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MICROSECOND PULSE TECHNIQUE FOR HEAT CAPACITY MEASUREMENT

Tang-Hua Chen
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MICROSECOND PULSE TECHNIQUE FOR HEAT CAPACITY MEASUREMENT

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ABSTRACT

A refined thermal pulsing technique for measuring heat capacity of metals at high pressure is described. The technique originally involved measurements of the rate of temperature rise in the sample when a constant current power input was added for a short period of time. When the technique was applied to a highly conducting sample, the results were found to be poor because the heat leak from the sample to the surrounding medium was appreciable. Efforts were therefore directed towards improving measuring techniques and refining mathematical equations to account for the heat leakage. The technique was improved to render an essentially constant heat capacity of aluminum with pressure at room temperature. The major limitation at present still lies in the lack of quality measuring devices. Suggestions for future improvement are discussed.

Heat capacity of iron in vacuum between room temperature and 1100 K has been measured with the thermal pulsing technique to demonstrate its versatility. Differences in heat capacity between an annealed sample and a cold-worked sample were noted. The drastic change in heat capacity of iron in the vicinity of the magnetic phase transition was measured with an error less than 2%.
The electrical resistance of iron was measured between liquid nitrogen and room temperatures at seven different pressures. The dependence of the electrical resistance of iron on the three-halves power of the absolute temperature at pressures greater than 20 kbar previously reported was not observed.
I. INTRODUCTION

The importance of heat capacity lies in the fact that it relates two fundamental physical quantities; temperature and entropy. Various methods have been developed in the past for measuring heat capacity. Most of these are adiabatic in nature and are mainly suited for measurements at 1 atmosphere or in vacuum.

With the advance in high pressure technology, it is a desirable step to investigate pressure effects on heat capacity. The realization that heat capacity over the temperature and pressure domain could lend itself readily for calculating equations of state (see II.A.) provided another major thrust for this measurement.

Due to the huge mass associated with high pressure apparatus, adiabatic measurements of heat capacity at high pressure are precluded. A pulsing technique, first described by Avamescu, offered a solution to the problem.

The method was originally developed for heat capacity measurement of metals in vacuum and a large storage battery was employed to generate heat through discharge. In the rigorous sense, the discharge of a battery did not give a pulse and, in addition, the total energy of the discharge could not be measured precisely enough to yield good results. However, the idea, that a fast enough thermal pulse sent through the sample will be consumed solely by raising the sample temperature (since a time lag always exists between the temperature rises of the sample and the surrounding medium), appeared extremely good.
The basic pulsing technique was implemented by Stark\textsuperscript{8} when he first undertook the formidable task of high pressure heat capacity measurements. The use of a constant current pulse instead of a exponentially decaying current was developed. An ingenious technique of dc offset to enhance sensitivity for measuring sample temperature rise was also devised by him. The heat capacity of iron between liquid nitrogen and room temperatures was measured isobarically at high pressure with success. Yee\textsuperscript{9} continued the work by building a constant current pulse generator which gave fast switching time and accurately controlled constant current pulse. Five isobaric heat capacity measurements of iron between liquid nitrogen and room temperatures were conducted with an uncertainty of 2\%.

Both Stark and Yee derived heat capacity results from very short pulses which lasted no more than 300 μsec. The reason, as pointed out earlier, was to get the heat capacity near the beginning of the pulse so that a minimum of the energy input had the chance to leak from the sample to the surrounding. This worked fine for iron. When more electrically conducting samples were used, one was faced with the problem of a compromise between a decrease in sample diameter for better resistance measurement (the key to accurate temperature measurement) and an increase of sample diameter for smaller surface to volume ratio to reduce heat leak. Aluminum was a metal for which a small sample diameter had to be used and one was confronted with the heat leak problem directly. In order that the constant current pulse be made a more general technique, aluminum was chosen as the
sample for testing to improve the method.

The approaches adopted were along two directions. First, mathematical equations were developed on theoretical and semiempirical grounds to account for the heat leak. Second, efforts were spent on improving measuring techniques so that significant data could be secured to test out various equations. The pulse technique has been refined to the limits of available instrumentation.

It was realized that the constant current pulsing technique was valuable not only for high pressure but also for vacuum heat capacity measurements. In the latter case, one should enjoy the accuracy of energy input of the constant current pulse over that of the battery discharge. The heat leak would also cease to be a serious problem until very high temperature is reached where radiation loss predominates. To demonstrate the effectiveness of the constant current pulse technique, heat capacity of iron in vacuum between room temperature and 1100 K was measured.
II. HIGH PRESSURE HEAT CAPACITY

A. Theory

1. Thermodynamic Functions

In the absence of electric, magnetic, and gravitational field the equation of state of a one-component solid relates stress-strain, and temperature. To simplify the picture, we shall confine ourselves to a solid under hydrostatic pressure only. The equation of state for such a solid can then simply be written either as

\[ f(P, V, T) = 0 \]

or

\[ V = V(P, T) \]

The thermodynamic functions that are of interest are the heat capacity at constant volume \( C_v \); the heat capacity at constant pressure \( C_p \); the entropy \( S \), the internal energy \( E \), the enthalpy \( H \), the Helmholtz free energy \( A \), and the Gibbs free energy \( G \) in terms of two independent variables. Obviously thermodynamics would not be useful if all the functions had to be measured experimentally. In fact only some of the functions need to be determined and the rest can be deduced through thermodynamic relations.

One method of calculating the thermodynamic functions requires the equation of state and an isobaric heat capacity as a function of temperature. An alternative method, on the other hand, requires the heat capacity as a function of pressure and temperature along with
one pressure-volume isotherm. Both approaches shall be described briefly.

First Method:

By definition heat capacity is

\[ C = \lim_{{\Delta T \to 0}} \frac{\Delta Q}{\Delta T} . \]

From the second law of thermodynamics, we know that

\[ Q_{\text{rev}} = T \Delta S , \]

and that the heat capacity for a reversible process is therefore

\[ C = T \cdot \frac{dS}{dT} . \]

The heat capacities at constant pressure and constant volume are

\[ C_p = T \cdot \frac{dS}{dT} \]

and

\[ C_v = T \cdot \frac{dS}{dT} \]

respectively.

The \( C_p \) value at any pressure and temperature can be calculated from

\[ C_p(P,T) = C_p(P',T) + \int_{P'=P}^{P} \left( \frac{\partial C_p}{\partial P} \right) dP \]

and

\[ \left( \frac{\partial C_p}{\partial P} \right)_T = \left( \frac{\partial}{\partial P} \left( T \frac{\partial S}{\partial T} \right)_P \right)_T = T \left( \frac{\partial}{\partial T} \left( \frac{\partial S}{\partial P} \right)_T \right)_P = T \left( \frac{\partial}{\partial T} \left( - \frac{\partial V}{\partial T} \right)_P \right)_P \]

\[ = - T \left( \frac{\partial^2 V}{\partial T^2} \right)_P , \]
where \( C(P', T) \) is measured directly and \( (\partial^2 V/\partial T^2) \) is available from the equation of state.

\( C_v \) can be calculated easily from \( C_p \) by the thermodynamic relation

\[
C_p - C_v = -T(\partial V/\partial T)^2/(\partial V/\partial p)_T .
\]

To calculate \( E(P, T) \), we can write

\[
E(P, T) - E(P_0, 0) = \int_{T=0}^{T} \frac{dE}{dP} = \int_{T=0}^{T} P \frac{\partial E}{\partial T} dT + \int_{P=0}^{P} P \frac{\partial E}{\partial P} dp ,
\]

\[
(\partial E/\partial P)_T = T(\partial S/\partial T)_p - P(\partial V/\partial T)_p = -T(\partial V/\partial T)_p - P(\partial V/\partial T)_p
\]

through differentiation of \( dE = TdS - PdV \) with respect to \( P \) at constant \( T \); use of the Maxwell relation \( (\partial S/\partial P)_T = -(\partial V/\partial T)_P \); and

\[
(\partial E/\partial T)_P = T(\partial S/\partial T)_P - P(\partial V/\partial T)_P = C_p - P(\partial V/\partial T)_P .
\]

Combining the above equations,

\[
E(P, T) = E(P_0, 0) + \int_{T=0}^{T} \frac{dE}{dP} \left[ C_p - P(\partial V/\partial T)_P \right] dT - \int_{P=0}^{P} \left[ T(\partial V/\partial T)_P + P(\partial V/\partial T)_P \right] dp
\]

is obtained.

The enthalpy \( H \) is \( H = E + PV \).
The entropy is found to be

\[ S(P,T) = S(P,0) + \int_{T=0}^{T} \left( \frac{\partial S}{\partial T} \right)_{P} dT = 0 + \int_{T=0}^{T} \left( \frac{C_{P}}{T} \right) dT \]

because the entropy of a perfect crystal at absolute zero is zero irrespective of pressure.

Once \( S, E, \) and \( H \) are known, \( A \) and \( G \) can be determined from their definitions

\[ A \equiv E - TS \]
\[ G \equiv H - TS \]

It is now obvious that from \( V(P,T) \) and \( C_{P}(P',T) \) to calculate \( C_{P} \) at other pressures and other thermodynamic functions. It is necessary at first to differentiate volume with respect to temperature twice. This imposes limitation on the reliability of the results so obtained.

**Alternative Method:**

Equation (T1) can be integrated at constant \( P \) to yield

\[ \int_{T=0}^{T} - T \left( \frac{\partial C_{P}}{\partial T} \right)_{T} dT = \int_{T=0}^{T} \frac{\partial V}{\partial T} \bigg|_{P} = \left( \frac{\partial V}{\partial T} \right)_{P} = \left( \frac{\partial V}{\partial T} \right)_{P} \bigg|_{T=0} = \left( \frac{\partial V}{\partial T} \right)_{P} \bigg|_{T} \]  

(T2)

The \( \left( \frac{\partial V}{\partial T} \right)_{P} \bigg|_{T=0} \) drops out because

\[ \left( \frac{\partial V}{\partial T} \right)_{P} \bigg|_{T=0} = \left( \frac{\partial S}{\partial P} \right)_{T} \bigg|_{T=0} = 0 \]

Equation (T2) can be further integrated at constant \( P \) to give

\[ V(P,T) - V(P,0) = \int_{0}^{T} dV = \int_{0}^{T} \left( \frac{\partial V}{\partial T} \right)_{P} dT = \int_{0}^{T} dT \int_{0}^{T} - T \left( \frac{\partial C_{P}}{\partial T} \right)_{T} dT \]  

(T3)
Thus we can generated the whole $V(P,T)$ and other functions through integrations of $(\partial G/\partial P)_T$ with the help of $V(P,T=0)$, or of $V(P,T')$ and $(\partial V/\partial T)_{P,T=T'}$. This is obviously a better way to go about all the thermodynamic functions, because integration of experimental data yields answers with less error than differentiation.

Both approaches discussed assume that there is no phase transition between $T=0$, $P=0$ and $T,P$. However, the basic idea is still valid if a polymorphic transition does occur. All we need to do is to determine the volume change and the enthalpy of transition between the phases. The equations outlines above are modified to include the additional terms involving $\Delta V$ and $\Delta H$. For example,

$$S(P,T) = \int_{T=0}^{T_1} C_p d\ln T + \frac{\Delta H_T}{T_1} + \int_{T=T_1}^{T} C_p d\ln T .$$

Experimentally, $\Delta V$ can be measured directly. $\Delta H$ can subsequently be evaluated by Clapeyron equation

$$dP/dT = \Delta H/T\Delta V .$$

Measurement of $\Delta H$ directly is now underway by this group. The preliminary result seems encouraging. At worst, directly measured $\Delta H$ can be used to check the deduced value from Eq. (T4).

The preceding methods are purely experimental. Theoretical calculations of thermodynamic functions can be realized by statistical mechanics. A model of the solid is first set up to describe its coordinates, and momenta. Its energy levels and partition function are computed next. From the partition function, all the thermodynamic
functions ensue. Apparently the choice of the model is both important and difficult.

2. Heat Conduction in Solids

The heat flow, \( f \), per unit area along the thermal gradient of an isotropic and homogeneous substance is

\[
  f = -K \left( \frac{\partial T}{\partial n} \right)
\]

(\( H1 \))

where \( K \) is the heat conductivity and \( \left( \frac{\partial}{\partial n} \right) \) is differentiation along the outward normal to the isothermal surface. The negative sign indicates that the heat flow is in the opposite direction as that of the thermal gradient.

Consider a stationary infinitesimal volume element consisting of an isotropic, homogeneous substance in which heat is generated at a rate of \( A \) per unit volume per unit time. The substance has a density of \( \rho \) and heat capacity of \( c \) per unit mass. The outgoing heat flow across the volume boundary is \( \iint f \cdot dS \), the heat generated inside the volume is \( \iiint A \cdot dv \), and the difference between the two is consumed in heating the substance inside the volume because no work is involved and the energy must be conserved. This relationship is expressed as

\[
  \iint f \cdot dS + \iiint A \cdot dv = \iiint \rho c \left( \frac{\partial T}{\partial t} \right) \cdot dv
\]

(\( H2 \))

By using divergence theorem,

\[
  \iiint f \cdot dS = \iiint (\nabla \cdot f) dv
\]

(\( H3 \))
Eq. (H2) can rewritten as

$$- \iiint (\nabla \cdot f) dv + \iiint \nabla \cdot A \ dv = \iiint \rho c \left( \frac{\partial T}{\partial t} \right) dv .$$

(H4)

If Eq. (H4) holds true for any infinitesimal volume, the integrands on both sides must be equal to each other. That is,

$$- \nabla \cdot f + A = \rho c \left( \frac{\partial T}{\partial t} \right) .$$

(H5)

Substituting Eq. (H1) in Eq. (H5), we get

$$k\nabla^2 T + A = \rho c \frac{\partial T}{\partial t} \quad (H6)$$

and further

$$\nabla^2 T - \frac{1}{k} \frac{\partial T}{\partial t} = - \frac{A}{K} \quad (H7)$$

where \( k \equiv \frac{K}{\rho c} \) is called the diffusivity or the thermometric conductivity.

The temperatures on both sides of a boundary, which separates two different solids, are identical provided the surfaces are optically flat and held tightly together. If the previous condition is not met, temperature difference will persist, and the conductive heat flow is proportional to this temperature difference.$^{13}$

Another heat transfer mechanism is black body radiation. The heat loss is proportional to the fourth power of the absolute temperature. At room temperature and under high pressure the radiative heat transfer is negligible in comparison with that due to the conductive heat flow.
To understand what occurs when a constant current pulse passes through the sample, it is necessary to study heat conduction in solids.

The physical setup of the sample is illustrated in Fig. 3. Because the cross section of the sample is small comparing with its length, the sample can be considered to be a cylinder instead of a circular ring so that the cylindrical coordinate system can be used, which simplifies the mathematics. If we take a cross section of the sample, the whole system will look like that shown in Fig. 1, a is the radius of the sample; l the length of the sample; medium 1 the sample, medium 2 the surrounding; and T the temperature. The reason \( \theta \) (the azimuthal angle) does not come into the picture is that both the sample and the surrounding are considered isotropic.

Differential equations corresponding to the above conditions can easily be written. Solution of the differential equations depend on the initial and boundary conditions, and energy conservation determines the final solutions.

Before a pulse, both the sample and the surrounding are at thermal equilibrium so that the initial condition is simply

\[ T_1 \bigg|_{t=0} = T_2 \bigg|_{t=0} = 0. \]  

To simplify the problem further, the sample, being a good electrical and thermal conductor compared to the surrounding, is treated as a perfect thermal conductor. This means that \( T_1 \) will no longer depend on \( r \), that is, the sample will have a uniform temperature. Therefore
Fig. 1. The cylindrical coordinate system used for treating the heat conduction problem.
we can write

\[ T_1 = T_1(t) \]  \hfill (H9)

At \( r=\alpha \), i.e.; at the boundary between media 1 and 2, the heat transfer is proportional to the temperature difference. It can be written as

\[ f = H(T_1 - T_2) \]  \hfill (H10)

The differential equations thus obtained are

\[ \frac{\partial T_1}{\partial t} = I^2 R - 2\pi aH(T_1 - T_2) \quad \text{at } r < \alpha \text{ in medium 1} \]  \hfill (H11)

\[ H(T_1 - T_2) + k_2 \frac{\partial T_2}{\partial r} = 0 \quad \text{at } r = \alpha \]  \hfill (H12)

\[ \nabla^2 T_2 = \frac{\partial T_2}{k_2 \partial t} = \frac{\partial^2 T_2}{\partial r^2} + \frac{\partial T_2}{\partial r} \quad \text{at } r > \alpha \text{ in medium 2} \]  \hfill (H13)

By taking the Laplace transform \(^{14}\) of Eq. (H12) and making use of the initial condition Eq. (H8), we get

\[ \frac{\partial^2 T_2}{\partial r^2} + \frac{1}{r} \frac{\partial T_2}{\partial r} - q^2 T_2 = 0 , \]  \hfill (H14)

where \( q_2^2 = p/k_2 \) and \( p \) is the variable from the Laplace transform.

Making

\[ r \equiv z/q \]  \hfill (H15)
and substitute $r$ into Eq. (H14), it takes a new form of

$$\frac{\partial^2 T_2}{\partial Z^2} + \frac{1}{Z} \frac{\partial T_2}{\partial Z} - (1 - \frac{0}{z^2}) T = 0. \quad (H16)$$

This is a standard differential equation with a solution of

$$\bar{T}_2 = BI_0(z) + CK_0(z) \quad (H17)$$

where $I_0$ and $K_0$ are the zeroth order hyperbolic Bessel functions of the 1st and 2nd kind respectively. Since $T_2$ remains finite and $I_0$ becomes infinity when $z$ approaches infinity, it is obvious that the coefficient $B$ in Eq. (H17) has to vanish. Therefore,

$$\bar{T}_2 = CK_0(q_2 r) \quad (H18)$$

Defining $A = l^2 R$ and $H' = H_{2\pi a}$, where $l$ is the length of the sample, the Laplace transform of Eq. (H11) is

$$C_{pp} \bar{T}_1 = \frac{A}{p} - H'(T_1 - \bar{T}_2) \quad (H19)$$

and on further simplification becomes

$$\bar{T}_1 = (A/p + H' \bar{T}_2 )/(pC_p + H'), \quad (H20)$$

where $p$ is the variable through the transformation. Similarly the Laplace transform of Eq. (H13) is

$$H(\bar{T}_1 - \bar{T}_2) = -K_2 \frac{\partial^2 \bar{T}_2}{\partial r^2} \quad (H21)$$
Substituting Eq. (H20) into Eq. (H21), we get

\[
\left( \frac{A/p + H'T_2}{pCp + H'} - \frac{T_2}{a} \right) + \frac{K_2}{H} \left( \frac{\partial T_2}{\partial r} \right)_a = 0. \tag{H22}
\]

Equation (H22) can be simplified by making use of Eq. (H18) and the fact that

\[
\frac{\partial K_0(x)}{\partial x} = -K_1(x)
\]

to be

\[
\frac{A/p - PCpK_0(q_2a)}{pCp + H'} - \frac{K_2}{H} C q_2 K_1(q_2a) = 0. \tag{H23}
\]

From Eq. (H23), we get

\[
C = \frac{A}{pq_2} \cdot \left[ \frac{pCpK_0(q_2a)}{q} + \frac{pCpK_2}{H} K_1(q_2a) + 2\pi a K_2 K_1(q_2a) \right]. \tag{H24}
\]

Once C is determined, \( \bar{T}_1 \) and \( \bar{T}_2 \) can be written out explicitly by substituting Eq. (H24) into Eqs. (H18) and (H20),

\[
\bar{T}_2 = C K_0(q_2r) \tag{H25}
\]

\[
\bar{T}_2 = \left[ \frac{A}{F} + H'C K_0(q_2r) \right] / (pCp + H') \tag{H26}
\]

\( T_1 \) and \( T_2 \) can be obtained by transforming \( \bar{T}_1 \) and \( \bar{T}_2 \) respectively by

\[
T(t) = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \bar{T}(p) e^{pt} dp. \tag{H27}
\]
Because both Eqs. (H25) and (H26) are very complicated, direct solution by inverse transformation is not possible. However, approximation solutions can be arrived at by expanding the modified Bessel functions in ascending powers, for the very short and very long time regions.

The criterion for the short-time approximation to be valid is

$$k_2 t/a \ll 1,$$

(H28)

and the approximate solution is

$$\Pi_1 = \frac{A}{\pi \alpha^\alpha} \left[ \frac{1}{2} - \left( \frac{2H}{\alpha} \right) \frac{1}{3} + \left( \frac{2H^2 k_2}{\alpha K_2} \right) \frac{1}{p^{1/2}} + \mathcal{O} \left( \frac{1}{p^4} \right) \right],$$

(H29)

where

$$\alpha \equiv \frac{C_p}{\pi \alpha}$$

(H30)

Transforming Eq. (H29), we get

$$T_1(t) = \frac{A}{\pi \alpha^\alpha} \left[ t - \frac{H^2 k_2}{15 \alpha K_2} \frac{t^{5/2}}{p^{1/2}} + \mathcal{O}(t^3) \right]$$

[H31]

$$= \frac{I^2 R}{C_p} \left[ t - \frac{H \pi \alpha}{C_p} t^2 + \frac{16}{15 \sqrt{\pi}} \cdot \frac{H \pi \alpha}{K_2} \cdot \frac{H}{K_2} \cdot t^{5/2} + \mathcal{O}(t^3) \right].$$

The approximate solution for the long-time limit includes a lnT term, and terms in the $T^{-1}$ and $T^{-2}$. 

-16-
For the general problem where the sample cannot be considered as a perfect thermal conductor, the differential equations and the conditions take the form of:

\[
\nabla^2 T_1 + \frac{A}{K_1} = \frac{1}{k_1} \frac{\partial T_1}{\partial t} \quad \text{at} \quad r < a , \tag{H32}
\]

\[
H(T_1 - T_2) = -K_1 \left( \frac{\partial T_1}{\partial r} \right) = -K_2 \left( \frac{\partial T_2}{\partial r} \right) \quad \text{at} \quad r = a , \tag{H33}
\]

while Eqs. (H8), (H13), and (H18) still hold true.

Taking the Laplace transform of Eqs. (H32) and (H33), we get

\[
\bar{T}_1 = C_1 I_0(q_1 r) + C_2 K_0(q_1 r) + A/K_1 \rho \tag{H34}
\]

and

\[
(\bar{T}_1 - \bar{T}_2) = -\frac{K_1}{H} \left( \frac{\partial T_1}{\partial r} \right)_{a} = \frac{K_2}{H} \left( \frac{\partial T_2}{\partial r} \right)_{a} \tag{H35}
\]

Since \(K_0\) becomes infinity and \(\bar{T}_1\) remains finite when \(r\) approaches zero, the coefficient \(C_2\) has to be zero and Eq. (H34) becomes

\[
\bar{T}_1 = C_1 I_0(q_1 r) + A/K_1 \rho \tag{H36}
\]

Making use of Eqs. (H36), (H18), and (H35), we get

\[
C_1 I_0(q_1 a) + \frac{A}{K_1 p} - C_2 K_0(q_2 a) = -\frac{K_1 q_1}{H} C_1 I_1(q_1 a) , \tag{H37}
\]

\[
C_1 I_0(q_1 a) + \frac{A}{K_1 p} - C_2 K_0(q_2 a) = \frac{K_2}{H} q_2 C_2 K_1(q_1 a) , \tag{H38}
\]
and

$$C_2 = -\frac{K_1 q_1 I_1(q_1a)}{K_2 q_2 K_1(q_2a)} C_1.$$  \hfill (H39)

Combining Eqs. (H39) and (H37),

$$C_1 = -\frac{A}{K_1^p [I_0(q_1a) + \frac{K_1 q_1 I_1(q_1a) K_0(q_2a)}{K_2 q_2 K_1(q_2a)} + \frac{K_1 q_1}{H} I_1(q_1a)]}$$  \hfill (H40)

can be obtained and when it is substituted into Eq. (H36) it yields

$$T_1(r) = \frac{K_0(q_2r) K_1 q_1 I_1(q_1a)}{K_1^p[I_0(q_1a) + K_1 q_1 I_1(q_1a)\left(\frac{1}{H} + \frac{K_0(q_2a)}{K_2 q_2 K_1(q_2a)}\right)] K_2 q_2 K_1(q_2a)}.$$  \hfill (H41)

Equation (H41) can be treated in the same way as Eq. (H26) was to get an approximate solution for the short-time limit. Other than radial distance dependent terms, the solution has the functional dependence on \(t\) as Eq. (H31) does.\textsuperscript{17}

A series of problems of heating an underground electric cable have been treated and approximate solutions cited by Carslaw and Jaeger.\textsuperscript{13}
B. **Experimental**

1. **High Pressure Apparatus and Sample Assembly**

The high-pressure generating apparatus used in the present work is a Bridgman Opposed-anvil system used in conjunction with a hydraulic press.

The hydraulic pump system is powered by compressed air. A block diagram is shown in Fig. 2. Compressed air is first filtered so that it is water and dirt free, and is then sent to the S. C. hydraulic pump, which uses a relatively large air-operated piston to drive a smaller piston that provides fluid flow at high pressure.

Compressed air goes through valve A, water trap, regulating valve R, filter, and another valve into the hydraulic pump. Oil from the reservoir is sucked through an oil filter and is compressed through the tube to connector C.

To increase the load, valves D and DB are closed and valves U and UB are open. High pressure oil at connector C goes through the open valve U to the lower cylinder of the press, and forces the piston to go up. Excess oil at the upper end is bled through connector B, valve UB back to the reservoir.

To decrease the load, valves U and UB are closed and valves D and DB are open. Compressed oil at connector C goes through the open valve D, connector B, and into the upper cylinder of the press to force the piston to go down. Excess oil in lower cylinder is bled through the open valve DB back to the reservoir.
Fig. 2. The pressure generating apparatus.
When the piston goes up, it compresses the Bridgman anvils and other filler blocks in between it and the press yoke. Pressure is thereby generated.

Calibration of pressure was made by assuming a linear relationship between load and pressure, and taking advantage of the known three phase transitions of bismuth. Details of the calibration procedures are described by Jura, et al.\textsuperscript{19} Souers\textsuperscript{20} and Yee's\textsuperscript{9} theses also include useful information about the system generally used by this group. Various books,\textsuperscript{21-29} conference proceedings,\textsuperscript{30-33} and review articles\textsuperscript{34-42} should be consulted for additional information on different aspects of high pressure research.

For the present work the sample and pressure cell assembly was similar to that described by Yee.\textsuperscript{9}

The sample was an aluminum wire with a diameter of 0.002" with a nominal purity of 99.99%. It was purchased from California Fine Wire Company and was annealed at 400°C for 12 hours in an argon atmosphere.

The pressure transmitting medium, silver chloride, was purchased from Harshaw Company in the form of 5"×6"×0.025" plates. A strip of 1"×3" was cut off and rolled down to a thickness of 0.0065". One side of the silver chloride sheet was evenly sprayed with acrylic to form a protective thin film lest the sample should be oxidized by silver chloride. The silver chloride sheet thus sprayed was dried for more than 24 hours. The final thickness of the sheet was 0.007". For each pressure run two circular disks with diameter of 5/16"
were punched out of the prepared sheet and rough edges were carefully trimmed off.

Pyrophyllite (a volcanic lava with a chemical composition of \( \text{Al}_2\text{Si}_4\text{O}_{12}\text{H}_2 \)) gasket rings with outside diameter of 0.5", inside diameter of 5/16", and thickness of roughly 0.011" were prepared by D. Newhart of IMRD, LBL. The pyrophyllite rings were carefully and evenly ground down to 0.010" and painted with a mixture of ferric oxide powder suspended in propanol to further increase the friction for a better seal.

The procedures for assembling the pressure cell were as follows:

The sample wire of proper length, roughly 0.55", was wound around an aluminum cylindrical rod of 0.190" in diameter, or a #11 drill, to form an almost complete loop. The sample loop was then centered on a trimmed silver chloride disc with the acrylic side facing the sample. A shim of 0.008" in thickness was placed around the silver chloride disc and light pressure was applied so that the sample loop was slightly imbedded in the silver chloride. The silver chloride disc together with the sample loop was next put on the anvil face. One prepared pyrophyllite ring was put around the disc.

Four 0.005" platinum wires of 4" in length were placed, two to each end of the loop, with ends touching the loop (see Fig. 3). The wires were further taped down on the anvil, which had already been covered with mylar tape to insure electrical insulation. Of these four leads, two were for delivering current to the sample, the other two were for measuring the voltage drop across the sample.
Fig. 3. Sample assembly.
A 0.005" alumel-chromel thermocouple junction was also installed near the gap of the sample loop. The thermocouple monitored the temperature of the sample.

Another silver chloride disc, with the acrylic side facing downward, and another pyrophyllite ring were put on top of the one already laid down. Three guides were secured around the anvils by gear type clamps. The top anvil was then lowered slowly. It was found that if three lumps of duxeal were placed on the lower anvil near the guides, the upper anvil could be lowered with more ease. The duxeal lumps served as shock absorbers so that there was less worry the upper anvil might crush the brittle pyrophyllite rings.

With back-up blocks on each side of the paired anvils, the assembly was ready to be put in between the hydraulic pump piston face and the press yoke. A load cell, with manganin wire as an arm of a bridge circuit, and filler blocks were added to fill up the empty space between the anvil assembly and the press yoke.

With the load cell connected to the strain indicator, a Baldwin Lima-Hamilton Type 20, and the leads properly connected to power supplies and measuring devices, the whole assembly was then ready to be compressed and measured.

During the temperature runs to find the temperature coefficient of electrical resistance, a tank was inserted in the column assembly (Fig. 4). White oil was used to fill up the tank, in the middle of which the sample lay. Two heating blades and an electric stirrer were used to heat up the oil slowly so that the sample could experience a steady and slow temperature increase, during which the resistance
Fig. 4. Column setup for temperature run.
and temperature of the sample were measured.

2. Measurements of Voltage, Resistance, Temperature, and Pressure

a. Voltage. A Newport Model 2400A digital microvoltmeter with full range of ±40 mV and resolution of 1 μV was employed for all the measurements of steady dc voltages. A Lambda Model LS511 precision voltage power supply with a range of 0-10 V, a resolution of 0.1 mV, was used as the primary standard to calibrate the digital voltmeter. The nonlinearity of the Newport digital voltmeter was found to be ±2 μV. An appropriate switch mechanism permitted the digital voltmeter to measure the voltage drops across the sample, a standard resistor, and determine the thermocouple potential (Fig. 5).

b. Resistance. The use of Ohm's law, which states that the electrical resistance is proportional to the voltage drop was used to determine the resistance of a sample by passing a known current through the sample and measuring the voltage drop. A variable dc constant current power supply (LRL-226084) was used throughout this work to provide a 0.1 ampere current through the sample and a standard resistor of 1.000000±0.000001 Ω. A voltage divider of known ratio, approximately 0.1, stepped down the voltage across the standard resistor to bring it within the range of the digital voltmeter. From the known resistance of the standard resistor and the voltage divider ratio, the constant current can be measured accurately. The voltage across the sample divided by the current gave the sample resistance.
Fig. 5. Diagram for current, resistance, and temperature measurements.
The advantage of using four leads instead of two for the resistance measurement is that the lead resistance is excluded in the measurement. Another switch box that changed the direction of the constant current made it possible to eliminate thermal emfs that might exist along the sample.

The accuracy of resistance measurement was estimated to be 0.00005 Ω.

c. Temperature. The measurement of temperature was made by measuring the emf of an alumel-chromel thermocouple with the Newport digital microvoltmeter. The accuracy of temperature measurement was estimated to be 0.1°C.

d. Pressure. The pressure was determined indirectly by measuring the load experienced by the load cell through the use of the BLH Type 20 strain indicator. A calibration run with 0.005" bismuth wire through the three known phase transitions at 25.4, 26.9, and 88 kbars, where the electrical resistance of bismuth manifests drastic changes, was used to establish the relationship between load and pressure. The accuracy of pressure was roughly 5%.

3. Measurements of Pulse Voltage

A constant current pulse power supply designed by Yee and modified by me was used through this project. A block diagram of the circuitry is shown in Fig. 6.
Fig. 6. Block diagram of electronics for pulsing.
The purpose of the circuitry is to generate and determine a constant current through the sample, and to amplify the sample voltage signal.

A constant voltage from the Lambda LS511 power supply was stepped down to one tenth of its magnitude by a voltage divider, and was fed to the noninverting input of an Analog Device Model 350B comparator. The inverting input of the comparator was connected to the voltage drop by the pulsing current through a 0.1 Ω shunt resistor. The comparator has a bistable output; a 0 V output when the shunt resistor voltage is smaller than the stepped-down Lambda voltage and a -6 V output otherwise. By varying the current output so that the comparator output fluctuated between 0 and -6 V, the shunt voltage was made equal to the reduced Lambda voltage. From the Lambda setting, the ratio of the voltage divider, and the shunt resistance, the pulsing current could be accurately controlled and determined to ±1 mA.

When a constant current pulse went through the sample, the voltage versus time looked like a curved triangle superimposed on a rectangle as shown in Fig. 7. The component $\Delta E$ is $\Delta E(t) = I(R(t)-R_0)$, where $R_0$ was the sample resistance prior to and at the beginning of the pulse ($t=0$), $R(t)$ was the sample resistance at time $t$. Because the sample temperature increased through Joule heating, $R(t)$ increased with time. Yet the rate of increase was slower than linear, since the heat leakage from the sample increased with time too. This accounted for the curved shape. The rectangular component was $E_0 = I R_0$. For a pulse of 2 to 3 A and 1 msec duration through the sample, the
Fig. 7. (a) $I(t)$ vs $t$
(b) $E(t)$ vs $t$.
maximum $\Delta E$ was about 2% of $E_0$. Details of $\Delta E$ vs $t$, the region where information was stored, were desired. It was obvious that either an ultrahigh resolution voltage recorder be used or only the $\Delta E$ portion of the signal be amplified. It was estimated that an analog-to-digital converter with a 17-bit resolution (roughly one part in one hundred thousand) at 1 V was required. This was too stringent a requirement, and consequently the second alternative became necessary.

The block diagram Fig. 6 shows the components used.

The voltage drop across the sample was first amplified by a factor of 10 with an Intertech LED 21530 differential amplifier, and was then fed to the inverting input of a Burr-Brown Model 3061/16 instrumentation amplifier. The voltage across the 0.1 $\Omega$ shunt resistor was amplified by an Analog Device Model 148B operational amplifier. A switch box enabled the gain of the AD-148B to be chosen to be any of the following values: 2, 10, 20, 30, 40, 50, and 100. A fraction of the amplified shunt signal could then be obtained through a 10-turn 2,000 $\Omega$ potentiometer, and was fed to the non-inverting input of the BB-3061/16 amplifier. The BB amplifier amplified the difference between the two inputs by another factor of 10, and this was the final output signal that was recorded.

To express all the relations in arithmatical form, the following quantities shall be defined first.

$$R \equiv \text{resistance of sample},$$
$$R_o \equiv (R)_{t=0},$$
$$R_s \equiv \text{resistance of the shunt resistor},$$
A_1, V_1 \equiv \text{amplification factor and output voltage of the Intertech amplifier},

A_2, V_2 \equiv \text{amplification factor and output voltage of the AD-148B amplifier},

A_3, V_3 \equiv \text{amplification factor and output voltage of the BB-3061/16 amplifier},

F \equiv \text{ratio of the 2KΩ 10-turn voltage divider},

V \equiv \text{voltage of the final output signal}.

The following relationships can be written immediately.

\[ V = V_3 \]

\[ = A_3(V_1 - V_2 F) \]

\[ = A_3(A_1 IR - A_2 RsF) \]

\[ = IA_3(A_1 R - A_2 RsF) \] \hspace{1cm} \text{(E1)}

By varying A_2 and F, V could be adjusted to a convenient level to be measured easily.

At t=0,

\[ V_0 = IA_3(A_1 R_0 - A_2 RsF) \] \hspace{1cm} \text{(E2)}

From Eq. (E1) and Eq. (E2),

\[ V - V_0 = IA_3A_1(R - R_0) \] \hspace{1cm} \text{(E3)}

The true value of the voltage across the sample was
\begin{align}
E &= IR \\
&= I(R_0 + (R - R_0)) \\
&= IR_0 + I(R - R_0) \\
&= E_0 + (V - V_0)/(A_3 A_1). \tag{E4}
\end{align}

In order to get \( E \), the values the values of \( A_3 \), \( A_1 \), \( V_0 \), and \( V \) must be determined. \( A_3 \) and \( A_1 \) were determined by sending voltage output from the Lambda power supply to the inputs of the BB and Intertechn amplifiers and the amplified outputs therefore were measured with the digital voltmeter respectively.

The constant current square pulse was far from ideal, that is, it took a finite time, usually 50 \( \mu \)sec, to attain the final constant current value. By this time the sample had already been heated up and a precise determination of \( V_0 \) was not possible.

To circumvent this difficulty, variable resistors with very large heat capacities were wound noninductively out of \#14 gauge insulated copper wire and inserted in the circuit in series with the sample and the shunt resistor. The variable resistor could be adjusted to within 1 miliohm of that of the sample. Because the variable resistor had very large heat capacity, its temperature increase by the pulse was negligible and, therefore, its resistance remained unchanged during the pulse. The ratio of the 2 \( K \) \( \Omega \) voltage divider could be continually varied until

\begin{align}
V &= I \cdot A_3 (A_1 \cdot R_v - A_2 \cdot R_s \cdot F) = 0 \tag{E5}
\end{align}
when the switch connected the voltage across the variable resistor to the Intertech amplifier. Then,

$$A_1 \cdot R_v = A_2 \cdot R_s \cdot F.$$  \hspace{1cm} (E6)

Without changing either the variable resistor nor the F, the Intertech amplifier input could be connected back to the sample voltage, and from Eq. (E6) and Eq. (E2) we have

$$V_o = I \cdot A_3 \cdot (A_1 \cdot R_o - A_1 \cdot R_v)$$

$$= I \cdot A_3 \cdot A_1 \cdot (R_o - R_v).$$  \hspace{1cm} (E7)

Since all of $R_o$, $R_v$, $I$, $A_3$, $A_1$ could be measured precisely, consequently $V_o$ could be determined accurately too.

During the first part of this work, all the output signal were sent to a Tektronix 531A oscilloscope with wide-band Type B plug-in unit, and was triggered externally by the signal from the shunt resistor. Polaroid pictures of the output signals were taken. A 3"x3" capacity X-Y measuring device with a resolution of 0.0002" was designed and made. It was used to measure the voltage and time relationship as recorded on the Polaroid film.

The optics of the cathode-ray-tube of the oscilloscope was found to be far from ideal under the high resolution power of the X-Y device. For refined measurements this optical system was not too reliable.

A system which can make fast accurate voltage measurements and provide a buffer memory storage would be ideal (more about the ideal system will be said in discussion). Unfortunately, the ideal system proved to be financially inaccessible at the present time.
The latter part of this work was performed by using the a LAB-8 Basic averager in conjunction with a Digital PDP-81 minicomputer of Professor Myers' group.

The PDP-81 has 4096 memory addresses, each of which is of 12 bits. The LAB-8 has an analog-to-digital converter (ADC) with full range of \( \pm 1.024 \) V and a resolution of 9 bits, i.e., an actual resolution of 2 mV (0.5 part in 512 for 2.048 V). The fastest sampling rate of 30 \( \mu \)sec/point was used.

In order to command the Averager to start to take the data points and to store and add corresponding ones in the computer memory, an external triggering signal of no less than 3 V with negative slope and no shorter than 30 \( \mu \)sec was required. A simple amplifier circuit of Zel-1, an operational amplifier, was added to the circuitry to reverse the polarity and to boost the magnitude of the output from AD-1480 by a factor to ensure a satisfactory triggering signal. The negative going leading edge of the triggering signal was found indeed to lead the output signal by about 20-30 \( \mu \)sec. This was desirable because all the information contained in the output can be recorded.

The resolving time of 30 \( \mu \)sec was a bit too slow and the voltage resolution of 2 mV was not as fine as desirable. However, this was the best system available to me at the time and I had to live with the 30 \( \mu \)sec resolving time. For the voltage resolution, it was effectively enhanced by sending the signal more than once and having the sum stored to be averaged later. A sum of 8 signals was used because the ratio between the memory word length (12 bits) and the ADC resolution (9 bits) is \( 2^{12}/2^{9} = 2^3 = 8 \). This means that if each
individual signal was about 2 V, full scale for the ADC, 8 was the maximum number of signals the memory could handle without overflow. Experimentally, 8 pulses could be put through the sample in a reasonable length of time with enough interval in between pulses so that the sample had ample time to relax back to the starting temperature.

Because the PDP-8I system was immobile, it was necessary to string cables to carry over the distance of 400 ft. in between Prof. Myers' laboratory and ours. Two twisted pair aluminum-foil shielded cables were used, one for the signal and the other for the external triggering signal. Simple calculations showed that the amplifiers with output current rating at 10 mA and output impedance at 0.1 Ω were enough to drive the signal against the 30 pf/ft capacitance associated with the cable. A 5 mil iron wire with 4 leads contained in a box was used as a testing sample for the purpose of checking the possible attenuation. At first, with the pulsing system and the iron sample in our laboratory, cables were connected to the PDP-8 system and output signals were recorded. Next, the pulsing system and the iron sample were moved to Myers' laboratory and short cables were used for the output signals to be recorded. The two pieces of data were compared. For the same time interval, E's were 525 and 524 mV respectively for the local and the remote cases. A plot of the local E(t) vs. the remote E(t) gave a straight line with a slope of 1.01. If there was no attenuation nor distortion in the remote case, the plot should yield a slope of 1.00. The difference in the obtained
and the theoretical slopes was accounted for by the limited resolution of the ADC because $E = S \cdot E' = (1.01 - 1.00) \cdot 500 \text{ mV} = 5 \text{ mV} = 1$ bit of the ADC. It was therefore concluded that the 400 ft cables did not distort the signal within experimental error. When more than one point of the whole system were grounded, the groundloop caused a serious noise problem. Through experiences, it was found the best technique to reduce noise was to let the pulsing system and the sample float and to ground them and shields of the cables over the PDP-8 end.

The output from the PDP-8 could be in either teletype printout or paper tape. In this work, only the printout was obtained and cards were later punched for analyses in the CDC7600 computer of LBL. Due to the small size of the PDP-8 memory core, it was not possible to utilize it for the lengthy calculations involving more than one method.

Since all the signals were digitized by the ADC, it was found advantageous to use it as the primary standard. Everything was therefore calibrated against the ADC. The constant pulse current was also determined by sending it to the ADC, instead of using the Lambda precision voltage power supply and the comparator, to reduce groundloop noise and to speed up the experiment. The LAB-8 averager was capable of accepting two different signals simultaneously (by sampling alternatively between the two) and in principle could accept the output signal and the current sensing signal. This, even though is very desirable in the sense that both the output signal and the actual current could be measured simultaneously in real time, was not attempted during this work because the sampling rate would have to be
sacrificed to be even longer than 30 \mu sec. Instead, for each pressure and current setting, the output signal and the current sensing signal were recorded separately.

During the experiment, either the input or the sum of the inputs could be viewed on a scope by the PDP-8. Efforts were made to utilize the full 9 bits of the ADC whenever possible.

C. Data Treatment

A constant current, I, flowing through a sample with resistance R generates a Joule heating of I^2R. Part of this power, which is proportional to the temperature difference between the sample and the medium surrounding the sample, leaks from the sample. The rest of it heats up the sample at a rate of C(dT/dt). Writing in mathematical form, it is

\[ I^2R = Cd\frac{dT}{dt} + H(T-Ta) \quad (D1) \]

where H is the surface conductance, T the temperature of the sample, and Ta the temperature of the medium in contact with the sample. If everything is carried on at constant pressure, Eq. (D1) can be written as

\[ Cpd\frac{dT}{dt} = I^2R-H(T-Ta) \quad (D2) \]

and further

\[ \frac{dT}{dt} = \frac{d}{dR}(dR/dE)(dE/dt) = (1/R')(1/I)(dE/dt). \quad (D3) \]
Combining Eq. (D2) and Eq. (D3), we get

$$C_p\left(\frac{1}{IR'}\right)(dE/dt) = I^2R-H(T-Ta)$$ \hspace{1cm} (D4)

and

$$dE/dt = \left(\frac{I^3RR'/Cp}{IR'/H/Cp}\right)(T-Ta)$$ \hspace{1cm} (D5)

Of all the variables in Eq. (D5), $E$, $t$, $I$, $R$, $R'$ and $T$ can be measured directly. $C_p$, $H$, and $T_a$ are the unknowns that have to be determined. $E$, $T$, and $T_a$ are dependent on time. Different approximations can be applied to Eq. (D5) at different time regions; different forms of equations are derived for the solutions for $C_p$ and $H$.

1. **Short-time Limit.**

   In the short-time limit, the sample temperature $T$ is not significantly changed from its original value before the pulse and $(T-Ta)$ is so small such that $H(T-Ta)$ is negligible compared with $I^2R$. This reduces Eq. (D5) to a very simple form, i.e.,

$$\left(\frac{dE}{dt}\right)_{t=0} = \frac{I^3RR'/Cp}{IR'/H/Cp}$$ \hspace{1cm} (D6)

Since $R$ is considered constant, and so are $R'$, $C_p$, and $I$, $dE/dt$ is therefore a constant. Integrating $dE = I^3RR'dt/Cp$ results a $E$ linear in time. In other words, where the short-time approximation is valid the $E$ vs $t$ will be a straight line, and

$$C_p = \frac{I^3RR'/(dE/dt)_{t=0}}{\left(\frac{dE}{dt}\right)_{t=0}}$$ \hspace{1cm} (D7)

Pictures of pulses for which the short-time limit applies are shown in Fig. 15.
2. Constant Medium Temperature

A time lag exists between the temperature rises of the medium and the sample. Therefore, for some time interval, $E$ is definitely nonlinear, yet $T_a$ is effectively unchanged, that is, it remains to be $T_0$, the temperature of both the sample and the medium at the beginning of the pulse. Equation (D5) can then be rewritten as

$$\frac{dE}{dt} = \left(\frac{I^2 RR' /C_p}{(IR'H)/C_p}\right)(T-T_0). \quad \text{(D8)}$$

Equation (D3) can be modified to

$$(T-T_0) \equiv \Delta T = (\frac{1}{IR'})(dE/dt)\Delta t = (\frac{1}{IR'})\Delta E = (\frac{1}{IR'})(E-E_0), \quad \text{(D9)}$$

where $E_0$ is the sample voltage at time 0. Equation (D9) makes it possible to express $T$ in terms of $E$ easily. Combining Eq. (D8) and Eq. (D9), we get

$$\frac{dE}{dt} = \left(\frac{I^2 RR' /C_p}{(H-Cp)}(E-E_0)\right)$$

$$= \left(\frac{I^2 R'E/C_p}{(H/Cp)}(E-E_0)\right)$$

$$= \left(\frac{(I^2 R'-H)/C_p}{(H/Cp)}E + (H/Cp)E_0\right). \quad \text{(D10)}$$

a). Equation (D10) is nothing but a linear equation of $dE/dt$ vs $E$ with an intercept $HE_0/C_p$ and a slope of $(I^2 R'=H)/C_p$. Making

$$B \equiv \frac{HE_0}{C_p} \quad \text{(D11)}$$

and

$$A \equiv \frac{(I^2 R'-H)/C_p}{(H/Cp)} \quad \text{(D12)}$$
we can easily get

$$H = \frac{(I^2 R'B)}{(AEo+B)}$$  \hspace{1cm} (D13)

and

$$Cp = \frac{(I^2 R'Eo)}{(AEo+B)}$$  \hspace{1cm} (D14)

Therefore by plotting $dE/dt$ vs $E$, we can get both $Cp$ and $H$.

Figure 8 is a typical plot of $dE/dt$ vs $E$. It shows that in the early portion of the pulse, corresponding to roughly 300 microsecond, the assumption of a constant $T_a$ is a sound one. However, the uncertainty in the values of $Cp$ and $H$ so obtained is about 5%, due to error introduced in differentiation.

b). Another way of treating the data is by rearranging Eq. (D10) to get

$$\frac{dE}{((I^2 R' - H)E + HEo)} = \frac{dt}{Cp}$$  \hspace{1cm} (D15)

which upon integration becomes

$$\left(\frac{1}{I^2 R' - H}\right) \ln \frac{(I^2 R' - H)E + HEo}{(I^2 R' - H)Eo + HEo} = \frac{t}{Cp}$$  \hspace{1cm} (D16)

and

$$(I^2 R' - H)E + HEo = I^2 R'Eo \exp\left[\frac{(I^2 R' - H) \cdot t}{Cp}\right].$$  \hspace{1cm} (D17)

By differentiating Eq. (D17) again, we get

$$dE = \frac{(I^2 R'Eo)(1/Cp)\exp [(I^2 R' - H) \cdot \frac{t}{Cp}]}{\exp [(I^2 R' - H) \cdot \frac{t}{Cp}]dt}$$  \hspace{1cm} (D18)
Fig. 8. \( \frac{dE}{dt} \) vs E.
and
\[
dE/dt = (I^2 R'Eo/Cp) \exp[(I^2 R'H)t/Cp], \quad (D19)
\]
\[
dE/dt = (I^3 RR'/Cp) \exp[(I^2 R'H)t/Cp], \quad (D20)
\]
or
\[
\ln(dE/dt) = \ln(I^3 RR'/Cp) + [(I^2 R'H)/Cp]t. \quad (D21)
\]
This expresses \(dE/dt\) in terms of time \(t\) instead of \(E\). From the slope and intercept of \(\ln(dE/dt)\) vs \(t\), \(Cp\) and \(H\) can be calculated.

c). Equation (D10) can also be rearranged to become
\[
dE = \frac{I^2 R'H}{Cp} \left( \frac{Edt + HE_{odt}}{Cp} \right) (D22)
\]
and integrated from a reference time \(t_r\) to any other time \(t\). If two \(t\)'s are included, we get two simultaneous equations for two unknowns and \(Cp\) and \(H\) can be uniquely determined. In practice more than two \(t\)'s were used and a least square fit was made to determine the best values of \(Cp\) and \(H\) for the data.

d). Rewriting Eq. (D10) by using definitions of \(A\) and \(B\), we get
\[
dE/(AE+B) = dt. \quad (D23)
\]
Upon integration, Eq. (D23) becomes
\[
\int_{E_r}^{E_i} dE/(AE+B) = \int_{t_r}^{t_i} dt, \quad (D24)
\]
\[
(1/A) \ln \frac{AE_i+B}{AE_r+B} = t_i - t_r, \quad (D25)
\]
When Eq. (D27) is substituted into Eq. (D26), we get

\[ (AE_1 + B) = (AE_r + B) \exp(A(t_i - t_r)) \]. \tag{D26} \]

If \( t_i - t_r \ll 1 \), then

\[ \exp(A(t_i - t_r)) = 1 + A(t_i - t_r) + \left(\frac{1}{2!}\right)(A(t_i - t_r))^2 + \left(\frac{1}{3!}\right)(A(t_i - t_r))^3 + \ldots \]. \tag{D27} \]

When Eq. (D27) is substituted into Eq. (D26), we get

\[ AE_1 + B = (AE_r + B) + (AE_r + B)(A(t_i - t_r)) + (AE_r + B)(A^2/2)(t_i - t_r)^2 + \]

\[ + (AE_r + B)(A^3/6)(t_i - t_r)^3 + \ldots \]. \tag{D28} \]

Defining

\[ \Delta E \equiv E_1 - E_r \] \tag{D29} \]

and

\[ \Delta t \equiv t_i - t_r \], \tag{D30} \]

Eq. (D28) becomes, after rearranging,

\[ \Delta E = (AE_r + B)\Delta t + (AE_r + B)(A/2)\Delta t^2 + (AE_r + B)(A^2/6)\Delta t^3 + \ldots \]. \tag{D31} \]

and can be written as

\[ \Delta E = C\Delta t + D\Delta t^2 + F\Delta t^3 + \ldots \], \tag{D32} \]
By varying the point \( i \), a set of simultaneous equations were least square fitted to get the coefficients, \( C, D, \) and \( F \). It was found best to vary point \( i \) from \( i = r - m \) to \( i = r + m \), where \( m \) is a constant, so that any effect due to error in \( E \) can be minimized. More than two \( C \)'s were obtained by varying the reference point \( r \), and another least square fit was performed to obtain \( A \) and \( B \) through Eq. (D33). From \( A \) and \( B \), it is straightforward to calculate \( C_p \) and \( H \) according to Eqs. (D13) and (D14).

3. Constant Rate of Increase of Medium Temperature

Since all the pulses were of the order of 1 msec, a fairly short time, it was felt that if the medium temperature, \( T_a \), did increase, it could be described sufficiently well as a linear function in time. That is,

\[
T_a = T_0 + \alpha t.
\]  

\( (D34) \)

Substituting Eq. (D34) and Eq. (D9) into Eq. (D5), we get

\[
\frac{dE}{dt} = \left( I^3 R' /C_p \right) - \left( I R' H /C_p \right) (T - (T_0 + \alpha t))
\]

\[
= \left( I^3 R' /C_p \right) - \left( I R' H /C_p \right) (T - T_0) + \left( I R' H /C_p \right) (\alpha t)
\]

\[
= \left( I^2 R' /C_p \right) - \left( H /C_p \right) (E - E_0) + \left( I R' H /C_p \right) (\alpha t)
\]

\[
= \left( I^2 R' - H /C_p \right) E - \left( H /C_p \right) E_0 + \left( I R' H /C_p \right) (\alpha t).
\]  

\( (D35) \)
a). Rearrangement of Eq. (D35) gives

$$dE = \left(\frac{I^2 R'}{Cp} - H\right) Edt + \frac{H}{Cp} Eodt + \frac{R'\alpha}{Cp} t dt,$$

(D36)

and

$$\int_{E_r}^{E} Eodt = \frac{Cp}{H} \int_{E_r}^{E} dE + \frac{1 - I^2 R' / H}{Cp} \int_{E_r}^{E} Edt - \frac{I R' \alpha}{Cp} \int_{E_r}^{E} t dt.$$

(D37)

Defining

$$C_1 = \frac{Cp}{H},$$

(D38)

$$C_2 = 1 - I^2 R' / H,$$

(D39)

and

$$C_3 = I R'$$

(D40)

Eq. (D37) is further simplified as

$$\int_{E_r}^{E} Eodt = C_1 \int_{E_r}^{E} dE + C_2 \int_{E_r}^{E} Edt - C_3 \int_{E_r}^{E} t dt.$$

(D41)

By varying the lower and upper limits of the integration in Eq. (D41), more than three simultaneous equations can be obtained for a least square fit to get the coefficients, $C_1$, $C_2$, and $C_3$. Once they are obtained, $Cp$, $H$, and $\alpha$ are solved from Eqs. (D38) to (D40) to be

$$H = \frac{I^2 R'}{(1-C_2)}$$

(D42)

$$Cp = \frac{C_1 H}{C_3}$$

(D43)
and

\[ \alpha = \frac{C_3}{IR'} . \]  

(D44)

b). In addition to the definitions of A and B in Eqs. (D11) and (D12),

\[ L \equiv IR'a/Cp \]  

(D45)

is defined, which changes Eq. (D35) to

\[ \frac{dE}{dt} = AE + B + Lt. \]  

(D46)

Eq. (D46) can be rewritten in the form of

\[ \frac{dE}{dt} = AE = B + Lt. \]  

(D47)

Using the integrating factor \( \exp(-At) \), we get

\[ E = \exp(At) \left[ \int \exp(-At)(B+Lt)dt + G \right] \]

\[ = \exp(At) \left[ - \frac{B}{A} \exp(-At) - \frac{L}{A^2} \exp(-At) - \frac{Lt}{A} \exp(-At) + G \right]. \]  

(D48)

When \( t=t_r \), \( E=E_r \), and when both are substituted into Eq. (D48), the integration constant \( G \) is found to be

\[ G = \left( E_r + B/A + L/A^2 + Lt_r/A \right) \exp(-At). \]  

(D49)

Therefore,

\[ E_1 = \left( -B/A - L/A^2 - Lt_r/A \right) + \left( E_r + B/A + L/A^2 + Lt_r/A \right) \exp(A(t_i - t_r)) . \]  

(D50)
When \( \exp(A(t-t_\tau)) = \exp(A\Delta t) \) is expanded into power series as in Eq. (D27), Eq. (D50) becomes

\[
E_i - E_r = \Delta E = (AE_r + B + Lt) \Delta t + (AE_r + B + Lt + L) \frac{A}{A'} \frac{A}{2} \Delta t^2 + \ldots
\]

\[
\equiv C' \Delta t + D' \Delta t^2 + \ldots
\]

The same least square fit was performed by varying point \( i \) to get \( C' \), and by varying point \( r \) to get \( A, B, \) and \( L \). \( C_p \) and \( H \) were calculated from \( A \) and \( B \).

D. Results and Discussion

1. Heat Capacity

Of all the methods outlined in Data Treatment, it was found that methods C.2.d and C.3.b yielded the most consistent results. Table 1 shows results for the heat capacity and heat leak constant of aluminum in silver chloride at 100 kbar and 298 K as a function of the current, obtained with method C.2.d. It shows that both the heat capacity and heat leak constant vary randomly with respect to current. The average deviation in both \( C_p \) and \( H \) is about 2%.

Figure 9 shows heat capacity results of aluminum at 298 K obtained previously by this group. The enormous increase of \( C_p \) with pressure is judged to be incorrect.

From the thermodynamic point of view, Eq. (T1)

\[
(\partial C_p/\partial p)_T = -T(\partial^2 V/\partial T^2)_p
\]
Table I. Aluminum at 100 kbar and 298 K.

<table>
<thead>
<tr>
<th>I (amp)</th>
<th>$C_p \times 10^{-4}$ (Joule/ K)</th>
<th>$H \times 10^{-1}$ (Joule/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>1.303</td>
<td>1.843</td>
</tr>
<tr>
<td>2.2</td>
<td>1.392</td>
<td>1.678</td>
</tr>
<tr>
<td>2.3</td>
<td>1.341</td>
<td>1.807</td>
</tr>
<tr>
<td>2.4</td>
<td>1.311</td>
<td>1.783</td>
</tr>
<tr>
<td>2.5</td>
<td>1.328</td>
<td>1.801</td>
</tr>
<tr>
<td>2.6</td>
<td>1.366</td>
<td>1.755</td>
</tr>
<tr>
<td>2.7</td>
<td>1.335</td>
<td>1.742</td>
</tr>
<tr>
<td>2.8</td>
<td>1.342</td>
<td>1.764</td>
</tr>
<tr>
<td>2.9</td>
<td>1.353</td>
<td>1.773</td>
</tr>
<tr>
<td>3.0</td>
<td>1.341</td>
<td>1.825</td>
</tr>
</tbody>
</table>
Fig. 9. The heat capacity of aluminum at 298 K as a function of pressure.
dictates that the change of constant pressure heat capacity with pressure be in the direction opposite to the second derivative of volume with respect to temperature at constant pressure. As \((\partial^2 V/\partial T^2)_p\) of most materials start at zero at absolute zero temperature and increases with increasing temperature (one prominent exception is water between 0 and 4°C), the heat capacity should decrease with increasing pressure.

If the heat capacity is dominated by lattice contribution, it is also expected to decrease with pressure. This is because higher pressure decreases the interatomic distances and constrains the freedom of atoms to move, making it more difficult for them to accept additional thermal energy. This results in a smaller heat capacity.

When the Debye model is applied, both the heat capacity and electrical resistance can be related to each other. Raimondi actually calculated the heat capacity of aluminum as a function of pressure by determining the Debye temperature from the electrical resistance. His calculated results showed a 1% decrease of heat capacity between 30 and 100 kbar.

Since the heat leak constant increases with pressure, as we shall presently see, an appreciable amount of the Joule heating power intended for the sample was drained out from the sample to the surrounding, resulting in a larger apparent heat capacity at higher pressure. This is believed to be the source of the enormous increase in heat capacity obtained in the previous work.
Results of the present work as shown in Fig. 9 shows the heat capacity of aluminum to increase by 5% between 30 to 50 kbar and to remain constant between 50 and 100 kbar. When this result is checked against Raimondi's semiempirical data, it does not look very impressive, however, it is a significant improvement over the previous data which showed a 33% increase in heat capacity. The modest achievement of the present work has been hard won by painstaking carefulness in calibration and conducting the experiments and by checking the data fairly exhaustively against the possible ways to treat them.

One of the major factors that impede us from getting better result is the lack of better pulse voltage measuring devices.

In order to get more accurate data, further improvement on several accounts are needed. Among them are

**Devices:**

A constant current pulse power supply with a faster switching time in the order of a few microsecond will be helpful to get information closer to time zero, the time when heat leakage is not severe and treatment of data is simple.

An analog to digital converter with a window time of 1 µsec and preferably a 17 bit voltage resolution. With the fast sampling time more data points can be taken to enhance signal to noise ratio. In principle, an ADC with a 17 bit resolution is capable of converting the whole pulse and at the same time rendering a 1 part per thousand resolution for the temperature rise of the sample. This converter will make the dc offset (bucking) voltage unnecessary and in consequence eliminate sources of errors.
A storage device which can store data points as fast as the ADC can provided them. It also needs to have enough storage capacity to accommodate enough data points so that averaging manipulation is feasible.

A processing unit, such as a PDP-8 minicomputer, which will enable us to do real time decision and on-line experiments.

An output device which displays the pulses and results, and an input device so that relevant control parameters can be fed to the processor.

**Determination of Decay Curve Experimentally**

If the constant current pulse power supply is modified such that it is capable of producing two consecutive constant current pulses with variable interval in between them, the decay of the sample temperature as a function of time can be obtained. Figure 10 shows pulses of ideal shape. By varying $T$ and monitoring the starting points of the second pulses, the decay curve can be very easily gathered. From the slope of the decay curve, it is easy to calculate the heat loss due to leakage, and the correction can be applied to the leading pulse. This is much more desirable than treating the data on purely theoretical grounds since a measurable quantity is used instead. Taking into account of the fact that the pulse shape is not ideal, that it overshoots, it is nevertheless easy to get an envelope of the trailing pulses to obtain the decay curve.
Fig. 10. The (a)'s show pulses current vs time; the (b)'s show temperature vs time. The gap \( t \) between the two consecutive pulses increases from 0 and up. When all the (b)'s are superimposed on top of each other, the temperature decay curve is shown by the dash-dotted line in (5).
The second scheme to measure the decay curve is to have the pulse current superimposed on top of a small constant current, as shown in Fig. 11. Points C and D correspond to right before and after the termination of the pulse. The curve between point D and E is the decay curve. The monitoring is made possible by the application of the constant current i. The decay curve can be electronically amplified and analyzed in the same fashion as described above.

2. Heat Leak Constant

One of the by-products of measuring heat capacity at high pressure with the pulse method is the heat leak constant.

The heat leak constant as a function of pressure for aluminum in the silver chloride medium is graphically presented in Fig. 12. Looking at Fig. 12, it is evident that the heat leak constant goes through a discontinuous change in the neighborhood of 85 kbar. Recalling that a phase transition of silver chloride at 90 kbar had been observed by Drickamer, this break of heat leak constant is attributed to the phase transition.

For the sample geometry employed for this work, silver chloride starts plastic flow around 25 kbar and acts as a good quasi-hydrostatic pressure transmitting medium thereafter. As pressure increases further, the interface between aluminum and silver chloride is expected to remain unchanged. The thermal properties of aluminum do not change much with pressure and the thermal conductivity of aluminum is so much larger than that of silver chloride, one expects the heat leak constant to be determined by the thermal properties of silver chloride.
Fig. 11. (a) The current vs time curve shows a small constant current persists through all the time, while a constant current pulse begins at point A and ends at D. (b) The temperature vs time curve shows the temperature response to the pulse. (c) Blow-up view of the circled region from (b) showing the decay curve.
Fig. 12. The heat leak constant when silver chloride is used as the surrounding medium, as a function of pressure at 298 K.
only. In other words the thermal properties of the material in which the highly conducting wire sample is imbedded can be measured.

The utilization of the µsec pulse method to detect phase transitions and to measure the heat conductivity of materials in addition to its original function as a calorimeter is a very intriguing thought. It shows that one can hardly overestimate the potential of this all powerful method.
III. HEAT CAPACITY OF IRON AT ZERO PRESSURE

To demonstrate the versatility of the pulse method, the heat capacity of iron was measured in vacuum between room temperature and 1100 K.

Iron wire of 2 mils diameter, which was purchased from California Fine Wire Co. with 99.99% purity, was used. Except for one sample, all sample wires were annealed at 700°C in Ar atmosphere for 24 hours.

The experimental setup is shown in Fig. 13. The sample wire was wound in a loop of 0.4" in diameter and multiple leads were welded onto the sample wire for current, voltage, and temperature monitoring. Another alumel-chromel P thermocouple with one junction near the center of the sample loop was used for temperature control. A temperature controlling power supply was built to control the sample temperature by regulating the power to the furnace which enclosed the sample chamber. The whole assembly was put inside a quartz tube of 1 1/2" in diameter and 20" in length. Electrical connections were made possible by using heavy copper wires and feedthroughs. The vacuum system used was a simple one with a mechanical forepump and a diffusion pump. The vacuum inside the sample chamber was roughly $10^{-4}$ Torr.

All the power supplies and amplifiers employed were identical to the ones used in the high pressure heat capacity measurements. The Newport Digital Microvoltmeter was used for monitoring the resistance and the temperature. The pulses were recorded through a Tektronix 531 oscilloscope onto polaroid pictures.
Fig. 13. Block diagram of the vacuum heat capacity measurement setup.
The typical sample resistance at room temperature was around 0.05 Ω, and a steady current of 10 mA was used to measure the resistance. Usually four pulses were recorded on each picture and the same current setting was used.

Figure 14 shows two pictures of pulses through the iron sample at around room temperature and 1100 K. It was observed that all the pulses were fairly straight, indicating very little heat loss. Therefore the short-time limit treatment of data as outlined in Eq. (D7) was applicable. \( (\frac{dE}{dt})_{t=0} \) was measured by a protractor with a 0.0005 resolution in the 100 to 300 μsec region on the pictures. \( I \) and \( R \) were also determined in the usual fashion. \( R' \), the temperature derivative of the resistance, was determined by

\[
R' = \frac{dR}{dT} = \frac{dR}{d\xi_{TC}} \cdot \frac{d\xi_{TC}}{dT},
\]

where \( \xi_{TC} \) was the thermocouple emf.

In Fig. 15 \( \frac{Cp}{R'} \) values for two samples, one had been annealed as described and the other not annealed, are plotted against normalized resistance. The temperature span is from room temperature to 1100 K. The unannealed sample showed a break around 7 on the normalized resistance scale, which corresponded to roughly the annealing temperature.
Fig. 14. Pulses through Fe samples in vacuum at (a) 1100 K (b) 298 K.
Iron sample wire as purchased
Iron sample annealed in Ar
at 700°C for 24 hours

Fig. 15. Cp/R' vs R of Fe samples.
The precision of the heat capacity measurement in vacuum was estimated to be around 1%. The major source of error was in the determination of the thermal coefficient of resistance. The final heat capacity of the annealed iron is compared with Austin's compiled data\textsuperscript{51} in Fig. 16. Keeping in mind that Austin's data was selected from various sources and smoothed out, and comparing the data with more recently compiled data,\textsuperscript{52,53} it is easy to see that the microsecond pulse method yielded very good results.

If efforts are exercised in employing a more sophisticated vacuum system to avoid possible oxidation of the sample, the pulse technique will certainly prove to be the most precise and fastest method for getting relative heat capacity of electrically conducting materials at high temperature.
Fig. 16. Comparison of literature and present values for the heat capacity of iron from room temperature to about 1100 K.
APPENDIX

A $T^{3/2}$ dependence of electrical resistance was found at zero pressure for iron and nickel between 4 to 20 K by Kondorsky and coworkers$^{54}$ and between 1.2 to 4.3 K by Semenko.$^{55}$ The scattering of electrons by spin-waves (magnon) was attributed for this 3/2 temperature dependence.

During the study of iron and cobalt, Stark$^8$ observed that when the pressure was higher than 20 kbar, the electrical resistances were also proportional to $T^{3/2}$ between 150 and 300 K. He made some rough calculations and checks, and felt that no definitive conclusion could be drawn from the then available data. However, he did suggest the possibility of a dominant magnon scattering mechanism over the phonon scattering mechanism for the electrical resistance to manifest the $T^{3/2}$ behavior.

To clarify this uncertain point, resistance of iron was studied more carefully between 77 to 300 K at 0 to 100 kbar.

Experimental:

The sample wires of iron were of a diameter of 0.005", purchased from California Fine Wire Co., and were annealed in argon atmosphere at 700°C for twenty-four hours. The sample assembly was identical to the description in Fig. 3 except that a tank was put in between the column, similar to the setup in Fig. 4. The alumel-chromel thermocouple
junction was placed adjacent to the sample ring and all the current and voltage leads used were 0.005" platinum wires. The thermocouple was calibrated at ice-point and liquid nitrogen temperatures. Temperature measurements were made by using a Leeds & Northrup potentiometer with one of the thermocouple junction in an ice-water mixture. The accuracy of temperature measurement was 0.1 K. Resistances were measured by using a Muller bridge with a 17 V mercury battery as the current source. A simplified circuit shows the essential arrangement of leads with a three-pole double throw switch to eliminate lead resistances. The typical current flowing through the sample was 40 mA and the Joule heating was judged negligible in view of the high thermal conductive path from the sample to the intimately contacted surrounding. The precision of the resistance obtained was estimated to be 0.00002 Ω.

Duxeal was used to fill the gap between the pair of Bridgman anvils and the same sample was used throughout for several isobaric runs between room temperature and liquid nitrogen temperature. The whole tank was filled with lead shots to further increase the thermal mass and to improve thermal equilibrium throughout the sample region so that no appreciable temperature gradient existed along the sample ring.

During the start of each isobaric run the sample was at first pumped to the desired pressure at room temperature. The tank was then filled with liquid nitrogen and due to the thermal contraction of the column blocks additional pumping was necessary to keep the sample at the same pressure. It usually took roughly half an hour
for the whole system to cool down to 77 K and another hour or two for all the liquid nitrogen to boil away. The temperature rose quite rapidly from then to 100 K and gradually (5 min /K) up to room temperature.

To make sure about the precision of the temperature and resistance measurements, isobaric runs at 30 Kbar were performed twice. Resistances for the two runs were checked by plotting \((\bar{R}_2/\bar{R}_1)_T^{-1}\) vs T, where \(\bar{R}\) is a normalized resistance with respect to the 290 K value and the subscripts refer to two different samples. The resulting curve, in which any deviation from 0 reflects inconsistency between the two sets of data, is shown in Fig. 17. It is obvious from it that the scatter was less than 0.2% at low temperature and less than 0.1% at higher temperature. Also there was no apparent systematic deviation between the two sets of data.

Results:

Seven isobaric runs between 77 and 300 K on the same iron sample were taken. The resultant electrical resistance data are graphically presented in Fig. 18.

When \(\log R\) was plotted against \(\log T\) and a least square fitted straight line was put through the points, it was found that the slopes for the various pressures vary between 1.3 and 1.4 with lower pressures having larger slopes. It was realized that any residual resistivity \(\rho_0\), as real samples always have, shows up in the total resistivity as

\[
R = \rho_0 + \rho_T, \quad (R1)
\]
Fig. 17. Scatter of $\Delta R$ vs $T$ as an indication of reproducibility of $R$ measurements.
Fig. 18. Isobaric $R(T)$ of iron.
according to Matthiessen's rule, where $R_T$ is a temperature dependent 
term. The ratio between $R_T$ and $R_0$, $a \equiv R_T/R_0$, depends on the 
irregularity of the sample. Equation (R1) can be written as

$$R = (1/a + 1)R_T,$$

and the logarithm of $R$ obviously depends on $a$. Since resistance data 
near absolute zero were not available for me to assess $a$ directly, 
I got around the problem by trying to fit data numerically to an 
equation of the form of

$$R = c_1 + c_2 T^{c_3}.$$

In addition, following theoretical guidelines, equations of

$$R = c_1 + c_2 T + c_3 T^{1.5},$$

$$R = c_1 + c_2 R_{BG} + c_3 T^{1.5},$$

$$R = c_1 + c_2 R_{BG} + c_3 T^{c_4}$$

were used for the fittings, where $R_{BG}$ is the Bloch-Grüneisen\textsuperscript{50} 
resistance. Of all the various equations that have been tried, none 
produced a good enough fit to render a random deviation between the 
fitted and the experimental data. The systematic deviation was 
always larger than that could be accounted for by experimental errors. 
The fittings were also applied to data in different temperature 
regions. It was found that only when data was in an narrow range 
of about 30 K that the fittings were good.
In view of the quality of the data and the poor fit, and more careful review of Stark's raw data, it is felt that Stark's findings about the $T^{3/2}$ dependence of iron resistance could have been due to an artifact of the residual resistance.
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