Experiment 47. Low-temperature Heat Capacity of Solids

The heat capacity of solids has played a lively role in many theoretical developments of the past and continues to present challenging problems even today. As early as 1818 Dulong and Petit stated as an empirical law that the heat capacity of a chemical element in the solid state was approximately 6 cal deg^{-1} g-atom^{-1}. This law played a significant role in the determination of atomic weights from chemical combining weights. Soon after the development of statistical mechanics, this law was given a theoretical foundation based on classical mechanics. However, it was then observed experimentally that heat capacities at low temperatures were much smaller than those at room temperature, in contradiction with the classical Dulong-Petit theory which predicted a constant $\bar{C}_v$ independent of temperature. Einstein's semiquantitative explanation of the fact that C_v approaches zero as T approaches 0°K was one of the early triumphs of quantum theory.

In the present experiment the heat capacity of aluminum will be determined at several temperatures over the range from 7 to 300°K, and the data will be interpreted in terms of the Debye theory of specific heats.

THEORY

We shall be concerned with developing a theory of the *lattice heat capacity* at constant volume for macrocrystalline solids. Special phenomena such as transition points will not be considered; the contribution of electronic specific heats in the case of metals will be mentioned only briefly. For simplicity the discussion will be limited to monatomic solids with a simple crystal structure (one atom per primitive unit cell), but the results will be applicable at low temperatures to any crystalline solid.

Let us consider a *large single crystal* consisting of N atoms (all of the same kind) which interact with harmonic forces. That is, the atoms are assumed to obey Hooke's law, whereby the restoring force on an atom is directly proportional to the displacement from its equilibrium position. It can be shown that such a crystal is equivalent to a set of $3N$ *independent*, one-dimensional harmonic oscillators.[†] Therefore, we can write the vibrational energy of the crystal as

$$E = \sum_{i=1}^{3N} (\bar{\epsilon})_i \tag{1}$$

where $(\bar{\epsilon})_i$ is the average energy of the ith oscillator. The classical theory of the equipartition of energy[1] (see Exp. 4) states that the average energy in each vibrational degree of freedom (each normal mode) is kT. Thus, on the basis of classical statistical mechanics

$$E = 3NkT$$

$$\bar{C}_v = \left(\frac{\partial \bar{E}}{\partial T}\right)_v = 3R = 5.96 \text{ cal deg}^{-1} \text{ g-atom}^{-1} \tag{2}$$

which confirms the law of Dulong and Petit. As one might expect of a classical

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[†]To be exact there are (3N-6) vibrational degrees of freedom and there should be (3N-6) oscillators corresponding to the normal modes of vibration (see Exp. 41).

treatment of vibration, Eq. (2) is not adequate at low temperatures.   Indeed, this equation is not always valid even at room temperature (see Fig. 1).

The variation of C_v with temperature is a consequence of the existence of discrete, quantized energy levels for each of the one-dimensional oscillators, as required by quantum mechanics.   For a harmonic oscillator with vibrational frequency ν, the allowed energy states are

$$\epsilon_n = (n + \tfrac{1}{2})h\nu \qquad n = 0, 1, 2, 3, \ldots \tag{3}$$

In order to find $\bar{\epsilon}$ for this oscillator at a temperature T one must use the Boltzmann distribution law[2] for the population of the various energy states.   The probability of finding a harmonic oscillator in the state with energy ϵ_n is

$$P_n = \frac{e^{-\epsilon_n/kT}}{\sum\limits_{n=0}^{\infty} e^{-\epsilon_n/kT}} = \frac{e^{-nh\nu/kT}}{\sum\limits_{n=0}^{\infty} e^{-nh\nu/kT}} \tag{4}$$

The average energy $\bar{\epsilon}$ is obviously

$$\bar{\epsilon} = \sum_{n=0}^{\infty} P_n\epsilon_n = \frac{1}{2} h\nu + h\nu \frac{\sum\limits_{n} n e^{-nh\nu/kT}}{\sum\limits_{n} e^{-nh\nu/kT}} \tag{5}$$

Since $\sum\limits_{n=0}^{\infty} x^n = (1 - x)^{-1}$ and $\sum\limits_{n=0}^{\infty} nx^n = x(1 - x)^{-2}$, we find that[†]

$$\bar{\epsilon} = \frac{1}{2} h\nu + \frac{h\nu}{e^{h\nu/kT} - 1} \tag{6}$$

Combining Eqs. (1) and (6), we obtain for the entire crystal

$$E - E_0 = \sum_{i=1}^{3N} \frac{h\nu_i}{e^{h\nu_i/kT} - 1} \tag{7}$$

where E_0 is the zero-point energy of the crystal.   For the sake of completeness one can include the lattice energy U (see Exp. 46) in E_0 and write

$$E_0 = E_0(\text{vib}) + U = \sum_{i=1}^{3N} \tfrac{1}{2}h\nu_i + U \tag{8}$$

In both Eqs. (7) and (8) ν_i is the frequency of the ith oscillator (ith normal mode of vibration of the lattice).   Since E_0 depends only on the volume (both U and all ν_i are functions of the volume per atom) and is independent of temperature, we can obtain immediately a general expression for the lattice heat capacity of any harmonic solid:

$$C_v \equiv \left(\frac{\partial E}{\partial T}\right)_v = k \sum_{i=1}^{3N} \left(\frac{h\nu_i}{kT}\right)^2 \frac{e^{h\nu_i/kT}}{(e^{h\nu_i/kT} - 1)^2} \tag{9}$$

Einstein used Eq. (9) to calculate heat capacities in semiquantitative agreement with experiment by making the simplifying assumption that the atoms oscillate

[†] This result could also have been obtained directly from $\bar{\epsilon} = kT^2(\partial \ln z/\partial T)$ where z, the vibrational partition function, is given[3] by

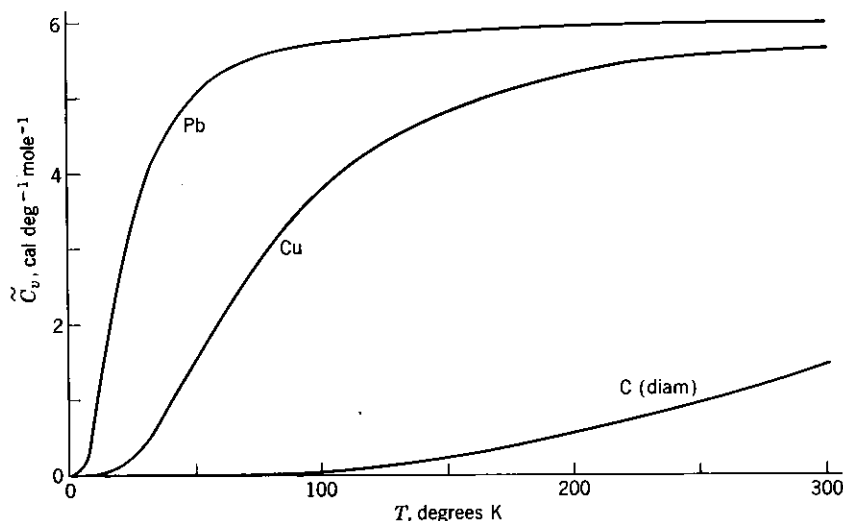$$z \equiv \sum_{n=0}^{\infty} e^{-(n+1/2)h\nu/kT} = \frac{e^{-h\nu/2kT}}{1 - e^{-h\nu/kT}}$$

FIG. 1. Low-temperature molar heat capacities of lead, copper, and diamond.

independently and all the oscillators have the same frequency ν_0 (i.e., all $\nu_i = \nu_0$). This model explains in a crude way the great difference in C_v for lead and diamond (see Fig. 1). In a lead crystal the atoms are heavy and the forces between atoms are weak (Pb has a high compressibility); thus ν_0 for lead should be very low and the classical limit will be achieved well below room temperature. In diamond the atoms are light and the forces between atoms are strong (diamond has a low compressibility); thus ν_0 for diamond will be much higher and the classical limit is not achieved even at room temperature. The Einstein model is, however, inadequate at very low temperatures, where it predicts that C_v will approach zero exponentially as T approaches $0°K$. The actual dependence of the (lattice only) heat capacity on T at low temperatures has been found experimentally to be T^3.

The failure of the Einstein theory to predict correctly the low-temperature behavior of C_v is due to the crudeness of the simplifying assumption that all $\nu_i = \nu_0$. Actually, of course, atomic motions are strongly coupled through interatomic forces, and the $3N$ normal modes have many different frequencies, as would be expected from our knowledge of molecular vibrations (see Exp. 41). The frequencies of the $3N$ normal modes range from very near zero (sonic vibrations; wavelengths comparable to the dimensions of the crystal) to some highest value (wavelength comparable to the interatomic spacing).

For a large crystal there are about 10^{24} normal modes which are so closely spaced in frequency that it is possible to treat the distribution as continuous and define a *distribution function* $g(\nu)$ such that $g(\nu)\,d\nu$ is the number of normal modes in the interval ν to $\nu + d\nu$. Using this distribution function, Eqs. (7) and (9) can be rewritten as

$$E - E_0 = kT \int_0^{\nu_{max}} \frac{u}{e^u - 1} g(\nu)\,d\nu \tag{10}$$

$$C_v = k \int_0^{\nu_{max}} \frac{u^2 e^u}{(e^u - 1)^2} g(\nu)\,d\nu \tag{11}$$

where $u = h\nu/kT$ and ν_{max} is the highest frequency. Thus the problem of the lattice thermodynamic properties of a solid becomes a question of evaluating $g(\nu)$.

Debye Theory. The theory of specific heats was greatly improved by Debye, who assumed that a monatomic solid could be treated as a continuous elastic medium with no dispersion. That is, the mass of the crystal is considered as smeared out uniformly over the entire volume instead of being localized at discrete lattice sites, and the velocity of waves traveling through the solid is taken as independent of their frequency. Such a model provides a reasonable description of the low-frequency modes, since their wavelengths are much longer than the unit cell dimensions of the lattice. Thus the Debye theory should be valid at very low temperatures where only low frequencies contribute significantly to the C_v integral. The brave step taken by Debye was to propose this model for describing a solid over the entire temperature range.

For the Debye model, $g(\nu)$ can be shown[4] to be proportional to ν^2:

$$g(\nu) = \frac{12\pi V}{c^3}\nu^2 \tag{12}$$

where V is the volume of the solid and c is an "average" elastic wave velocity.† For a lattice of N atoms there are $3N$ normal modes and the dynamics of the motion gives a highest frequency ν_{max}, just as in the case of a polyatomic gas molecule. But the Debye theory is based on a continuum model, and one must introduce an artificial cutoff frequency ν_D to restrict the total number of vibrations to $3N$. This cutoff frequency is obtained from

$$3N = \int_0^{\nu_D} g(\nu)\, d\nu = \int_0^{\nu_D} \frac{12\pi V}{c^3}\nu^2\, d\nu = \frac{4\pi V}{c^3}\nu_D{}^3 \tag{13}$$

Therefore, we can rewrite Eq. (12) as

$$\begin{aligned} g(\nu) &= \frac{9N}{\nu_D{}^3}\nu^2 \qquad 0 \leqslant \nu \leqslant \nu_D \\ &= 0 \qquad\qquad \nu > \nu_D \end{aligned} \tag{14}$$

With this Debye distribution function Eqs. (10) and (11) can be written as

$$E - E_0 = \frac{9NkT}{\nu_D{}^3}\int_0^{\nu_D}\frac{u}{e^u - 1}\nu^2\, d\nu = 9NkT\left(\frac{kT}{h\nu_D}\right)^3\int_0^{h\nu_D/kT}\frac{u^3}{e^u - 1}\, du \tag{15}$$

$$C_v = 9Nk\left(\frac{kT}{h\nu_D}\right)^3\int_0^{h\nu_D/kT}\frac{u^4 e^u}{(e^u - 1)^2}\, du \tag{16}$$

At this point it is appropriate to introduce a new variable Θ, called the "Debye characteristic temperature" and defined by

$$\Theta = \frac{h\nu_D}{k} \tag{17}$$

† This is defined by

$$\frac{3}{c^3} = \left\langle \frac{1}{U_l{}^3} + \frac{1}{U_t{}^3} + \frac{1}{U_t{}'^3}\right\rangle_{av}$$

In general, the three ultrasonic velocities (one longitudinal and two transverse) depend on the direction of propagation. Many derivations of the Debye theory assume an isotropic medium for which $U_t = U_t{}'$ and all velocities are independent of direction, but this is not basic to the Debye model.

We can now give expressions for the energy and heat capacity *per gram atom* in terms of this single parameter which characterizes the solid:

$$\frac{\tilde{E} - \tilde{E}_0}{3RT} = 3\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{u^3}{e^u - 1} \, du \tag{18}$$

$$\frac{\tilde{C}_v}{3R} = 3\left(\frac{T}{\Theta}\right)^3 \int_0^{\Theta/T} \frac{u^4 e^u}{(e^u - 1)^2} \, du \tag{19}$$

For a "Debye crystal" the zero-point vibrational energy $\tilde{E}_0$(vib) is equal to $\% R\Theta$; this can be derived from Eq. (8) in a manner exactly parallel to the treatment given above.

The integrals in Eqs. (18) and (19) cannot be evaluated analytically as a function of Θ/T, but numerical values have been tabulated.[5] However, at very low temperatures ($T < \Theta/16$) the values of the integrals are substantially equal to the definite integrals from 0 to ∞ (which are known). Thus, one obtains the famous Debye T^3 law:

$$\frac{\tilde{C}_v}{3R} = \frac{4\pi^4}{5} \left(\frac{T}{\Theta}\right)^3 \tag{20}$$

As a demonstration of the Debye theory we shall replot the data in Fig. 1 as $\tilde{C}_v/3R$ vs. T/Θ; these are shown in Fig. 2 along with the curve predicted by Eq. (19). The Θ values used in Fig. 2 were chosen empirically to give the best possible fit to the theoretical curve, but Θ values could be calculated from experimental low-temperature ultrasonic velocities using the expression

$$\Theta = \frac{h}{k} \left(\frac{3N}{4\pi V}\right)^{1/3} c \tag{21}$$

which is derived from Eqs. (13) and (17). In general the agreement between Debye theory and experiment is quite good but not perfect; in particular, there is often a disagreement between the empirical value of Θ chosen to fit the heat capacity and the ultrasonic value given by Eq. (21). Such difficulties are not surprising,

FIG. 2. A plot of $\tilde{C}_v/3R$ vs. T/Θ for lead, copper, and diamond. The solid line is the theoretical curve given by the Debye theory.
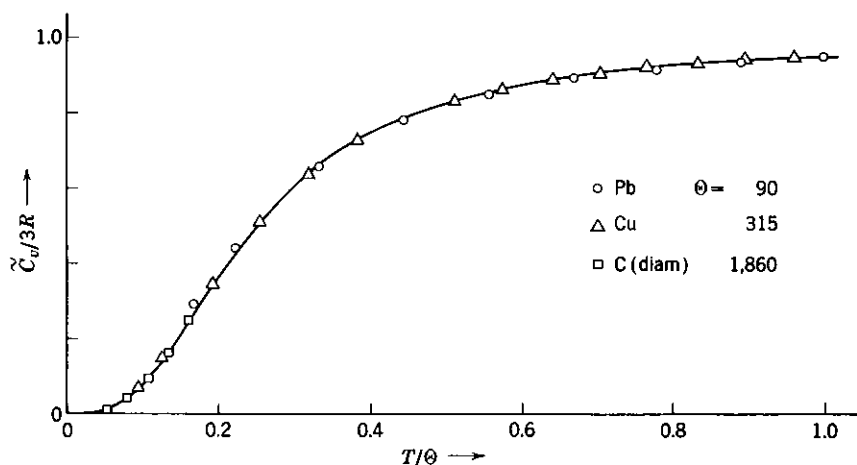
since the Debye theory is based on a quite simplified model for a solid. More recently, considerable progress has been made using the theory of lattice dynamics[4, 6] which is based on a more realistic model but is much more complicated mathematically. It should be emphasized that the Debye theory is still perhaps the best one-parameter theory available and is very useful in many problems because of its simplicity.

$C_p - C_v$ **Correction.** The theory presented above has been concerned with C_v, the heat capacity at constant volume, but the values measured experimentally for solids are almost always C_p, the heat capacity at constant pressure. The difference between C_p and C_v is given by thermodynamics[7] as

$$C_p - C_v = \frac{9TV\alpha^2}{\beta} \tag{22}$$

where 3α is the volume coefficient of expansion and β is the isothermal volume compressibility. Both 3α and β are functions of temperature, and they are often not known at low temperatures. It is common practice to replace this exact expression by an empirical approximation[7]—the so-called Nernst-Lindemann equation:

$$\tilde{C}_p - \tilde{C}_v \cong AT\tilde{C}_p{}^2 \tag{23}$$

where A is a constant evaluated from the room-temperature properties of the solid.

Electronic Specific Heats. In a metal there are a large number of conduction electrons which are relatively free to move throughout the crystal. The heat capacity of this "free-electron gas" must be considered in addition to the heat capacity due to lattice vibrations discussed previously. Because of the very small mass of the electron, this electron gas does not behave like a classical gas of atoms or molecules, and it is necessary to use quantum statistics to predict its properties. It has been shown[8] that the heat capacity of such a free-electron gas is

$$\tilde{C}_v(\text{el}) = \gamma T \tag{24}$$

where γ is a constant for a given metal and is usually of the order of 10^{-4} cal deg^{-2} g-atom^{-1}. Thus the electronic specific heat at room temperature is only about 3×10^{-2} cal deg^{-1} g-atom^{-1}, and it is almost negligible compared with the lattice heat capacity of about 6 cal deg^{-1} g-atom^{-1}. It becomes important, however, at very low temperatures, since $\tilde{C}_v$ (lattice) goes to zero more rapidly than $\tilde{C}_v$ (el).

METHOD

The method of determining C_p in this experiment is identical in principle with that used in Exp. 10: electrical work is degraded to "Joule heat" by a heating coil, and the resulting temperature rise ΔT is measured. The only difference is that now we wish to use Eq. (V-13a)

$$C_p = \frac{-w_{el}}{\Delta T} \tag{25}$$

to obtain C_p for the sample alone *without* any contribution due to the calorimeter itself. To achieve this we must isolate the sample as well as possible from its surroundings (including the walls of the calorimeter) and must reduce stray heat leaks to a minimum (see the discussion in Principles of Calorimetry, Chap. V).
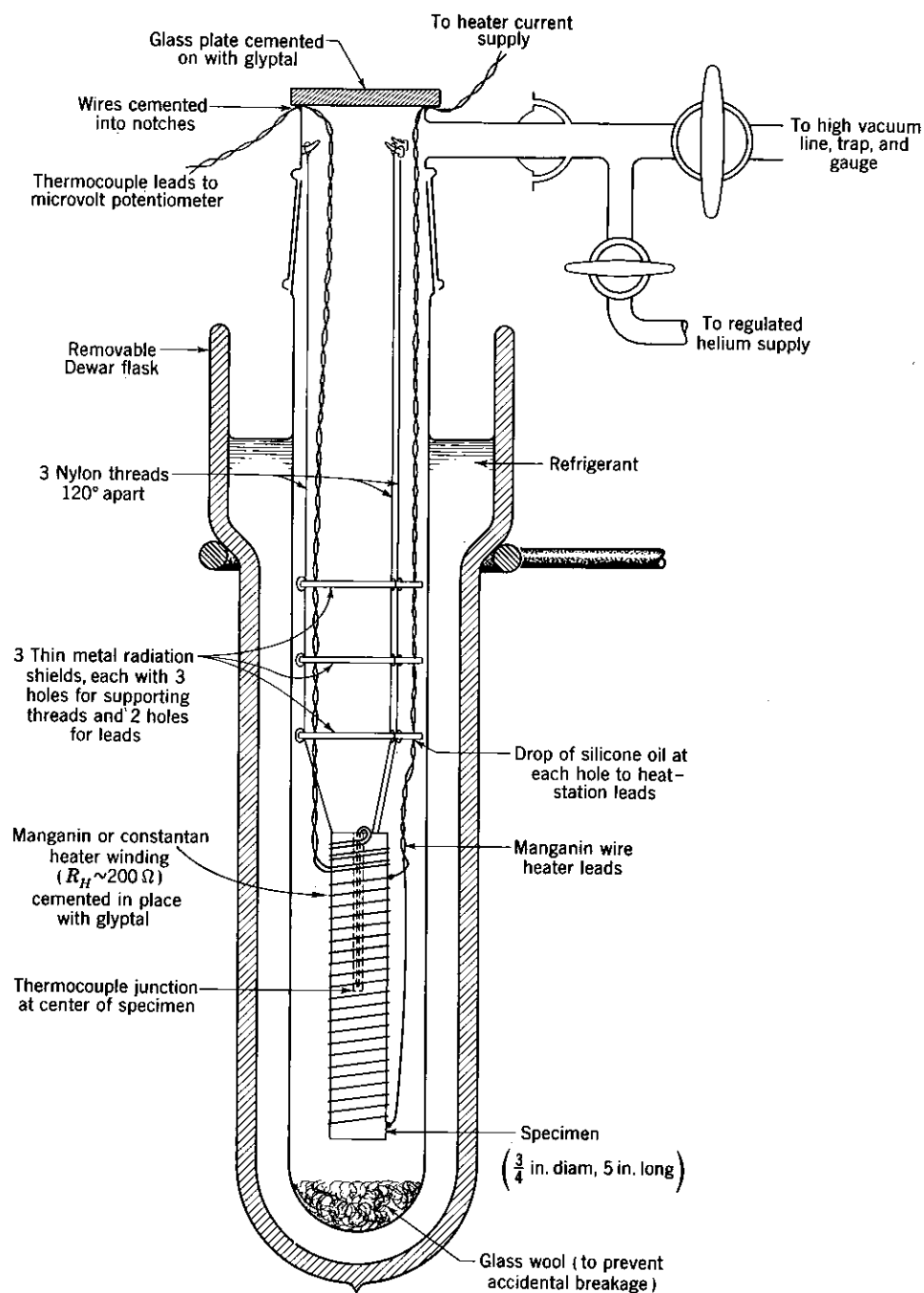
FIG. 3. A simple low-temperature calorimeter.

Calorimeter Design. A simple design for a low-temperature calorimeter is shown in Fig. 3. A large Pyrex tube containing the sample is immersed in a tall Dewar flask filled with the refrigerant. Suitable refrigerants for this experiment are liquid nitrogen and Dry Ice-acetone. The sample (preferably in the form of a cylinder) hangs by three nylon threads from three thin aluminum radiation shields,

which are hung from the top of a large, standard-taper joint. Heater and thermocouple leads are sealed tightly in tiny notches in the top edge by attaching a flat glass top plate with glyptal; they are also heat-stationed at the metal shields. Helium gas can be admitted to the system as a heat-transfer gas to bring the sample initially to the bath temperature; then the entire tube can be evacuated to eliminate gas conduction between the sample and the walls of the tube.

Heat leaks due to radiation, residual gas conduction, and conduction along the leads and threads are small but not negligible. This design is satisfactory only if the temperature of the sample is close to that of the bath; the procedure must be planned with this in mind.†

Note that the heat capacity which is measured is that of the sample alone except for a very small contribution due to the "addenda" (heater wire and cement). One may either neglect C_p(addenda) or calculate a value for it and subtract this correction term from the total C_p.

Heating Circuit. The heater should consist of many turns of fine constantan wire wound around the sample cylinder. If a metal sample is used, varnish the surface, and while it is still sticky, coat the sides of the sample with cigarette paper to provide electrical insulation. A convenient heating tape made of constantan wire and silk fibers interwoven (called "Silko ribbon") is available from De Bary and Co. Ltd., Basel, Switzerland. The heater wire must be attached to the sample with an adhesive that provides a reliable thermal contact between the two.

The electrical work in joules is given to a good approximation by

$$-w_{el} = \int i_H E_H \, dt \cong \bar{i}_H \bar{E}_H \, \Delta t \tag{26}$$

where $\bar{i}_H$ and $\bar{E}_H$ are the average heater current in amperes and the average potential drop across the heater in volts during a heating period of duration Δt sec. Figure 4 shows an electrical circuit designed to operate a heater of about 200 ohms using a 110-v dc source; this circuit can be easily modified to utilize lower voltage dc sources. Since i_H is about 0.06 to 0.08 amp in this circuit, E_H is approximately 14 v and a potential divider is necessary in order to use a potentiometer for measuring voltages. The potential divider is two high-resistance resistors in parallel with the heater (from a to b in Fig. 4). Use of the dummy heater enables one to achieve a steady current flow through the circuit before switching on the heater; thus i_H and E_H will vary only slightly during a heating period, and only a few values of each are required for each heating.

Combining Eqs. (25) and (26) we obtain for C_p in calories per degree

$$C_p = \frac{\bar{i}_H \bar{E}_H \, \Delta t}{4.184 \, \Delta T} = \frac{\bar{i}_H (\bar{E} - \bar{i}_H R_L) \, \Delta t}{4.184 \, \Delta T} \tag{27}$$

where $\bar{E}$ is the average potential drop across the heater and its leads (from a to b in Fig. 4) and R_L is the resistance of these leads (a to c and b to d in Fig. 4). The value of R_L is measured at room temperature and is assumed to be independent of temperature. The correction term $\bar{i}_H R_L$ takes account of the heat dissipated in the

† More complex designs[9] are possible in which the sample is completely surrounded by an adiabatic shield (i.e., a shield isolated from the sample but maintained at the same temperature as the sample at all times). Such designs will reduce heat leaks and permit operation at temperatures considerably above bath temperature, but they require a more complicated procedure and are difficult to construct.
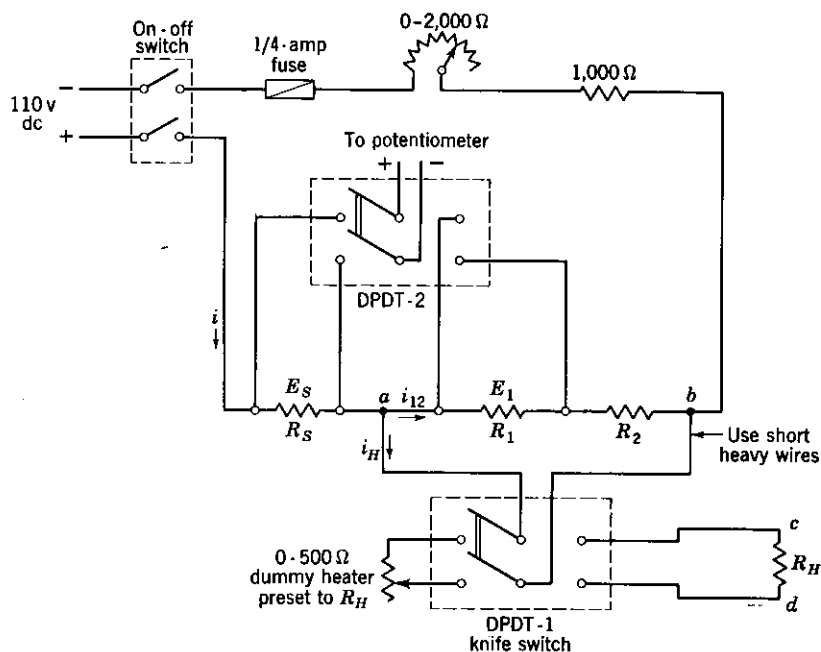
FIG. 4. A heater power-supply circuit designed to operate from a 110-v dc source. Typical values are $R_1 = 1,500$ ohms, $R_2 = 25,000$ ohms, $R_S = 10$ ohms, $R_H = 200$ ohms, and $R_L \cong 15$ ohms; R_L is the resistance of the leads from a to c and from b to d.

leads and is based on the assumption that none of this heat is delivered to the sample. (In the present design most of this heat flows to the radiation shield.) Now the directly measured quantities are E_S, the potential drop across the standard resistor R_S, and E_1, the drop across R_1. From $i_H + i_{12} = i = E_S/R_S$, where i is the total current and i_{12} is the current through the potential divider $(R_1 + R_2)$, and the fact that $i_H(R_H + R_L) = i_{12}(R_1 + R_2)$, one can easily derive an expression for $\bar{i}_H$:

$$\bar{i}_H = \frac{\bar{E}_S}{R_S[1 + (R_H + R_L)/(R_1 + R_2)]} \tag{28}$$

The term in brackets is very close to unity (1.008 for the values given in Fig. 4) and will be assumed independent of temperature; use the room-temperature value of R_H in calculating it. Also it is clear that $\bar{E}$ is given by

$$\bar{E} = \bar{E}_1 \frac{R_1 + R_2}{R_1} \tag{29}$$

Both E_S and E_1 can be measured with a Student Potentiometer circuit; see Chap. XV for details. Accurate room-temperature values of R_L and R_H must be determined before assembling the calorimeter and should be given. Values of R_1 and R_2 may be determined by the student or given by the instructor.

Temperature. The sample temperature is measured with a thermocouple which should be affixed in a small-diameter hole down the axis of the sample cylinder with an adhesive to ensure good thermal contact. Use either a copper-constantan or a chromel-alumel thermocouple (see Chap. XVI). Since the sensitivity of these thermocouples is ~15 μv deg^{-1} at 80°K and ~40 μv deg^{-1} at

300°K, it is necessary to use a precision potentiometer which will measure potentials in the 1- to 10-mv range to within ± 1 μv. One should also use heating periods which give ΔT between 5 and 10° to reduce the uncertainty in ΔT. Very large ΔT values should be avoided because heat leaks may introduce a serious error (radiation heat loss is especially serious at higher temperatures).

EXPERIMENTAL

It is assumed in the discussion below that an aluminum sample (with heater and calibrated thermocouple attached) has been mounted and that the calorimeter has been assembled. It is also assumed that values of R_1, R_2, R_S, R_L, and R_H as well as the mass of the sample and of the addenda are known.

Make all necessary connections to set up both a Student Potentiometer (for measurement of E_S and E_1) and a high-precision potentiometer (for thermocouple measurements); see Chap. XV. Standardize both potentiometers against a standard cell. At the same time, prepare an ice-water mixture in a 1-qt Dewar flask as the 0°C bath for the reference junction of the thermocouple. Fill the Dewar completely full of crushed ice, rinse the ice with a small amount of cold distilled water, and then add enough cold distilled water to fill the Dewar half full of liquid. Insert the junction well into the liquid.

With the sample at room temperature record the thermocouple emf and check the temperature corresponding to this reading with the reading of a mercury thermometer mounted close to the calorimeter.

With stopcock C closed, open stopcocks A and B. After pumping for 5 min, check the pressure. Continue to pump out the calorimeter until the pressure is less than 10^{-4} mm Hg. During this pumping period, close knife switch DPDT-1 so as to insert the dummy heater into the circuit and turn on the heater power supply. To facilitate later measurements, obtain approximate values of E_S and E_1 with current flowing through the dummy. The knife switch DPDT-2 permits the Student Potentiometer to be connected rapidly to either R_S or R_1. By adjusting the 0- to 2000-ohm variable resistor, obtain a current of between 0.06 and 0.08 amp and record the observed values of E_S and E_1.

When the vacuum is satisfactory, make a heat-capacity measurement at room temperature. Follow the procedure given below.

After this initial measurement is completed, make one or two measurements at liquid-nitrogen temperature. First close stopcock B and then open C slowly to fill the calorimeter with helium gas at about 1 atm. Now close stopcock A and slowly raise the Dewar flask, partially filled with liquid nitrogen, up over the calorimeter. Make sure that the top of the Dewar is above the uppermost radiation shield. After the Dewar is clamped in place, fill it to the top with liquid nitrogen. Check the temperature of the sample; it is necessary to reverse the thermocouple leads at the potentiometer in order to measure temperatures below 0°C. It may require about 40 to 50 min for the sample temperature to achieve a steady value. When the rate of drift is zero or very small, pump out the helium as before and check the pressure. After the pressure has dropped to 10^{-4} mm or less, make a C_p measurement as described in the procedure below. If possible, make a second measurement immediately after completing the first one.

Next make measurements at Dry Ice temperature. First remove the Dewar and empty out the liquid nitrogen. Partly fill the Dewar with a Dry Ice-acetone

mixture prepared in advance. Fill the calorimeter with helium gas as before, and then slowly raise the Dewar into place and fill it to the top. **Caution:** Dry Ice-acetone baths tend to foam badly; see Chap. XVI for the details of preparing and handling this refrigerant. When the temperature is almost steady but still slowly rising, pump out the helium and carry out one or two C_p measurements in the same manner as at liquid-nitrogen temperature.

At the end of the experiment, leave the calorimeter at room temperature.

Procedure for a Run. We shall assume that the sample temperature is close to bath temperature and that the calorimeter is already evacuated.

Record the thermocouple emf and the clock time every 30 sec for at least 5 min; the rate of change should be small and constant, if not zero. During this time check the standardization of the Student Potentiometer and then set it at the expected value of E_S.

Start a stopwatch and simultaneously turn on the heater by rapidly throwing the knife switch DPDT-1. Record the values of E_S and E_1 during the heating period. First read E_S and then throw switch DPDT-2 and read E_1; alternate the readings until several values of each have been recorded. After a temperature rise of about 7° (the desired thermocouple emf should be determined in advance), turn off the heater and simultaneously stop the stopwatch. Record the elapsed time Δt.

During the heating period it is only necessary to make occasional thermocouple readings in order to decide when to turn off the heater. However, as soon as the heater is turned off, the thermocouple emf must be recorded every 30 sec for 10 min or until the temperature is constant.

If dT/dt (that is, $d\mathscr{E}/dt$) is not too large, another measurement of C_p can be made immediately by using the postheating temperature drift rate as the preheating rate for a second heating period.

CALCULATIONS

For each heating period, calculate the average values $\bar{E}_S$ and $\bar{E}_1$, and use Eqs. (28) and (29) to obtain $\bar{\imath}_H$ and $\bar{E}$. Then determine the initial temperature T_1 and the final temperature T_2. Before electrical heating, the temperature should have changed only *very slowly*, if at all. However, after the heating period, the sample may have slowly cooled toward the bath temperature. If either the pre- or post-heating temperatures show a steady drift, plot the thermocouple emf vs. time for the entire run and extrapolate to the mid-point of the heating period to determine the emf corresponding to T_1 and T_2. Now calculate C_p from Eq. (27); this value is an average over the temperature interval and can be taken as corresponding to a mean temperature $T = (T_1 + T_2)/2$. If the heat capacity of the addenda is known at T, it should be subtracted from the total C_p given by Eq. (27). The molar heat capacity of aluminum is given by

$$\tilde{C}_p(\text{Al}) = \frac{26.97}{W}[C_p - C_p(\text{addenda})] \tag{30}$$

where W is the mass of the aluminum sample in grams. The constant-volume heat capacity can now be calculated from Eq. (23); the value of the constant A for aluminum[10] is 2.23×10^{-5} g-atom cal^{-1}. Tabulate the values of T, ΔT, C_p, $\tilde{C}_p$, $\tilde{C}_v$ for each run.

DISCUSSION

The coefficient γ which determines the electronic heat capacity of a metal is 3.5×10^{-4} cal deg^{-2} g-atom^{-1} for aluminum.[11] One can then calculate $\tilde{C}_v$(el) from Eq. (24) and, if necessary, correct $\tilde{C}_v$ to obtain $\tilde{C}_v$(lattice). The Debye characteristic temperature Θ which best fits the lattice heat capacity of aluminum[10] over the range 77 to 300°K is 391°K. Plot your values of $\tilde{C}_v$ vs. T, and for comparison, draw a smooth curve based on the predictions of the Debye theory. Comment on the agreement between your points and the theoretical curve; in particular state whether any deviations can be explained by systematic errors in the method used here.

APPARATUS

Low-temperature calorimeter, assembled containing an aluminum sample with heater attached and thermocouple installed; vacuum line; tall Dewar flask and clamp; 1-qt Dewar for ice; complete potentiometer setup for measuring current and voltage; high-precision potentiometer setup for thermocouple readings; heater power supply; two good-quality knife switches; clock and stopwatch; 0 to 30°C thermometer.

Supply of helium gas; refrigerants (liquid nitrogen and Dry Ice-acetone); distilled-water ice.

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GENERAL READING

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