0.280
2987	387.50	95.003	10.624	5.671	0.280
		20.002	210.600	5.931	0.289
		25.002	136.140	5.935	0.290
		34.999	70.575	5.939	0.290
		55.002	29.702	5.940	0.290
		75.008	16.821	5.940	0.290
3076	800.00	95.021	11.160	5.933	0.290
		20.009	223.820	6.225	0.300
		25.003	144.220	6.229	0.300
		34.999	74.488	6.234	0.300
		44.998	45.792	6.235	0.300
		55.006	31.088	6.232	0.300
3146	820.00	65.003	22.704	6.232	0.300
		75.008	17.416	6.229	0.300
		84.991	13.920	6.224	0.300
		95.012	11.440	6.219	0.300
		19.999	234.340	6.472	0.320
		24.999	150.950	6.479	0.320
		34.999	77.892	6.484	0.320
		45.005	47.831	6.488	0.320

Sample No. 2b (Xenon)(Continued)

$\bar{T}$ (°K)	R_A (Ω)	$\omega/2\pi$ (Hz)	$R_A C_A$ (Ω - μ F)	i_0 (A)	i (rms A)
		55.006	32.472	6.483	0.320
		65.003	23.682	6.483	0.320
		75.002	18.147	6.479	0.320
		84.983	14.481	6.475	0.320
		95.021	11.865	6.463	0.320

Sample No. 3 (Ar + I₂)

1117	125.00	95.003	3.135	1.822	0.200
		84.983	3.410	1.821	0.200
		75.002	3.785	1.822	0.200
		64.998	4.348	1.823	0.200
		54.999	5.248	1.824	0.200
		45.000	6.773	1.823	0.200
		35.001	9.785	1.823	0.200
		25.000	17.135	1.822	0.199
		19.999	25.535	1.823	0.200
		14.998	39.917	2.430	0.200
1490	175.00	85.012	4.372	2.430	0.200
		75.002	5.037	2.430	0.200
		65.003	6.034	2.430	0.200
		55.006	7.574	2.431	0.200
		44.994	10.322	2.433	0.200
		35.003	15.677	2.433	0.200
		25.000	28.749	2.433	0.200
		20.000	43.449	2.433	0.200
		14.994	51.130	3.195	0.200
		85.005	5.911	3.195	0.200
1854	225.00	74.991	7.027	3.196	0.200
		64.998	8.667	3.196	0.200
		54.990	11.327	3.195	0.200
		44.996	15.903	3.196	0.200
		35.003	24.971	3.196	0.200
		24.999	46.841	3.197	0.200
		20.000	71.996	3.197	0.200

Sample No. 4 (Ar + I₂)

$\bar{T}$ (°K)	R_A (Ω)	$\omega/2\pi$ (Hz)	$R_A C_A$ (Ω-μF)	i_0 (A)	i (rms A)
953	100.00	20.002	19.908	1.576	0.099
		25.001	13.518	1.575	0.100
		35.003	7.948	1.576	0.100
		45.005	5.658	1.576	0.100
		55.006	4.485	1.575	0.100
		65.011	3.813	1.575	0.100
		75.008	3.394	1.575	0.100
		84.998	3.105	1.575	0.100
		95.021	2.892	1.571	0.100
953	100.00	20.028	19.408	1.552	0.391
		25.002	13.228	1.552	0.300
		34.994	7.808	1.552	0.300
		45.000	5.588	1.552	0.300
		55.002	4.438	1.552	0.300
		64.998	3.783	1.551	0.300
		75.002	3.368	1.551	0.300
		84.991	3.098	1.552	0.300
		95.030	2.897	1.552	0.300
3200	800.00	20.003	228.180	6.652	0.501
		25.002	153.610	6.660	0.500
		35.005	79.316	6.666	0.500
		45.000	48.724	6.668	0.500
		54.999	33.112	6.671	0.500
		65.011	24.168	6.673	0.500
		75.008	18.552	6.674	0.500
		85.020	14.820	6.676	0.500
		95.057	12.168	6.677	0.500
3202	800.00	19.999	239.130	6.665	0.250
		24.998	154.170	6.672	0.250
		35.002	79.568	6.676	0.250
		45.002	48.864	6.680	0.250
		54.996	33.182	6.681	0.250
		64.998	24.236	6.684	0.250
		75.002	18.600	6.685	0.250
		85.012	14.848	6.685	0.250
		95.102	12.204	6.685	0.250
3346	840.00	19.999	249.040	7.148	0.251
		24.999	160.450	7.157	0.250

Sample No. 4 ($A_r + I_2$)(Continued)

T (°K)	R _A (Ω)	$\omega/2\pi$ (Hz)	R _A C _A (Ω-μF)	i ₀ (A)	i (rms A)
3383	850.00	34.993	82.849	7.167	0.250
		54.999	34.496	7.173	0.250
		74.996	19.270	7.176	0.250
		94.994	12.604	7.177	0.250
		19.999	250.180	7.278	0.250
		25.003	161.190	7.287	0.251
		34.996	83.173	7.294	0.250
		54.996	34.638	7.302	0.250
		74.996	19.363	7.305	0.250
		95.021	12.648	7.304	0.250
3418	860.00	20.001	250.410	7.405	0.250
		24.998	161.470	7.417	0.250
		34.997	83.325	7.428	0.250
		54.999	34.675	7.434	0.250
		74.991	19.367	7.435	0.250
		95.003	12.659	7.435	0.250

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