

AN APPARATUS FOR THE MEASUREMENT OF
THE SPECIFIC HEAT OF CADMIUM BELOW 1° KELVIN

by

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ABSTRACT

The electronic specific heat of Cadmium has been determined by a number of independent workers using two basic methods; magnetic and calorimetric. This thesis pursues the problem by a calorimetric determination using an aquadag thermometer and a thermal valve. Production of low temperatures is necessary as the transition temperature for this superconductor is about 0.56° K. Hence, the interest lies in attempting to determine the heat capacity of the metal both in the normal and superconducting states.

The experimental method and results for specific heat measurements for other superconductors is briefly reviewed. The design of the cryostat is discussed in detail in Chapter II. A rather unique method of preparing a paramagnetic salt pill is also given. Resistance thermometers and determination of temperature is very important and the temperature range is obtained by adiabatic demagnetisation.

The conclusion and results of this research project is given in Chapter III.

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INTRODUCTION

Many research workers have determined the electronic specific heat of Cadmium. This is so as Cadmium was the first metal for which the transition temperature using demagnetisation techniques was discovered. In determining the transition temperature the electronic specific heat was found. Of more interest, the electronic specific heat can be determined calorimetrically from the normal specific heat equation in which the linear term yields γ . Samoilov successfully investigated cadmium in this way. He used an interesting fact that a very weak thermal coupling allows one to raise the temperature only of the sample during the short heating period. A phosphor-bronze thermometer, calibrated against the susceptibility of Fe ammonium alum, was also employed. The author wishes to carry out a similar experiment using a thermal valve to break thermal contact between the salt and sample, and using an aquadag thermometer to determine the temperatures involved.

This thesis begins with a brief survey of the work done on specific heats of metals, mostly superconductors, in the very low temperature region. The development is chronological for the most part. One section deals with the electronic heat capacity and transition temperatures of superconductors alone. A brief review of the principles of adiabatic demagnetisation is also presented concluding Chapter I.

Chapter II is a necessary discussion of cryostat design for specific heat work. Special attention is given to preparing the sample and salt pill. The a.c. resistance bridge, monitored by a recorder, is discussed along with a susceptibility bridge.

The final chapter, III, deals with the experimental procedure for determining the specific heat of cadmium both in the normal and superconducting states. As the largest source of error is in determining the heat input and the corresponding temperature rise this subject is also dealt with. The results are also found in the final chapter.

CHAPTER I

Resume of Experimental Facts

Eucken published an article, "Energie and Warmeinhalte", in 1929 and since this date our knowledge of the specific heat of solids has steadily increased.

In 1930 accurate calorimetry in the liquid helium temperature range began, using thermometric techniques of the vapor pressure of liquid helium and phosphor-bronze thermometers. Actually, Kammerlingh Onnes in 1911 discovered superconductivity in the metal mercury and he and Holst attempted to measure the specific heat above and below the transition temperature.

The sensitive phosphor-bronze thermometer, greatly needed in this work, entered the scene in 1931. Keesom and Van den Ende¹ were able to detect a discontinuity in the atomic heat of tin at the transition temperature. A thermodynamical theory has been put forward, connecting latent heat, changes in entropy and heat capacity with the magnetic threshold curve. Heat capacity measurements of several elements and alloys have been performed and found to be in excellent agreement with the threshold curves in many cases. Hence, γ , the electronic specific heat can be determined by magnetic or calorimetric methods. A detailed discussion of the theory is given in section 3 of this chapter.

1. Specific Heat of Superconductors

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1. Keesom W.H., Van den Ende J.N., Proc. Acad. Sci. Amst., 35, 143, 1932

Table 1. Atomic heat of the elements at low temperatures.

The Atomic Number stands on the left, the Symbol on the right of the field. Below these are given Θ_0 ($^{\circ}$ K) and (boldface) γ (millijoules/mole deg²). Parenthesis indicates uncertain value. For superconductors, Θ_0 refers to the normal state and γ is the best estimate from calorimetric data.

Period	Group																		
	Ia	IIa	IIIb	IVb	Vb	VIb	VIIb	VIII			Ib	IIb	IIIa	IVa	Va	VIa	VIIa	0	
1	1 H																	2 He	
2	3 Li	4 Be 1160 0.226											5 B	6 C Diamond (2000) Graphite 391	7 N	8 O	9 F	10 Ne	
3	11 Na 158 1.8	12 Mg 406 (1.35)											13 Al 418 1.46	14 Si 658	15 P	16 S	17 Cl	18 Ar	
4	19 K (219) (0.38)	20 Ca	21 Sc	22 Ti 278 3.34	23 V 273 8.83	24 Cr 402 1.54	25 Mn 13.8	26 Fe 467 5.0	27 Co 445 5.0	28 Ni 456 7.4	29 Cu 339 0.72	30 Zn 308 0.66	31 Ga	32 Ge 366	33 As	34 Se	35 Br	36 Kr	
5	37 Rb	38 Sr	39 Y	40 Zr 270 2.95	41 Nb 252 8.5	42 Mo 425 2.14	43 Tc	44 Ru	45 Rh	46 Pd 275 10.7	47 Ag 225 0.66	48 Cd 300 0.71	49 In 109 1.81	50 Sn White Gray 189 212 1.82	51 Sb	52 Te	53 I	54 Xe	
6	55 Cs	56 Ba	57* La 132 6.7	72 Hf	73 Ta 231 5.44	74 W (379) 1.48	75 Re	76 Os	77 Ir	78 Pt 229 6.8	79 Au 165 0.74	80 Hg (60-90)	81 Tl 89 3.1	82 Pb 94.5 3.0	83 Bi 117 (<0.08)	84 Po	85 At	86 Rn	
7	87 Fr	88 Ra	89** Ac			* 58—71 Lanthanide Rare Earths ** 90—103 Actinide Rare Earths													

* 58—71 Lanthanide Rare Earths

** 90—103 Actinide Rare Earths

Facings - 4-

As our primary interest is in superconductors a brief account will now be given of a particular few. Those in discussion will be both hard and soft superconductors; tin, aluminum, lanthanum, thallium, vanadium, niobium, and tantalum. Cadmium, a soft superconductor, is discussed separately. With reference to Table 1 the specific heats of the above metals are reviewed by Pearlman.¹ The choice of Sn, Al, La, Tl, V, Nb and Ta for discussion arises from the fact that at the lowest temperatures the electronic specific heat in the superconducting state has been proven to be exponential in form rather than cubic. In fact the empirical relationship is

$$C_s = \gamma T_0 a e^{-bT_0/T}$$

and in addition to being empirically applicable Corak et al² have pointed out that this could be expected to be true for a theory in which the levels occupied by superconducting electrons are separated by a gap from those occupied by the normal electrons. The idea of an energy gap of the order $\Delta E \approx kT_0$ has been discussed for many years and recently in particular by Frohlich³ (1954) and Bardeen (1955)⁴ and Biondi, Garfunkel and McCouberg⁵ (1956).

Further support for the energy gap theory was utilized

-
1. Keesom P.H., Pearlman N., H. Der Physik, Vol XIV, P. 282
 2. Corak W.S., Goodman B.B., Satterthwaite C.B., Wexler A.,
Phy. Rev., 96, 1442, 1954
 3. Frohlich H., Phys. Rev., 97, 845, 1950.
 4. Bardeen J., Phys. Rev. 97, 1724, 1955.
 5. Biondi, M.A., Garfunkel M.P., McCouberg A.O., Phys. Rev., 101, 1427, 1956.

by Tinkham¹ (1956). He concluded for lead a gap of the order of $3kT_0$ exists. Tinkham measured the ratio of power transmitted through thin films in the normal and superconducting states.

2. Measurements of Specific Heat of Superconductors to Determine γ

The temperature dependence of the specific heat for a normal metal is of the form

$$C_n = A \left(\frac{T}{\theta} \right)^3 + \gamma T \quad (1.1)$$

At low temperatures the linear term is predominant and γ , the electronic specific heat term is of the order of 10^{-4} cal/mole deg². It is not always possible to separate the electronic contribution from the total specific heat with great accuracy. It is desirable to have the lattice specific heat term as small as possible and this occurs, with reference to equation (1.1), for metals having large Debye temperatures. However, most soft superconductors which have excellent superconducting properties have relatively small θ 's. Sn (185) and Al (420) have fairly high θ 's and much work has been done on them. The hard superconductors, in periods IVa and V, have the desired larger Debye temperatures but are difficult to obtain with ideal superconducting properties.

One very striking fact of superconductivity is that when changing from a normal to a superconducting phase a discontinuity

1. Tinkham M., Phys. Rev., 104, 845, 1956.

in the specific heat appears. This discontinuous jump occurs through the transition temperature from a value of γT_0 to about $3\gamma T_0$. This was first seen by Keesom and Van den Ende,¹ at Leiden, in 1932. Shortly after Keesom and Kok² measured the magnitude of the discontinuity in the specific heat at transition to be about 0.0024 cal/mole deg.

Also, they noticed that no latent heat was associated with the transition. The same jump in the specific heat was noticed later in their experiments with thallium. Again, no evidence of latent heat during the transition was noted.

Sn

Before World War II more accurate work was performed by Keesom and Van Laer³ on tin. The transition temperature T_0 is conveniently located in the He range, $T_0 = 3.73$ K. If the threshold magnetic field is parabolic it can be shown that at T_0

$$\gamma = \frac{(\Delta C)_{T_0}}{2T_0} \quad (1.2)$$

corresponding to the jump of the atomic heat. The value $(\Delta C)_{T_0}$ is obtained by extrapolation from atomic heat curves above and below T_0 . γ from $(\Delta C)_{T_0}$ by Keesom and Kok is 10 mj/mole deg² and from (1.2) is 1.4 mj/mole deg². This is lower than calori-

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1. Keesom W.H., Van Den Ende J.N., Proc. Acad. Sci. Amst., 35, 143, 1932.
 2. Keesom W.H., Kok J.A., Physica, 1, 770, 1934.
 3. Keesom W.H., Van Laer P.H., Physica, 5, 193, 1938.

metric value, which is to be expected in this case.

Keesom and Van Laer¹ also investigated tin. A plot of C_n/T and C_s/T versus T^2 has been calculated from their data where C_n and C_s are the specific heats of Sn in the normal and superconducting states. For the normal metal Keesom expressed C_n in the usual manner

$$C_n = A'T^3 + \gamma T \quad (1.3)$$

and since the straight line representing C_s passes through the origin then $C_s = AT^3$. Hence,

$$\begin{aligned} \Delta C = C_s - C_n &= (A-A')T^3 - \gamma T \\ &= \frac{V_m T}{4\pi} \frac{d}{dT} \left(H_c \frac{dH_c}{dT} \right) \end{aligned} \quad (1.4)$$

Integrating this equation twice leads to a parabolic threshold curve

$$H_c = H_0 \left[1 - (T/T_0)^2 \right] \quad (1.5)$$

This leads to

$$\begin{aligned} \Delta C &= \frac{V_m T}{2 \cdot 2\pi} \frac{d}{dT} \left(H_c \frac{dH_c}{dT} \right) = \frac{V_m}{2\pi} \frac{H_0^2}{T^2} T \left[3(T/T_0)^2 - 1 \right] \\ &= \gamma T \left[3(T/T_0)^2 - 1 \right] \end{aligned} \quad (1.6)$$

hence,

$$\gamma = \frac{V_m}{2\pi} \frac{H_0^2}{T_0} \quad (1.7)$$

for $T = T_0$

$$(\Delta C)_{T_0} = 2\gamma T_0 = \frac{V_m}{4\pi} T_0 \left(\frac{dH_c}{dT} \right)_{T_0}^2 \quad (1.8)$$

From these equations we find that there are several ways in which γ , the coefficient of electronic atomic heat in the normal state can be obtained. It is connected directly with V_m , T_0 , and H_c by (1.8), with the jump in the atomic heat at the normal

transition point, and also with the initial slope of the threshold curve at T_0 by (1.8). Daunt and Mendelssohn¹ investigated Sn as well which showed that the linear term $C_n - C_s$ is of the right order of magnitude to justify its interpretation as the Fermi-Sommerfield specific heat term.

The reader should refer to a review by Eisenstein² for a comparison between calorimetric and magnetic determinations of γ . He concludes that the γ 's obtained from the threshold curve data are frequently in good agreement with the calorimetric determinations. However, in some cases discrepancies exist with the magnetic values usually lower than the calorimetric values.

Kok³ assumes that for $C_s = AT^3$ this implies a cubic dependence for the superconducting electronic specific heat. Using this and (1.7 or 1.6) one can write

$$C_s = 3\gamma T_0 (T/T_0)^3$$

but even in the case of tin, from which data Kok originally derived these relations, a deviation from the straight line on the plot of C_s/T vrs T^2 can be seen around $T^2 = 5$.

The fit of Sn data by Keesom and Van Laer⁴ to an exponential temperature dependence is certainly no worse than the fit to T^3 except in the immediate neighbourhood of the transition point

1. Daunt J.G., Mendelssohn K., Proc. Roy. Soc., A, 160, 127, 1937.
2. Eisenstein J., Rev. Mod. Phys., 26, 277, 1954.
3. Kok J.A., Physica, 1, 1103, 1934
4. Keesom W.H., Van Laer P.H., Physica, 5, 193, 1938.

where there are pronounced deviations from the exponential.

Corak, Goodman, Satterthwaite, Wexler¹ have given recent more precise measurements for the specific heat of Sn over a more extended range of temperature. Corak et al have revealed that the exponential form is correct except near T_0 . They have given the values for the constants a and b to be almost the same as for vanadium, 9 and 1.5 respectively, for the empirical formula for the superconducting specific heat as in equation (1.0).

$$C_s = \gamma T_0 a e^{-bT_0/T}$$

Al

Keesom and Kok² investigated Al in the temperature range of 1 - 20° K and found γ to be 1.46 mj/mole deg² calorimetrically. Al data gives a good representation of a sum of a cubic term and a linear term for the specific heat. The value of $(\Delta C)_{T_0}$ observed was 1.9 mj/mole deg² and this corresponds by (1.2) a γ of 0.85. This is smaller than either the calorimetric or magnetic determination.

Daunt and Heer³ also made electronic specific heat measurements and they indicated that it is very plausible to attribute the linear term of $C_n - C_s$ to the Fermi-Sommerfield specific heat of the normal state.

-
1. Corak W.S., Goodman B.B., Satterthwaite C.B., Wexler A.,
Phys. Rev., 96, 1442, 1954.
 2. Keesom W.H., Kok J.A., Physica, 1, 770, 1934.
 3. Daunt J.G., Heer C.V., Phys. Rev., 76, 715, 1949.

Goodman¹ in his plot of C_s/T vrs T^2 shows a distinct change ispresent in the slope indicating that again the electronic specific heat in the superconducting state leads to an exponential equation of the form of (1.0),

$$C_s = \gamma T_0 a e^{-bT_0/T}$$

Goodman indicates, as do others in this field, that this form can be expected if there was a small energy gap ΔE in the energy level spectrum of superconductors for then at the lowest temperatures a term of the form $e^{-\Delta E/kT}$ could be expected. The constants a and b have been found for Al to be 6.9 and 1.28 respectively.

La

Below 35° K the true T^3 region extends to about 6° K according to Parkinson² et al. A calorimetric determination of γ gives 6.7 mj/mole deg² and T_0 4.37° K. The value of $(\Delta C)_{T_0}$ is 58 mj/mole deg² which corresponds to the same value of γ given by (1.2). Lanthanum behaves as do the oabove superconductors with respect to the exponential form for the superconducting electronic specific heat.

Tl

Further support for the exponential law has been produced by

-
1. Goodman B.B., Conférence de Physique des Basses Temperatures, P.506.
 2. Parkinson D.H., Quarrington J.E., Proc. Phys. Soc., A, 57, 569, 1954.

Snider and Nicol¹ on thallium. Previous investigations were made by Keesom and Van den Ende and Keesom and Kok.² Keesom and Kok were the first to measure the size of the jump in the specific heat at T_0 and detected the absence of latent heat during the transition. T_0 was found to be 2.36 K. By equation (1.2) $\gamma = 1.3 \text{ mj/mole deg}^2$ which agrees excellently with the value obtained by the magnetic threshold field measurements. Calorimetric values which were obtained by a least squares fit of Keesom and Kok data above T_0 is much larger. There appears no obvious reason for this discrepancy.

V-Nb-Ta

These elements are of interest for investigation of the thermodynamics of the phase transition from the normal to the superconducting state. These hard superconductors have high θ 's and T_0 's which is an advantage. A slight disadvantage is that T_0 for V and Nb falls between 4 - 10 K where no cooling bath is available. One difficulty is that different samples give different results by the same investigators for no apparent reason.

Worley, Zemansky and Boorse³ investigated V and Ta. Worley et al observed positive deviations in C/T again indicating the possibility of the exponential form for V. For Ta, the data of Worley et al agree with those of Keesom and Desirant⁴ in the normal

1. Snider J.L., Nicol J., Phys. Rev. 105, 1242, 1957.
2. Keesom W.H., Kok J.A., Haag 1, 175, 503, 595, 1934.
3. Worley B., Zemansky M.W., Boorse T., Phys. Rev., 91, 1567, 1953.
4. Keesom W.H., Desirant B., Physica, Haag 8, 273, 1941.

state. The measurements of Desirant and Mendelssohn² give values of $(\Delta C)_{T_0}$ of 34 and 40 mj/mole deg at T_0 equal to 4.0 and 4.4°K respectively. By (1.2) these correspond to γ of 4.2 and 4.0 mj/mole deg² which are lower than both the calorimetric and magnetic values.

For V Satterthwaite³ et al did not report deviations in C/T vrs T^2 . However, the results of Worley et al give the empirical exponential equation with constants a and b as 9.17 and 1.5 respectively.

Nb was investigated by Brown, Zemansky and Boorse, between 2-20°K. T_0 is 8.9°K with γ a value of 8.5 mj/moledeg². Although the data needs revision Nb did support the exponential law.

Electronic Specific Heat - Cadmium

The standard method of obtaining heat capacities is similar to that of Rayne.¹ He used cylindrical samples connected to the salt pill by copper wire which is in thermal contact by the vane technique. A manganin heater was glued to the metal using glyptal. The magnetic temperature for copper sulfate was determined ballistically. The ratio of amounts of salt and metal was chosen in such a way that at about 0.5°K they had equal heat capacities. The specific heat of the salt was measured in a separate experiment. Plotting C/T vrs T^2 straight lines were found for Cu, Ag, Pt, and

1. Rayne J., Phys. Rev., 95, 1428, 1954.

2. Desirant B., Mendelssohn K., Nature, 148, 316, 1941.

3. Corak W.S., Satterthwaite C.B., Phys. Rev., 99, 1660, 1954.

others confirming the $C = AT^3 + \gamma T$ relationship. From the slopes of these lines γ was found to be in reasonable agreement.

¹
Samoilov determined the specific heat of cadmium in the following way. The sample was of cylindrical shape containing a heater, H_1 , glued in a helical groove on the surface. The cadmium was connected to the salt pill, Fe ammonium alum, by a copper wire, W_1 , 0.1 mm dia. 30 cm long. The dimensions are chosen such that after demagnetisation it took about an hour for the metal to cool to the temperature of the pill. The advantage is that for a short heating period the heat flow to the salt was negligible so that the heat capacity of the cadmium alone was measured. In other words the resulting thermal coupling was so weak that the heat supplied by the heater during a short period raised the temperature only of the cadmium. Hence, it gives the heat capacity directly which is an advantage over Rayne's method. Some difficulties were encountered above 0.5°K since here the specific heat of the salt becomes rather small and helium desorption from the salt begins, so that the temperature rise due to heat leak increases appreciably. One method around this is to connect a second wire W_2 , similar to W_1 , to a heater H_2 . The salt was kept at about 0.1°K and the temperature of the cadmium was kept at a higher equilibrium temperature by generating a constant

1. Samoilov B.N., Doklady Akad. Nauk, USSR, 81, 791, 1951.

heat flow through W_1 and W_2 .

The temperatures involved were measured with a phosphor-bronze thermometer which was calibrated against the susceptibility of Fe ammonium alum, the latter being determined ballistically. Supply wires to thermometer and heaters were of tinned constantan. Copper vanes, inserted in the wires, were embedded in the salt in order to decrease the heat leak to the cadmium. The vacuum of the calorimeter was improved with an adsorption pump.

The results of Samoilov's experiments were very good. It was found that

$$C_n = 1.942 \times 10^{10} (T/300)^3 + 7.11 \times 10^3 T \text{ (erg/mole deg)}$$

Accuracy reached in the superconducting state was small due to the small temperature region in which measurements could be made, $T_c \approx 0.56^\circ\text{K}$ and to the irregularities in the phosphor-bronze thermometer below 0.4°K . It also appeared that $C_s \propto T^3$ but the possibility of a small linear term was not excluded.

The first metal for which T_c was discovered with the aid of demagnetisation technique was Cd. Kurti and Simon¹ performed the first experiments using a compressed mixture of a paramagnetic salt and cadmium metal. The transition temperature in zero field was 0.54°K and the slope of this transition curve at T_c was 100

-
1. Kurti N., Simon F., Nature 133, 907, 1934.
Kurti N., Simon F., Proc. Roy. Soc. Lond., 151, 610, 1935

oersted/deg. The susceptibility of the pill consisted of a paramagnetic term due to the salt and a diamagnetic term due to the superconducting cadmium. The transition curve can be derived from observation of the heating curves of the pill for various values of magnetic field strength. A second method based on Mendoza's vane technique has the advantage that a field can be applied to the metal without influencing the temperature of the salt.

Smith and Daunt¹ found by the same method a T_c equal to 0.602°K . The transition curve could be represented by a parabola

$$H = H_0 \left[1 - (T/T_c)^2 \right]$$

and H_0 , the critical field at absolute zero, was calculated to be 33.8 oersted and a slope at T_c of 112 oersted/deg.. If the above equation is valid then the specific heat of the electrons in the normal state, assuming a reversible transition, obeys

$$C_{el} = \gamma T = \frac{V}{8\pi} \left(\frac{dH}{dT} \right)_{T=T_c} \cdot T$$

and $\gamma = 6.44 \times 10^3$ erg/mole deg².

Steele and Hein,² applying the same method, investigated small Cd grains of spherical shape. They found $T_c = 0.65^\circ\text{K}$ and the slope of the transition curve increased as the particle size decreased. Using the vane technique Goodman and Mendoza³ found T_c to be 0.560°K , $H_0 = 28.8$ oersted, slope at $T_c = 103$ oersted/deg

-
1. Smith T.S., Daunt J.G., Phys. Rev., 88, 1172, 1952.
 2. Steele M.C., Hein R.A., Phys. Rev., 87, 708, 1952.
 3. Goodman B.B., Mendoza E., Phil. Mag. 42, 594, 1951.

and $\gamma = 5.35 \times 10^3$ erg/mole deg².

Samoilov¹ also tried the vane technique but found that γ was 20% lower than his previous calorimetric determinations. He suggested that the difference might be due to a small linear term in the specific heat in the superconducting state. Clement showed that the discrepancy may also be solved by assuming a small term proportional to T^3 in the magnetic transition curve. Samoilov's results were $T_c \approx 0.547^\circ\text{K}$, $H_0 \approx 28.4$, slope at $T_c = 104$ oersted/deg and $\gamma = 5.56 \times 10^3$ erg/mole deg².

3. Theory of the Lattice and Electronic Specific Heat of a Normal Metal at Low Temperatures

The determination of specific heat and its variation at low temperatures has been a powerful tool in the study of the solid state. In the classical theory, each element of a lattice had a thermal energy $6 \times \frac{1}{2} kT$ (kinetic + potential), yielding a total energy per mole

$$E = 3NkT = 3RT \quad (1.30)$$

and therefore a constant specific heat

$$C_v = dE/dT = 3R \approx 6 \text{ cal/mole deg}$$

For most elements, reasonable agreement with experiment at room temperature was shown by the empirical law of Dulong and Petit, although a notable exception was the case of diamond.

Einstein Model The recognition by Einstein² of the relevance of

1. Samoilov B.N., Doklady Akad. Nauk, USSR, 81, 791, 1951.
2. Einstein A., Ann. Phys., Lpz., 22, 180, 800, 1907.

the quantization of energy levels in a simple (Planck) oscillator given by, ignoring the zero point energy, $\epsilon = nh\nu$ showed that this classical result could only be expected to hold for temperatures not small compared with a characteristic temperature of the lattice, θ_E , defined by $\theta_E = h\nu/k$ where h and k is the Planck and Boltzmann constant respectively. The lattice was simulated by an aggregation of N similar, independent, oscillators of frequency ν and Einstein showed:

$$E = 3RT \frac{h\nu/kT}{e^{h\nu/kT} - 1} = 3RT \frac{\theta_E/T}{e^{\theta_E/T} - 1} \quad (1.31)$$

$$C_V = 3R \frac{(\theta_E/T)^2}{(e^{\theta_E/T} - 1)(1 - e^{-\theta_E/T})} \quad (1.31a)$$

For $T \gg \theta_E$ we have $E = 3RT$, and $C_V = 3R$ in agreement with (1.30), while if $T \ll \theta_E$ then

$$E = 3RT \left(\theta_E/T \right) e^{-\theta_E/T} \quad (1.32a)$$

$$C_V \approx 3R \left(\theta_E/T \right)^2 e^{-\theta_E/T} \quad (1.32)$$

thus the specific heat falls rapidly to zero as T diminishes. This theoretical deduction added great weight to Nernst's Law, the Third Law of Thermodynamics, from which a basic deduction in its present formulation is the vanishing of the specific heat at absolute zero.

It was soon recognized that this Einstein model was too crude an approximation to reproduce the very low temperature specific heat sufficiently accurately. In particular the very

rapid decay, $e^{-\theta E/T}$, for $T \ll \theta$ arises because a minimum energy, $h\nu$, is necessary to excite the lowest mode of the Planck oscillator and the probability diminishes very rapidly as the temperature is lowered. Nernst and Lindemann¹ proposed a generalization of Einstein's formula

$$E = 3RT \frac{1}{2} \left[\frac{\frac{\theta}{T}}{e^{\frac{\theta}{T}} - 1} + \frac{\frac{\theta}{2T}}{e^{\frac{\theta}{2T}} - 1} \right] \quad (1.33)$$

with a corresponding expression for C_v . This yielded much better agreement with experiment down to temperatures of 20°K. The Nernst-Lindemann formula is regarded today as a very useful approximate expression.

In his original paper Einstein identified the frequency ν with a sharp resonance absorption in the infra-red, but was later led to consider the general connection with the elastic vibrations of the crystal. Thus, other things being equal a high θ would imply strong elastic binding, that is a more rigid solid. This conclusion is of general validity. Einstein himself also recognized that the coupling between neighbouring atoms would generally be so strong that the assumption of a monochromatic vibrational spectrum could only be regarded as a rough approximation.

1. Nernst W., Lindemann F.A., Phys. Z. 11, 609, 1910.

The Debye Model Debye's¹ approach was to consider the coupled vibrational modes of the atomic lattice, some $3N$ in all, as forming a continuum of elastic vibrations running from the longest wavelengths ($v \rightarrow 0$) to a short wavelength-limit of the order of the lattice structure. This model leads directly to a frequency density distribution

$$dn = \frac{4\pi V}{C^3} v^2 dv$$

where C is the velocity of elastic waves in the crystal assumed independent of v and isotropic. Associated with each proper vibration we have the energy of a Plank oscillator and thus

$$E = \frac{4\pi V}{C^3} \int_0^{\infty} \frac{h\nu^3 dv}{e^{\frac{h\nu}{kT}} - 1}$$

that is

$$E = 3kT \cdot 3\left(\frac{T}{\theta_D}\right)^3 \int_0^{\frac{\theta_D}{T}} \frac{x^3 dx}{e^x - 1}$$

where a characteristic Debye temperature, θ_D , is now defined by $\theta_D = h\nu_m/k$.

At high temperatures we have $E = 3kT$ again in agreement with the classical treatment, but at low temperatures

$$E = 9kT^4 \frac{1}{\theta_D^3} \int_0^{\infty} \frac{x^3 dx}{e^x - 1}$$

and the specific heat $C_v \approx 464 \left(\frac{T}{\theta_D}\right)^3$ cal/moledeg.

1. Debye P., Ann. Phys., Lpz. 39, 789, 1912.

Almost simultaneously with Debye's work, Born and v. Karman¹ discussed the complete dynamical treatment of the proper vibrations of a lattice starting from the atomic force constants. Basically, the problem was not new. Newton first attacked the analysis of the vibration of a one-dimensional lattice when considering the velocity of sound, and Kelvin was the first to consider a diatomic lattice of large and small coupled masses. This then yields two distinct vibrational modes, the acoustic and optical branches.

In this approach the velocity of propagation is no longer constant nor necessarily isotropic and the simple vibrational frequency density is not obtained. The problem of analysing the true spectrum for a particular crystal is very complex and difficult to generalize; consequently Debye's much simpler and very elegant approximation has been widely applied to the analysis and comparison of experimental data.

In the Debye theory, Θ_D is of course a constant parameter by definition; however in presenting experimental data it has become conventional to derive values at various temperatures for an effective Θ_D necessary to force agreement with the Debye theory and to plot thus a curve of Θ_D as a function of temperature. If a substance obeyed the Debye theory precisely then of course Θ_D would be constant. If this is not the case within experi-

1. Born M., v. Karman, Phys. Z. 13, 297, 1912; 14, 15, 1913.

imental error, strictly one may only say that the Debye theory is inapplicable, but in fact this approach is of considerable value when certain types of variation common to a number of substances can be recognized.

Electronic Specific Heat - In the case of the electronic contribution to the specific heat in metals this term dominates in the temperature range below 1°K . It will be remembered that on the classical theory the thermal status of the free or conduction electrons was very unsatisfactory; on the one hand, the concept of an electron gas in the Drude-Lorentz theory of thermal and electrical conductivity seemed very appropriate while, on the other, such a classical gas should have contributed an additional specific heat $\frac{3}{2} nR$ cal/gm atom where n is the number of free electrons per atom. To explain the magnitude of the conductivities a value of $n \approx 1$ was necessary for simple metals, while no corresponding specific heat was observed.

Modern quantum theory, in particular the application of the Pauli exclusion principle in Fermi-Dirac statistics, showed however, that except at very high temperatures only a very small fraction of the conduction electrons (those on the surface of the Fermi sphere) can interchange thermal energy with the lattice; consequently at normal temperatures, the electronic specific heat is negligible and the electron gas is said to be degenerate. More

generally, however, Sommerfeld¹ has shown that the free electrons should exhibit a specific heat linear in T at low temperatures; this consequently should become significant at sufficiently low temperatures where the lattice contribution is falling roughly as T^3 . The actual magnitude of the linear term will clearly depend on the density of electron states near the top of the Fermi distribution and information about the whole energy-band can only be obtained if measurements can also be made at sufficiently high temperatures and for all the electrons to contribute essentially. This depends of course on the actual degeneracy temperature and if this can be approached, so that the electron gas tends to become Maxwellian, then an electronic specific heat of the order of $3/2R$ should manifest itself in addition to the classical lattice heat. This increase is observable in some metals, particularly the transition elements, but in a simple metal the degeneracy temperature is too high.

It is clear that, to separate out the electronic heat at low ~~temperatures~~, the lattice heat must be known accurately and it has been customary, for the purpose, to express the specific heat in the form

$$C_v = 464 (T/\theta)^3 + \gamma T \quad (1.35)$$

where the validity of the Debye law for the lattice heat is implicit in the second term. Thus:

1. Sommerfeld A., Z. Phys., 47,1,1928.

¹
Keesom and Clark found for nickel in the range 1-10°K,

$$C_v = 464 (T/413)^3 + 1.74 \times 10^{-3} T$$

²
Kok and Keesom for platinum and copper between 1.2 and 20°K,

$$C_v = 464 (T/233)^3 + 1.6 \times 10^{-3} T$$

$$C_v = 464 (T/335)^3 + 1.78 \times 10^{-4} T$$

³
Keesom and van Laer found for tin between 1 and 3°K,

$$C_v = 464 (T/185)^3 + 4 \times 10^{-4} T$$

⁴
Duyckaerts for cobalt between 2 and 18°K finds,

$$C_v = 464 (T/443)^3 + 1.2 \times 10^{-3} T$$

⁵
Keesom and Kurrelmeyer for iron between 1.1 and 20.4°K,

$$C_v = 464 (T/462)^3 + 1.2 \times 10^{-3} T$$

⁶
Samoilov for cadmium between 0.4 and 1.1°K,

$$C_v = 464 (T/300)^3 + 7.11 \times 10^{-4} T$$

In most cases, in fact, the experiments have been made at a temperature sufficiently low to assume reasonably that the Debye continuum has been reached. The Sommerfeld free electron gas theory predicts $\gamma = 10^{-4}$ and it appears therefore quite justifiable, to conclude from this data, in general agreement with theory, that the density of states for certain bands is much higher in the transition metals than for a simple metal like Cu.

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1. Keesom W.H., Clark C.W., Physica, 2, 513, 1935.
 2. Kok J.A., Keesom W.H., Physica, 3, 1035, 1936.
 3. Keesom W.H., van Laer P.H., Physica, 5, 193, 1938.
 4. Duyckaerts, G., Physica, 6, 401, 1939.
 5. Keesom W.H., Kurrelmeyer B., Physica, 6, 817, 1939.
 6. Samoilov B.N., Doklady Akad. Nauk., USSR, 86, 281, 1951.

4. Thermal Valves

It is often desirable when cooling by demagnetisation to break the thermal link between salt and sample. This was first suggested by F. Simon.³ Hence, thermal valves or switches are very useful for specific heat work as it allows one to determine the specific heat of the sample directly.

Mendoza² was the first to construct a practical thermal valve. A very thin copper sheet was actually broken by force to break the heat contact. Using the fact that the thermal conductivity of liquid helium becomes poor at lower temperatures, Kurti designed yet another switch. He connected the salt and sample by a narrow tube, containing a moveable copper rod, filled with liquid helium. Hence, heat transfer is good along rod when rod is in proper position. Otherwise, the heat transfer through the liquid helium is poor.

The fact that the heat conductivity of solid helium is much worse than that of liquid helium can also be employed as a basis for a thermal valve. Wilkinson and Wilks¹ increased the pressure in their cryostat to solidify the helium thereby breaking the heat contact. Upon melting, the heat contact was restored.

Superconductors by far make the best thermal valves. The metal is kept in the normal state by the application of an external

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1. Wilkinson K.R., Wilks J., Proc. Phys. Soc. Lond., A64, 89 (1951)
 2. Mendoza E., Ceremonies Langevin-Perrin, P. 67 Paris 1948
 3. Simon F., Reunion d'etudes sur le magnetisme, Stratsbourg, P. 1 (1939)

magnetic field. Hence, thermal linkage is very good. With the valve below its transition temperature the external field is removed and the valve goes into the superconducting state providing a much lower thermal conductivity. The transition temperature should be well above 1° K and care should be taken that no flux is trapped in the superconducting state. A high degree of purity is also essential.

Several independent authors proposed a valve based on the above principle; Gorter,¹ Heer and Daunt,² and Mendelssohn and Olsen.³ Heer and Daunt demonstrated the practical application of the switch using a tantalum wire (56 cm long, 0.017 cm dia.) connecting the salt pill to the liquid helium bath. Steele and Hein used a superconducting thermal valve, replacing exchange gas, in their experimentation with superconducting cadmium particles. DeVries and Daunt⁵ employed a thermal switch for determining the specific heat of He³. After the demagnetisation the heat contact between the salt and helium container was broken allowing the specific heat of the liquid to be measured separately. Cascade demagnetisation is another application for thermal switches. This has been carried out using lead by the following workers; Darby, Hatton, Rollin, Seymour,⁶ Silsbee and Croft, and Falkner, Hatton and Seymour.⁷

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1. Gorter C.J., Ceremonies Langevin-Perrin, P. 76, Paris 1948.
 2. Heer C.V., Daunt J.G., Phys. Rev., 76, 854, 1949.
 3. Mendelssohn K., Olsen J.L., Proc. Roy. Soc. Lond., A63, 2, 1950.
 4. Steele M.C., Hein R.A., Phys. Rev., 87, 908, 1952.
 5. DeVries G., Daunt J.G., Phys. Rev., 93, 631, 1954.
 6. Darby J., Hatton J., Rollin B., Seymour E., Silsbee H.,
Proc. Phys. Soc. Lond., A64, 861, 1951.
 7. Croft A., Faulkner E., Hatton J., Seymour E.,
Phil. Mag., 44, 289, 1953

1

Heer, Barnes and Daunt give the following figures for pure coldworked lead below 1° K, which is adequate for design purposes:

$$\begin{aligned} K \text{ (normal)} &= 4TW \text{ -cm}^{\circ}\text{deg}^{-1} \\ K \text{ (super)} &= 0.08 T^3W \text{ -cm}^{\circ}\text{deg}^{-1} \end{aligned}$$

The ratio of the thermal resistance of a wire in the two states is therefore 500:1 at 0.3° K and 5000:1 at 0.1° K. To open and close the valve an external field of 800-850 gauss is required. The field is usually provided by an external solenoid. Goodman² used a superconducting solenoid, niobium, for his external field. It has a critical field much greater than that of lead and could produce a field of 2000 gauss with no power dissipation.

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1. Heer C.V., Barnes T., Daunt J.G., Rev. sci. Instrum, 25, 1088
 2. Goodman B.B., Conference de Physique des Basses Temperatures, P. 506.

5. Adiabatic Cooling

If U represents the internal energy, T the absolute temperature, S the entropy, H the applied magnetic field, and M is the magnetisation of a system then, from the second law of thermodynamics,

$$TdS = C_H dT + T \left(\frac{\partial M}{\partial T} \right)_H dH$$

For an isothermal change of field (reversible)

$$TdS = T \left(\frac{\partial M}{\partial T} \right)_H dH$$

For a finite change of field from H_i to H_f , the quantity of heat Q may be given by

$$Q = T(S_f - S_i) = T \int_{H_i}^{H_f} \left(\frac{\partial M}{\partial T} \right)_H dH$$

With a constant field, it is known that an increase in temperature of a paramagnetic solid causes a decrease in magnetisation.

Therefore, $\left(\frac{\partial M}{\partial T} \right)_H$ is negative and heat is rejected when the field is increased and is absorbed when the field is decreased isothermally.

On the other hand, if we change the field adiabatically

$$C_H dT = -T \left(\frac{\partial M}{\partial T} \right)_H dH$$

whence

$$T = - \int_{H_i}^{H_f} \frac{T}{C_H} \left(\frac{\partial M}{\partial T} \right)_H dH$$

Note that if T and C_H can be assumed to be constant (it is almost so at room temperature for most paramagnetic substances)

$$T = \frac{-T}{C_H} \int_{H_i}^{H_f} \left(\frac{\partial M}{\partial T} \right)_H dH$$

and so a decrease in temperature will occur if the field is decreased adiabatically.

The above equations gave rise to the so called magnetocaloric effect and led to the currently used methods of cooling substances to temperatures below one degree Kelvin. Debye and Giaque were the first to suggest magnetic cooling of paramagnetic salts. The latter actually first performed such cooling experiments in America.

The procedure is a fairly simple one in principle. A paramagnetic salt, such as Cr K alum, whose magnetic ions are sufficiently far apart that Curie's law is valid, is suspended in a vessel containing exchange gas (helium) at the lowest temperature available with a liquid helium bath. Then a magnetic field is turned on and after the temperature equilibrium is re-established, the exchange gas is pumped out leaving the salt thermally insulated. Adiabatic demagnetisation is accomplished either by switching off the magnet and rolling it away from the specimen or the specimen itself is removed from the poles of the magnet after the current has been cut off.

The next step consists in a determination of the temperature of the salt pill. For this purpose, the magnetic susceptibility is first determined for five or six temperatures in the known temperature range (as determined by vapour pressure measurements) so that the Curie-Weiss law is determined accurately. A plot of the reciprocal of galvanometer deflection per unit of current in the primary of the measuring coils against $(T - \Theta)$ determines a straight line whose extrapolation to low temperatures is boldly carried out. (Θ is a constant dependent on the characteristics of the substance under consideration). A new temperature (T^*), called the magnetic temperature is defined as:

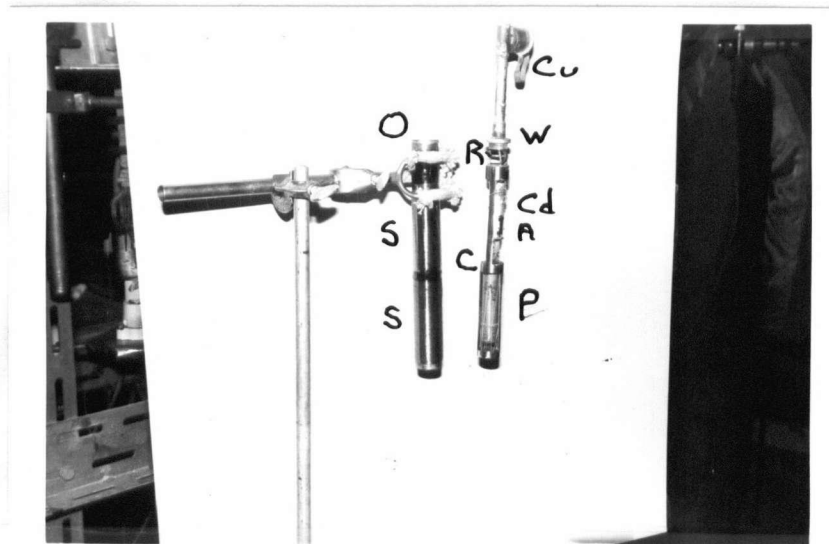
$$T^* = \frac{\text{Curie's constant}}{\text{susceptibility}} = \frac{CH}{M}$$

In the region where Curie's law holds, T is the real Kelvin temperature whereas in the region around absolute zero, T is expected to differ from T absolute. In order to determine T from T^* , one may use the relation

$$T = \frac{\Delta Q}{\Delta S} = \frac{\left(\frac{\partial Q}{\partial T^*} \right)_{H=0}}{\left(\frac{\partial S}{\partial T^*} \right)_{H=0}}$$

The plot of S vs T can be obtained from the initial conditions where a known magnetic field has changed S by a known amount.

Fig. 1



S - Secondary Coil
C - Cage
O - Outer Can
R - Radiation Trap
A - Aquadag Resistor

Cd - Cadmium Sample
P - Pill
Cu - Copper Braid
W - Wood's Metal Joint

SAMPLE SPACE AND OUTER CAN

CHAPTER II

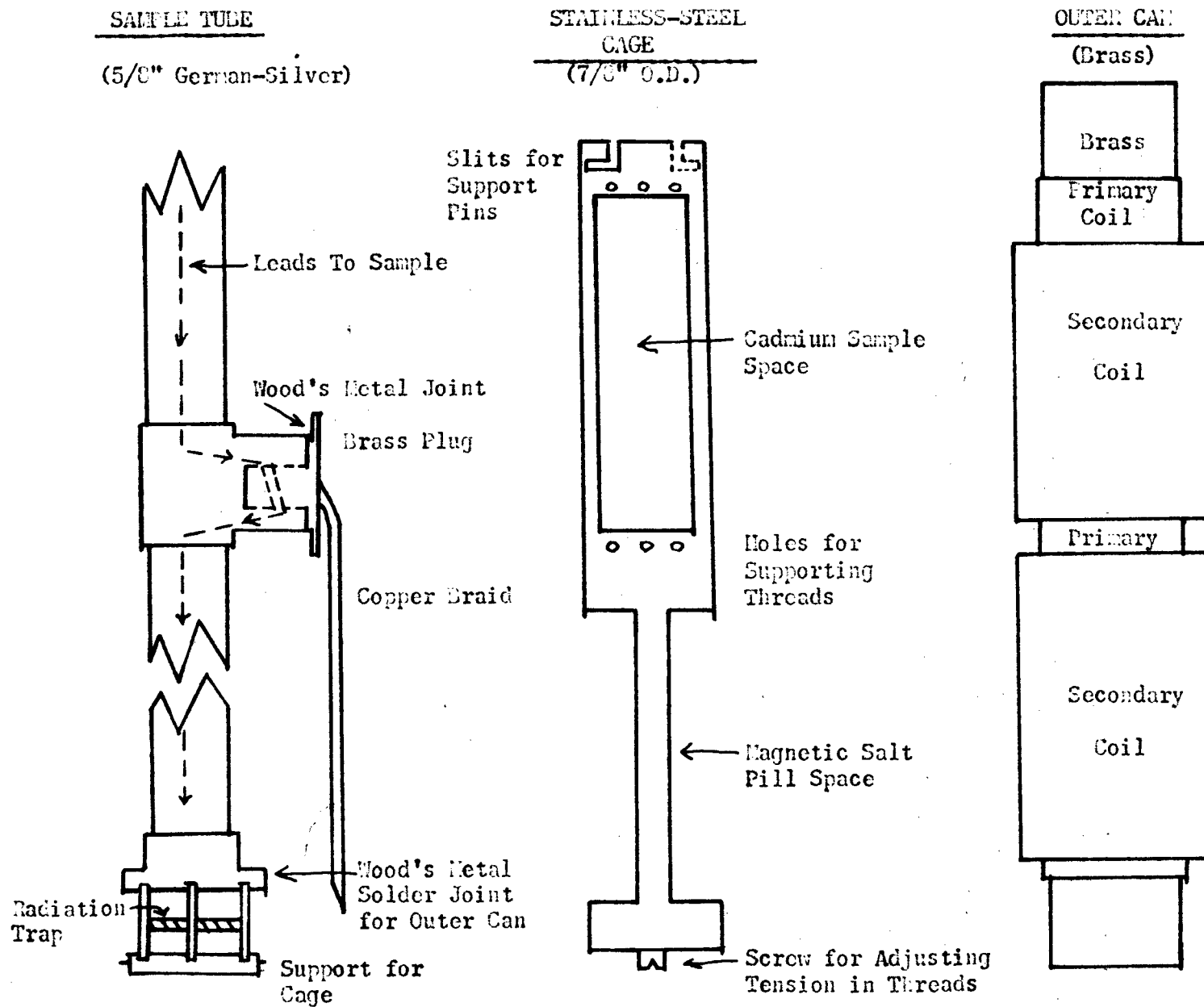
Design of Cryostat for Specific Heat Work

1. Cryostat and experimental space.

The cryostat is not unlike many that are used for demagnetisation work. Two glass dewars, an inner and an outer, are easily assembled concentrically about the experimental space. The dewars are silvered except for a small strip running the length of the dewars on both sides. This enables one to see the level of both the liquid nitrogen and liquid helium under experimental conditions. The dewar flasks also have long tails such that a large electromagnet can be rolled into position. The tails of the dewars, the inner one encumbering the paramagnetic salt pill, are exactly aligned between the poles of the magnet.

A stationary glass vacuum system with oil and mercury manometers and a Phillip's pressure gauge is an integral part of the cryostat. The low vacuum section is obtained by means of a backing pump. This offers a pressure of about 0.05 mm. of Hg to the mercury diffusion pump. A large backing volume, a 5 litre reservoir, was also in the backing system so that the rotary pump could be turned off when necessary. The diffusion pump can produce a pressure of about 10^{-6} mm. of Hg in the experimental space. This is necessary so that the exchange gas, in this case helium, can be removed during the demagnetisation process.

Fig. 2



(not drawn to scale)

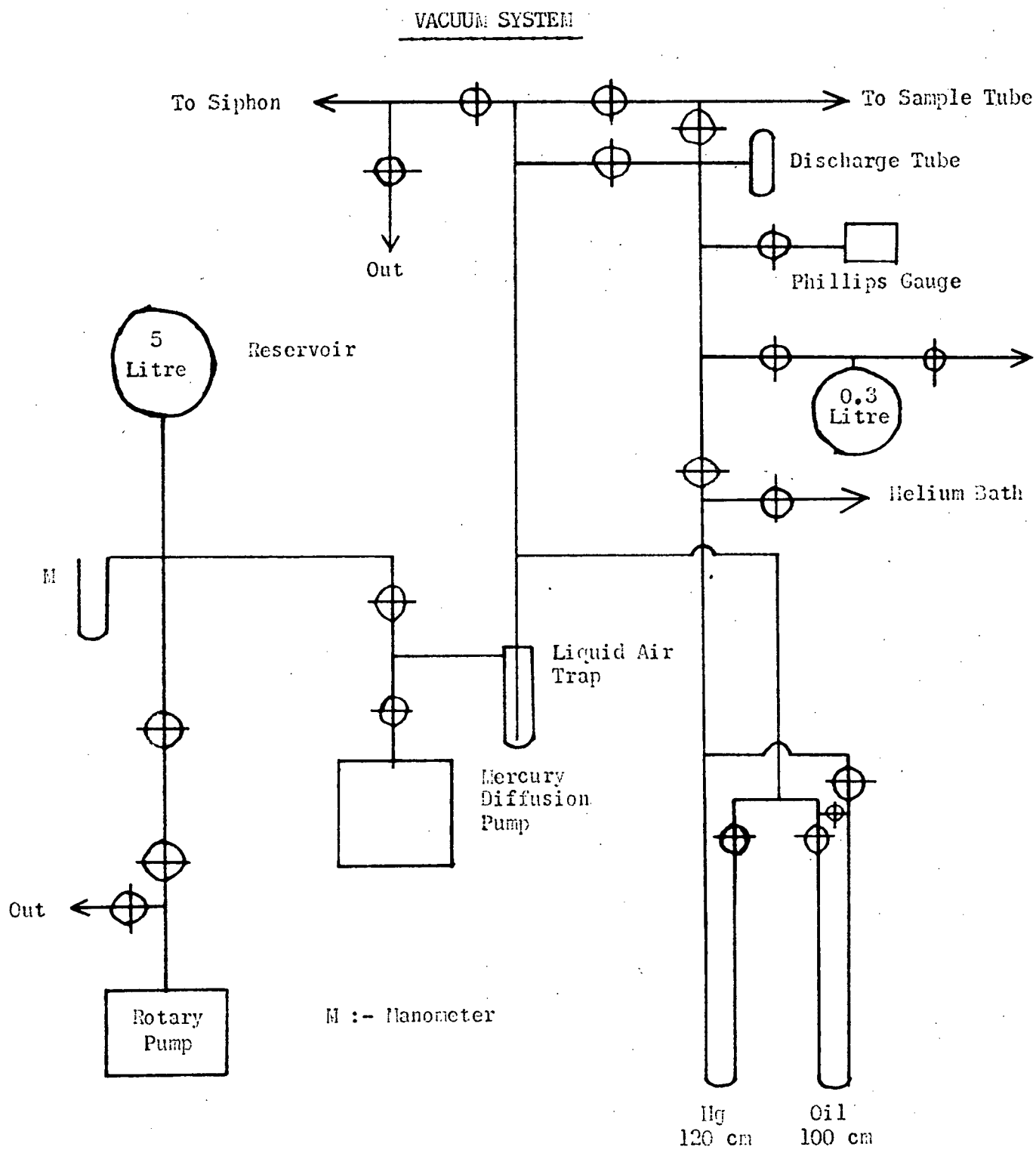


Fig. 3

A mercury and an oil monometer are provided in order to determine the temperature of the liquid helium using the vapor-pressure technique. By pumping on the helium one can lower the temperature from 4.2° K to about 1.3° K. This affords a good initial temperature with which to begin an adiabatic demagnetisation. A large capacity Kinney mechanical pump is used to pump on the helium bath.

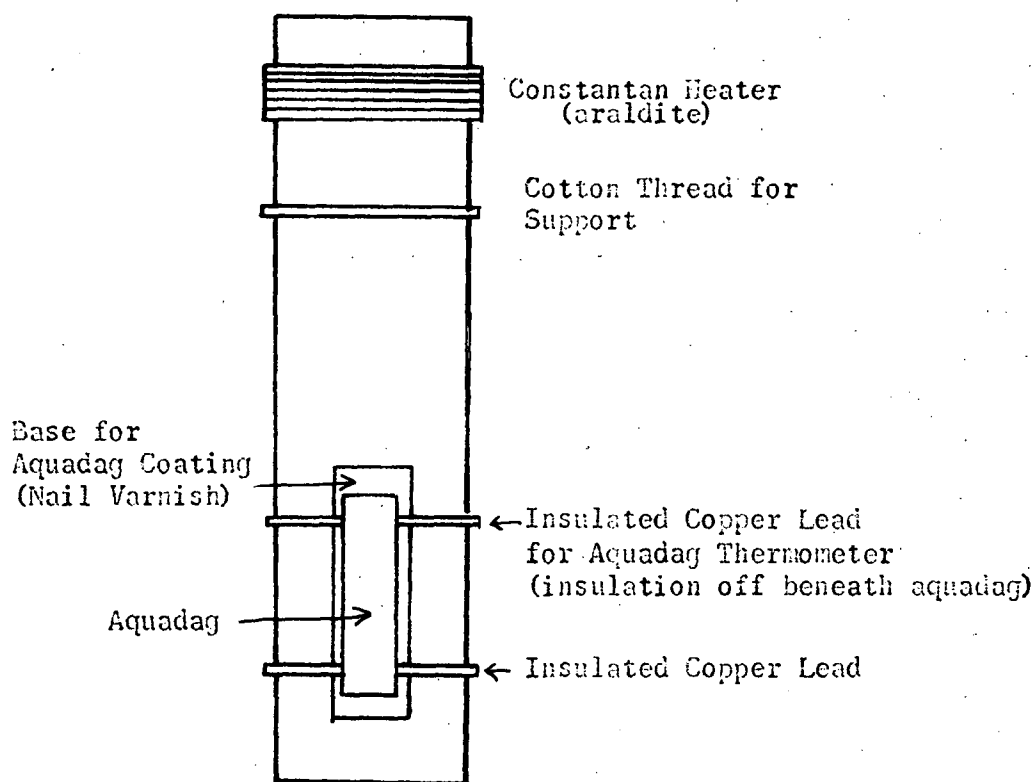
Also a susceptibility bridge is available to determine the temperature of the salt pill ballistically. Primary and secondary coils are wound on the can, containing the sample and salt.

The experimental space is the region which contains the cadmium sample and the paramagnetic salt. A long German-silver tube, connecting the high vacuum side of the mercury diffusion pump to the sample space, extends into the bath of liquid helium. A Wood's metal solder joint vacuum seals a brass can to the tube. Inside the can is a stainless steel cage which supports the cadmium and salt. Also, the leads are taken up the german-silver tube and out to the resistance bridge through a wax seal. The leads, #32 B.&S. constantan, are thermally anchored to the cage with Araldite.

The cadmium and salt are suspended in the cage by cotton fibres. Care must be taken that these substances do not touch the cage. To insure this the fibres were tightened by turning a screw at the base of the cage. This tends to keep the suspen-

CADMIUM SAMPLE

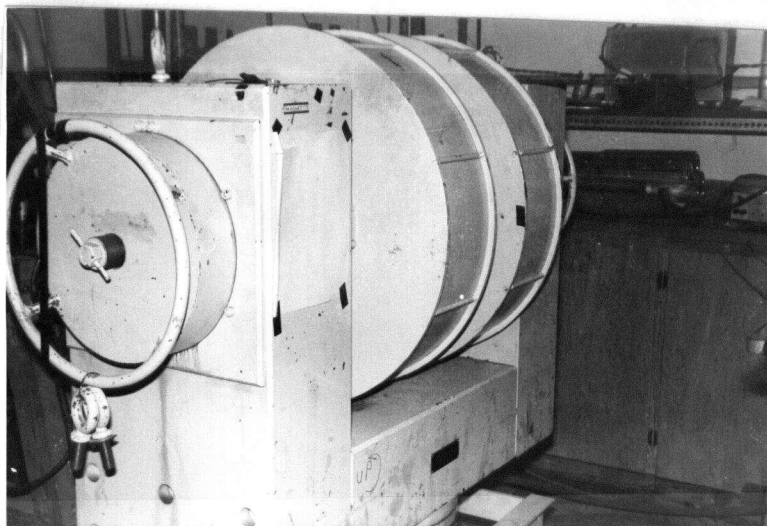
(mass - 55.508 grams)



(Scale: twice actual size)

Fig. 9

FIG. 5



MAGNET

sion centrally located.

An iron core, water-cooled electromagnet with adjustable gap and interchangeable pole pieces was used in this experiment. The magnet was operated at 160 volts and 200 amps. which provided a field of 21 kilogauss. The 2 ton magnet is easily rolled on tracks into position.

2. Preparation of Cadmium Sample

The sample of cadmium, five nines pure, was obtained from COMINCO through our metallurgy department. Its mass is 55.508 grams. The mass was determined before and after adding the heater, aquadag thermometer, and bonding agents so that estimates of the heat capacities of these substances could be given. This is important as it has been shown by Parkinson and Quarrington¹ that the heat capacity per gram of Araldite and Wood's metal are both far greater than that for copper between 2^o -20 K. Thus, even small amounts of these cements and solders used calorimetry contribute appreciably to its heat capacity and must not be neglected.

The heater is of #32 B.&S. constantan wire. Some ten turns were wound thoroughly about one end of the cylindrical cadmium sample, length 2" dia. 1/2", and glued with Araldite. Towards the other end, on the surface, two dabs of nail varnish were applied one about a centimeter above the other. Two turns of

1. Parkinson, D.H., Quarrington, J.E., Proc. Phys. Soc., A57, 569, 1954

insulated constantan wire were placed parallel to each other and running over the nail varnish. Each wire was bared a little over the nail varnish so that a thin strip of aquadag could be painted between them. Hence, the two turns of wire acted as leads with a carbon-suspension resistor between them. Finally a thin coat of varnish was painted over the aquadag to preserve it from flaking off.

The base of the cadmium was tinned with Wood's metal so that a small lead strip, a superconducting thermal valve, could easily be attached to the cadmium between it and the salt pill.

3. Preparation of a Paramagnetic Salt Pill

A very interesting and useful method of preparing a salt pill was suggested to the author by Dr. P. Matthews. The resulting thermal contact is nearly 10 times that of a compressed pill.

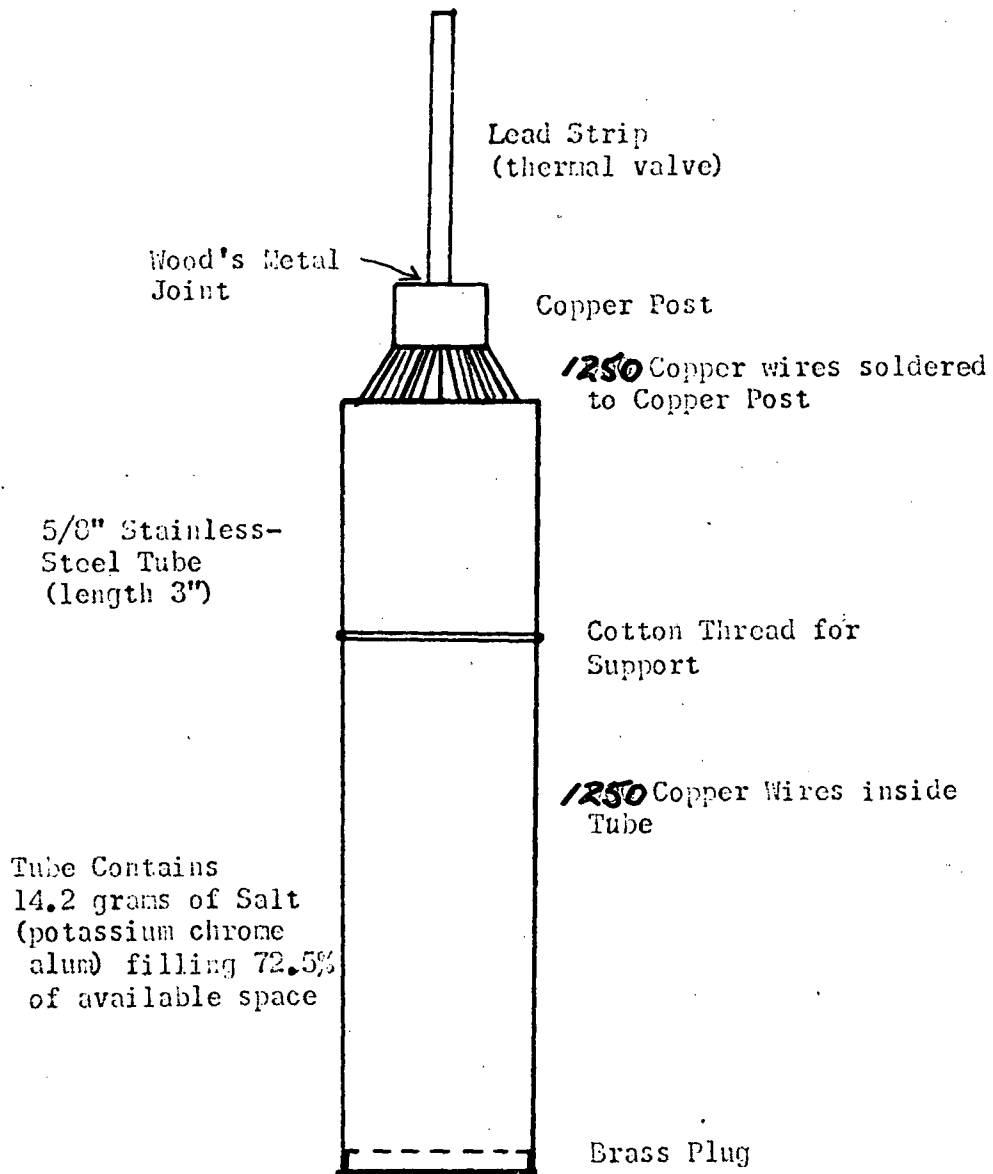
About 65 grams of chromium potassium alum was ground into a very fine powder. Two plate glass sections (18" x 6") had their surfaces roughened with steel wool. By placing small amounts of alum between these plates and passing the upper plate over the stationary lower plate, in a circular motion, produces a very fine powder indeed. The grain size very nearly resembles that of flour. About 80 grams of Apiezon oil is added to the powdered salt in a beaker and thoroughly stirred. A very fine suspension of salt

in oil is desired. A mixture, a thick liquid, of 5 grams of oil to 4 grams of salt is produced. This liquid is a slurry.

A stainless steel tube ($5/8$ " OD, length $21/2$ ") was chosen to be the pill container. Copper wires embedded in the salt are necessary for thermal contact. A desirable ratio of the area of copper wire to the area of the tube is of 5-10%. A ration of 7% was achieved by 1250 wires (#37 B.&S.). Actually 1250 turns of this copper wire was wound on a cylindrical mandrel (length 8" dia. $13/4$ "). The cylindrical solenoid of wire was then cut horizontally along the solenoid giving 1250 wires. As the ends were taped the wires could be rolled up tightly forming a cylinder of 1250 wires some 6 inches long. The ends were sheared to a convenient length and one end of the roll was put into a solid copper cap, crimped, and soldered in that position. This cap was later tinned with Woods metal and was the base for thermal contact to the salt.

The bundle of wire is then placed vertically inside the stainless-steel tube. One end of the tube is fitted with a plug containing a threaded hole and a glass filter. The hole is $8/32$ " dia. and the glass filter $5/16$ " dia.. The purpose of the threaded hole is to receive the syringe which is used to fill the tube

SALT PILL WITH LEAD STRIP



(not drawn to scale)

FIG. 6

with the slurry. The glass filter, a small circular one cut from a larger one, is designed to pass the oil from the slurry by pumping but to leave the salt particles behind.

The tube is now filled from the bottom up using a syringe. The slurry does not tend to flow easily and hence is forced in from the bottom in order to penetrate the mesh of wires. It also helps to tap the tube while filling. When full the syringe is removed and a threaded plug is inserted into the now vacant hole. Using a rotary pump one pumps on the tube, through the filter, and the oil is extracted and collected in a glass tube. While pumping the level of the slurry drops slightly indicating that as the oil is extracting and the particles of salt are being compressed onto the copper wires. A little slurry is now added to the open top each time the level drops. After $21\frac{1}{2}$ hours the level tends to remain stationary and coagulates. Pumping then ceases and the base plug is removed and is replaced by a similar one in size but it is a solid one. This plug is glued into place with Araldite. When removing the first plug one sees that heavy packing has taken place in the salt particles. This heavy packing about the copper vane of wires is responsible for the good thermal contact.

The mass of the extracted oil and unused slurry is then determined. This allows one to determine the mass and volume

of salt used with reference to the volume of free space available between the copper wires and stainless-steel tube. From this a figure for the packing fraction is found. About 14.2 grams of salt filled 72% of the available space and this is considered to be a good figure.

4. Determination of Temperature- A.C. Resistance Bridge

A 33 cps resistance thermometer bridge, suitable for precise temperature measurements in the liquid helium range, has been designed as a completely self-contained unit. The amplifier has a gain of 120 db, band width of 0.3 cps, and input impedance of 10k ohms. With a power dissipation of 2×10^{-8} watts in the thermometer, resistance changes of 0.1 ohm can be detected. For a typical resistance thermometer this corresponds to a temperature change of 4×10^{-6} K at 2°K . Other features include high rejection of line frequency pickup, short recovery time after saturation, and a combination gain band-width control which shortens the response time during preliminary operations. This circuit was designed by Blake, Chase and Maxwell¹ and the reader is referred to this paper for the circuit diagram.

Carbon resistance thermometers provide one of the most convenient and accurate methods of measuring small temperature changes at low temperatures.² The authors used a 1/2 watt

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1. Blake C, Chase C.E., Maxwell E., Rev. Sci. Instr., 29, 715 (1958)
 2. Clement J.R., Quinnell E.H., Rev. Sci. Instr., 23, 213 (1952)

carbon resistor of room-temperature resistance of 100 ohms. Near 2K the resistance is of the order of 15000 to 20000 ohms. The resistor has a temperature coefficient of about -3×10^4 ohms/deg. at this temperature. Such thermometers must be individually calibrated, during every run, but this disadvantage is offset by their high resolution and simplicity of operation. For greatest precision these thermometers must be operated in a suitable bridge circuit, and the power dissipation in them must be kept low.

The oscillator is of conventional design and its output is adjusted to 0.4 volts rms to provide a current of about 1 μ a in the thermometer. The linearity control adjusts the amount of feedback to minimize distortion of the output waveform. The components of the bridge are shielded from the oscillator and amplifier to minimize pickup and heating effects. The fixed arms of the bridge are wire-wound resistors of low-temperature coefficient. The decade resistor consists of six standard decade units which provides steps of 0.1 to 10k ohms, and is paralleled by a 250 μ f variable air capacitor which serves to balance capacity of the thermometer leads. The setting of this capacitor is independent of the resistive balance, and need be changed only if the capacitance in the

Improved Bridge for Low Temperature Measurements

W.L. BRISCOE

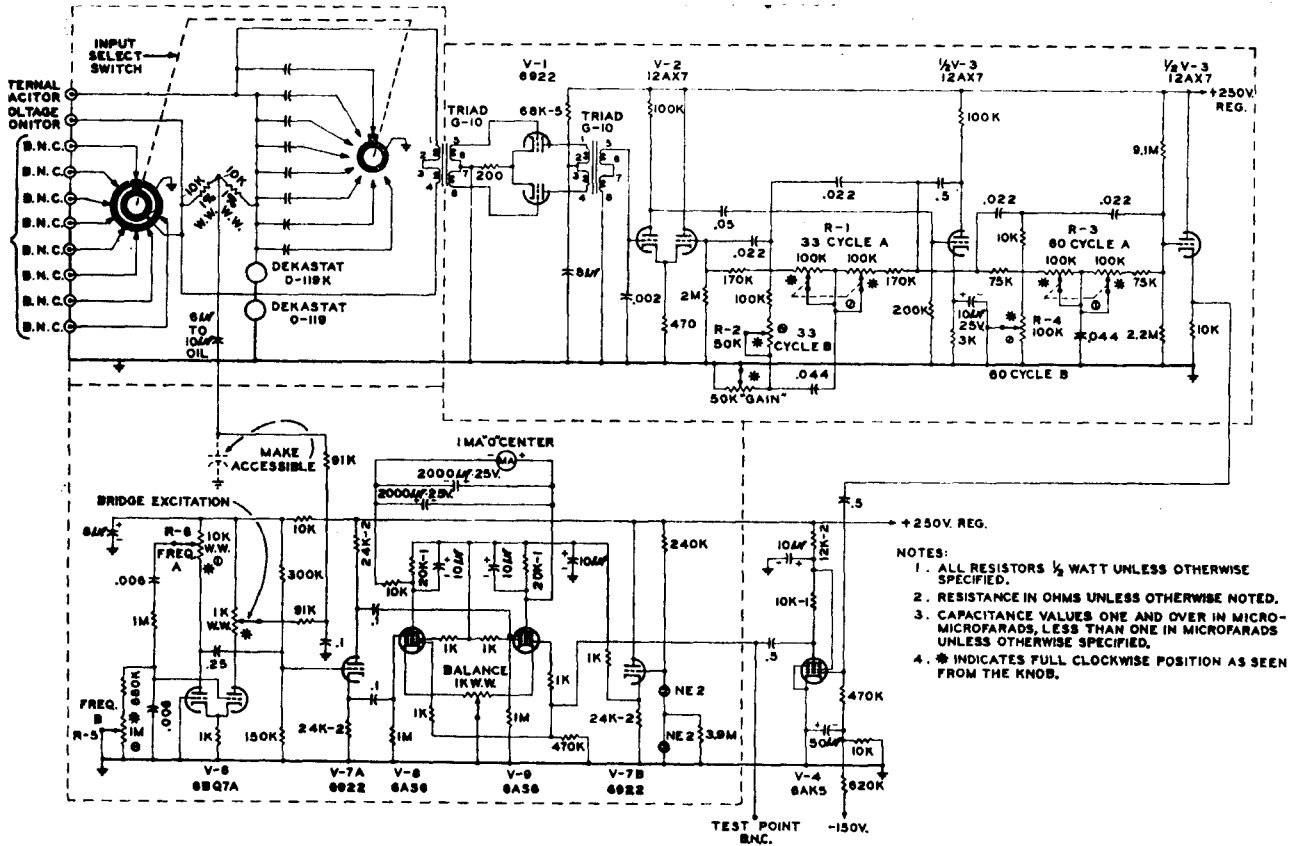


FIG. 1. Schematic circuit diagram of resistance thermometer.

(extension of Blake, Chase and Maxwell circuit to include
a means for self-indication of the bridge null)

FIG. 7

thermometer arm of the bridge changes. For a schematic diagram of this resistance bridge circuit the reader is to refer to the literature.

A very good modification of this circuit has been presented by W. L. Briscoe,¹ Improved Bridge for Low Temperature Measurements. Blake, Chase and Maxwell have met the basic requirement of sensitivity with a very small amount of bridge power; however, it has been found that its usefulness is limited by the need for peripheral equipment for null indication.. Hence, Briscoe presents a circuit as an extension of the Blake, Chase and Maxwell circuit to include a means for self-indication of the bridge null.

The basic difference is as follows; The output from the oscillator V-6, in addition to being fed to the bridge, is also fed to the inverter tube V-7A.. The original polarity and the inverted polarity are placed on the suppressor grids of the phase comparator tubes, V-8 and V-9, respectively. Type 6AS6 tubes are used for the phase comparator because of their relatively high suppressor sensitivity. A single stage of gain, V-4, amplifies the bridge output sufficiently to operate the control grids of V-8 and V-9 in parallel. For proper operation the circuit is adjusted so that the amplified bridge signal is in phase with the suppressor signal on V-9 on one side of the null and is in phase with the suppressor signal on V-8 on the other side of the null. With the plates of the comparator heavily

1. Briscoe W.L., Rev. Sci. Instr., 31,999(1960)

bypassed, they are essentially current sources, and it is current differences that are measured by the meter. The meter is also equipped with large electrolytic capacitors to integrate the noise that comes through the system. This integration is essential because an impulse at the input causes ringing or fluctuations of random phase. In regard to this noise, a user should not be alarmed if the noise as seen on a test bench seems excessive, because the noise appears to originate mostly in the temperature sampling resistor. When the temperature of this resistor is reduced to cryostatic values, very little noise remains.

The function of V-7B is simply to reduce the supply voltage to the proper value for the phase comparator. The portion of the circuit leading from the bridge excitation potentiometer to the bridge proper contains two filter sections that are used for adjusting the phase of the bridge signal as seen by the comparator.

The author of this thesis duplicated the bridge used by Briscoe and modified it slightly so that it could be adapted to temperatures below 1 K. The main modifications were three--fold; an aquadag resistor was used as the resistance thermometer in the bridge, an oscilloscope was always kept in the circuit at the point marked test-point balance, instead of detecting

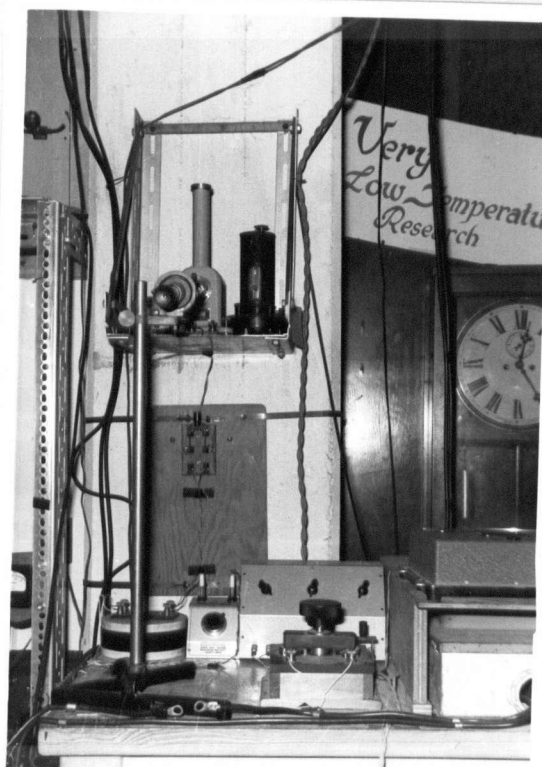
the null position with a meter a Honeywell recorder was used to monitor the output of the 6AS6's.

The preparation of the aquadag resistor has already been discussed. Its room temperature value is about 2500 ohms.

The oscilloscope is very useful in obtaining balance in the bridge before the recorder is switched on. Out of balance signal is very simple to detect at this point. Also, at a glance, the scope indicates quickly whether one is cooling or heating. This is very useful in the pre-cooling process and demagnetisation process as well as the actual heating process in the specific heat measurements.

Using a recorder to monitor the phase comparator output is very useful indeed. Rather than having a sharp null point indicating exact balance this section of the circuit was redesigned to give a linear output on each side of balance. This was achieved by cutting down the overall gain of the circuit and adjusting the impedance level at this point to match that of the Honeywell recorder. After obtaining balance, indication by oscilloscope, the recorder is started and traces any change in resistance of the thermometer. The recorder is reliable over the linear portion of the output of out of balance signal which was linear up to 500 ohms each side of the null position. Hence, the

FIG. 8



SUSCEPTIBILITY BRIDGE

heating curve is traced directly but care must be taken in determining the time lag of the stylus due to the time constant of the circuit so that the true heating curve can be arrived at.

4. Determination of Temperature- Susceptibility Bridge

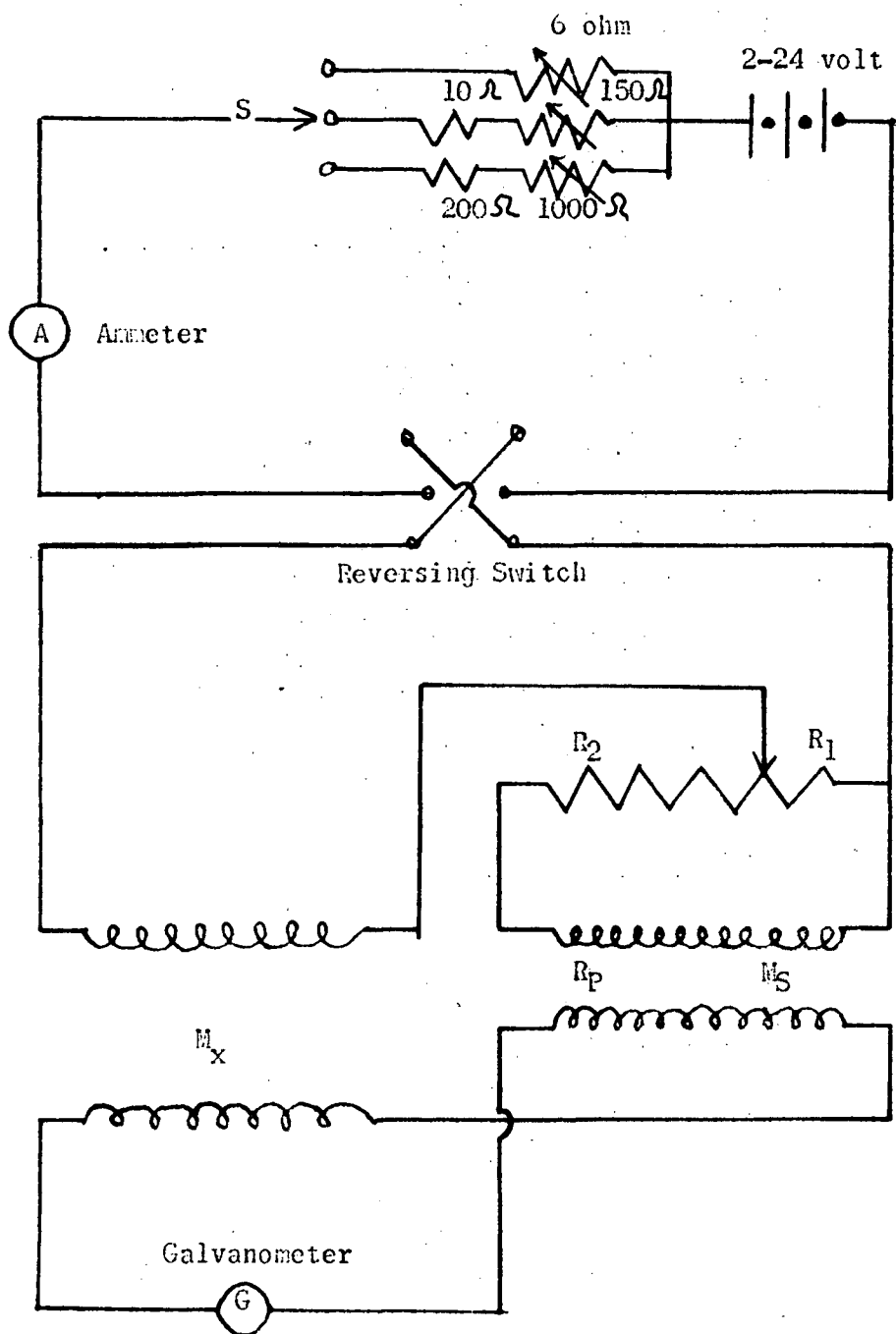
Many ballistic circuits for measuring the magnetic temperature and hence the absolute temperature of the chromium potassium alum are readily available in the literature. A very suitable one is that given by James Nicol.¹ This is a d.c. mutual inductance bridge. The mutual inductance coil around the paramagnetic sample is wound on the brass can in the experimental space. It consists of a primary and secondary coil. The primary is wound the length of the can. A secondary coil is usually wound over the primary with all the compensating inductance at room-temperature. A common practice in this laboratory is to wind the secondary as two coils of equal turns one in opposition to the other. S_1 is wound on the primary, in the same direction, near the bottom of the can. The paramagnetic sample is placed inside this coil. S_2 is wound in opposition about 1/2" above S_1 . This is the compensating inductance network. Now, only a small amount of compensating inductance need be in the circuit at room temperature.

The mutual inductor compensating coil is 40 mh in value.

1. Nicol J., Rev. Sci. Instr., 31, 211(1960)

SUSCEPTIBILITY BRIDGE

Fig. 9



This is much larger than necessary but balance is easily obtained. A heli-pot is used as a shunt in the primary of this coil with the center tap connected to the primary of the susceptibility coil. The secondary is in the galvanometer circuit and in series with the susceptibility secondary coils. The mutual inductance of the susceptibility coils with respect to the standard or compensating mutual inductance is given as

$$M_x = \frac{R_1}{R_1 R_2 R_p} \cdot M_s$$

This value is not necessary for the operation of the bridge as one need simply balance the circuit before demagnetisation.

The primary was wound with 932 turns of #37 B.&S. copper wire with polysol insulation. Room-temperature dc resistance was 125 ohms. The secondaries were wound with the same wire separated by a 1/2" gap. S_1 had 4500 turns and a dc resistance of 600 ohms (room-temperature), while S_2 had the same number of turns but wound in opposition. The brass can was first sprayed with a fast drying plastic film to prevent shorting through the thin insulation, which did tend to scrape off while winding with the lathe. Each layer of turns was also plastic coated.

CHAPTER III

Specific Heat of Cadmium

1. Apparatus - Procedures

The largest source of error in specific heat work lies in determining the heat generated in the heater coil to give the corresponding temperature rise. A known current i is passed through a constantan heater of 8.4 ohm resistance. In the liquid helium range R varies by about 0.1% per degree. However, a large resistor in the heating circuit allows the current to be kept constant. A high precision voltmeter (Hewlett-Packard) measures the voltage drop across the heater coil.

The heat generated in the constantan coil is $Q = i^2 R \frac{t}{J}$ where t is time and J is the Joule constant. As R has been measured with high precision during the heating intervals and as i is also accurately known the largest source of error in determining Q lies in the measurement of t . Hence, the precise heating interval must be known. This interval should not be less than 30 seconds and may be as long as 180 seconds. Precision switching and timing was greatly improved by adapting an electrical timer (Berkely) accurate to better than 1/10 seconds into the heater circuit. Hence, one switch controlled both heating and timing so that the timer records the exact time of the heating interval. Currents of 0.10 and 0.15 ma were used over intervals of 30 to 60 seconds and very little error was introduced in this way.

Thermometer Bridge - The a.c. resistance thermometer bridge

$\log_e R$ vrs $\log_e T$

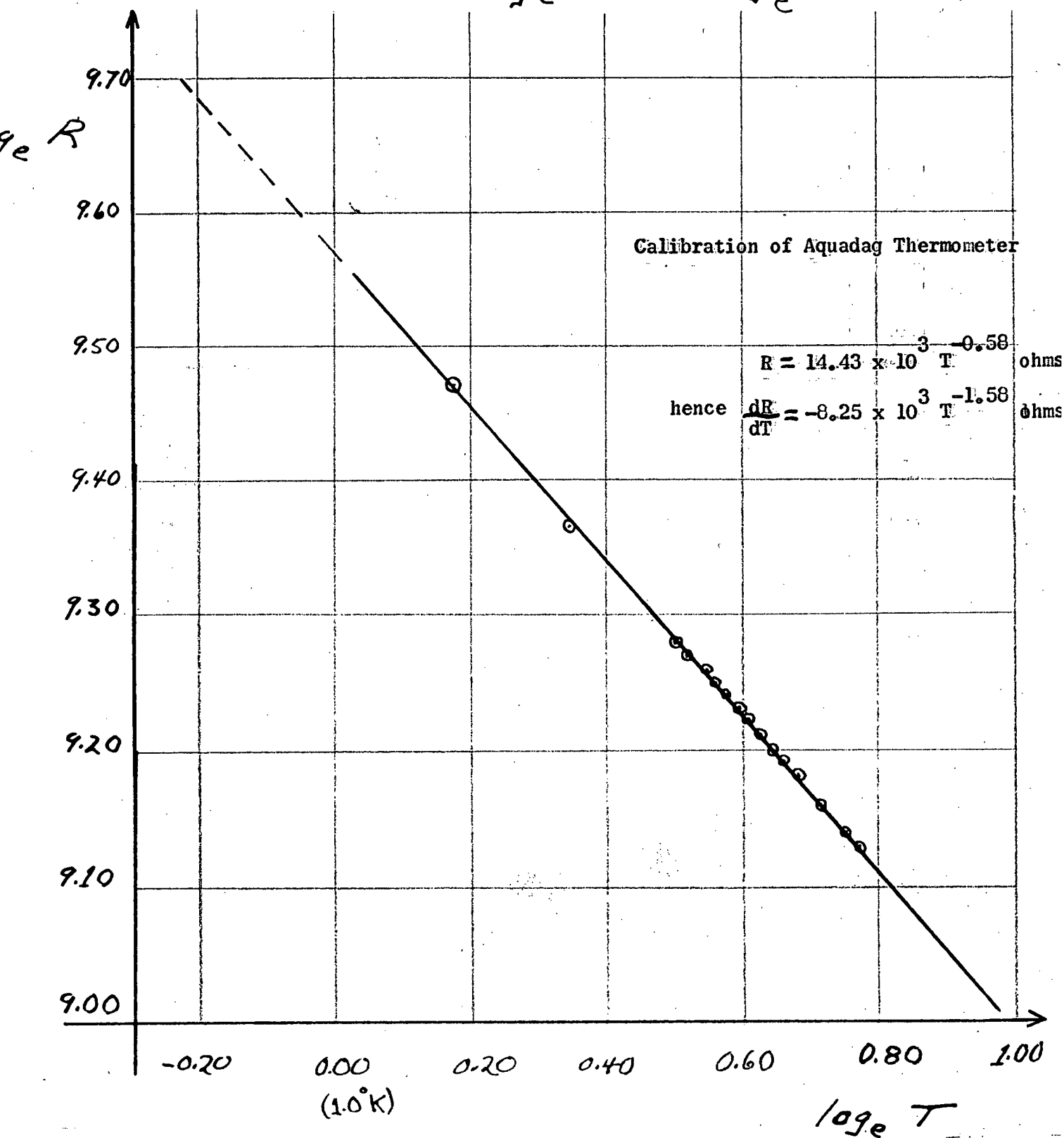


FIG. 10

performed well. During the pre-cooling stage one could readily detect any temperature change by observing the out of balance signal on the oscilloscope. The desired effect of adding exchange gas to the sample space and performing demagnetisations was readily seen in this way.

The Honeywell recorder, monitoring the out of balance signal, was only in the circuit when the bridge was very close to balance. A Gain control on the bridge allowed full scale deflection of the recorder for a resistance change of 1, 10, or 100 ohm steps on the decade resistance box.

Calibrating the aquadag resistor is a straight-forward procedure. Exchange gas was let into the sample space allowing the cadmium sample to achieve thermal equilibrium with the helium bath at about 4.2°K . The mercury and oil manometers were used to determine the temperature of the helium bath and hence the cadmium by vapour-pressure thermometry. The mercury or oil level could be held stationary at various points by adjusting the pumping speed. At these points with the recorder on a high sensitivity scale the resistance bridge was accurately balanced and the resistance setting on the decade boxes noted. In this manner various temperature and resistance readings were taken between 4.2 and 1.2°K .

After a demagnetisation to a lower temperature the bridge

was quickly balanced and the recorder put in the circuit.

Before any heat was put into the cadmium the recorder was calibrated with the decade resistance by putting the bridge out of balance by 1, 2, 5, or 10 ohm steps. This caused a step trace on the recorder. After adding a heat pulse at this temperature a corresponding temperature rise and hence a resistance change caused a deflection on the recorder. This deflection was then easily evaluated by comparing it with the known resistance steps previously recorded. This calibration was repeated often during each demagnetisation. The temperature rise was of the order of 50 millidegrees corresponding to a resistance change of 0.5 ohms in 20K ohms. The bridge and recorder unit worked very well.

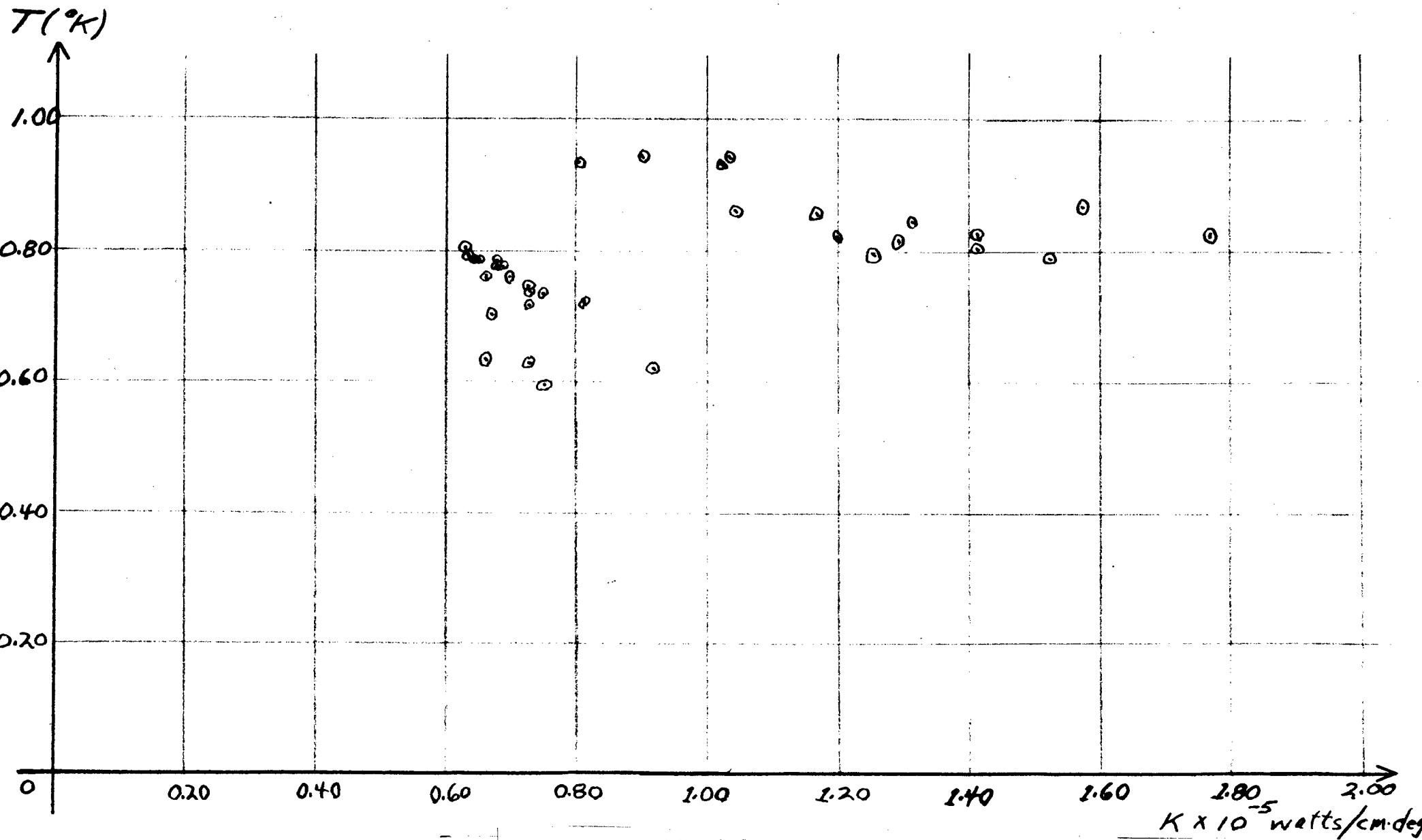
Susceptibility Bridge - Another method of determining the absolute temperature was attempted by use of a susceptibility bridge. The actual bridge set up was very good. All stray inductance was completely balanced out at room temperature and at liquid nitrogen temperature which indicated that the bridge would be successfully operable. With the bridge balanced at about 4.2°K one decreases the temperature through steps to 1.2°K as above using the vapour-pressure technique, and records increasing deflections on the galvanometer scale. However, this bridge did not yield a susceptibility curve.

2. Experimental Results-Conclusions

Specific Heat of Cadmium - The experimental conditions were good and throughout the experiment the apparatus performed well except for the recorder trace. Upon adding heat to the sample a temperature rise was observed on the recorder but when the heat pulse was terminated the recorder returned to its initial trace and hence indicated no net temperature change. Over six demagnetisations this recorder trace persisted for some thirty-six heat pulses. The initial deflection on the recorder certainly indicated a temperature rise of the proper magnitude but after the duration of the heating interval, 30 to 60 seconds, the trace returned to the initial temperature.

Due to the above results the specific heat of cadmium was not able to be found. Examination of these results indicates that the thermal contact between the cadmium and the salt pill via the lead strip was too good. The heat pulse did not warm up the sample but leaked away down the thermal valve, even though in the superconducting state, to the salt pill. The physical dimensions of the lead strip used (40mm x 5.0mm x 0.27mm) in conjunction with the equation of the thermal conductivity for lead in the superconducting state (Chapter I) clearly indicates that these results were to be expected. The cross-sectional area of the strip must be decreased some 500 times in order to achieve proper thermal contact between the

T vs K



Temperature vrs Thermal Conductivity
of Lead Strip

sample and the salt. This means producing very fine lead wire of the highest purity. Unfortunately this lead wire was not immediately available.

The data obtained should be a measure of the thermal conductivity of superconducting lead. Knowing the dimensions of the lead and assuming that all the heat travelled along it after a temperature rise was recorded on the recorder a measurement of the thermal conductivity was estimated. From the accompanying graph a well scattered pattern of points appear. The temperature range is from 0.6 to 1.0⁰ K. The cadmium is in the normal state while the lead is in the superconducting state. Unfortunately these points do not follow a curve and the order of magnitude, 10⁻⁵ watts/cm deg is not good. However, the purity of the lead and the heat leaks in the cryostat are very important.

Thermometer Bridge- The thermometer bridge with the Honeywell recorder was excellent. Changes of 0.1 ohms in 20K were easily detected. The aquadag thermometer was very good but had to be re-coated after every few runs and calibrated during each run. Calibration of this thermometer was good but before extrapolation below 1.2⁰ K a check of this thermometer vrs a susceptibility thermometer should be performed.

Susceptibility Bridge- This bridge met with difficulty for two reasons: a large pure conductor was in the compensating coil and, the secondary coils repeatedly became open circuits upon cooling to helium temperatures.

The bridge could be balanced at room temperature and at liquid nitrogen temperature but a net deflection of some 4 or 5 cm persisted at 4.2°K . This deflection of a simple kick was in either direction depending on the position of the reversing switch. However, upon cooling a double kick was observed. The first kick was as above and very quickly reversed itself and kicked very largely in the opposite direction. Upon cooling the initial throw remained the same but the second one became much larger. This was obviously the one to measure. This double kick phenomena is caused by the presence of a very pure and large conductor, the cadmium sample, which is concentricly located in the compensating secondary coil. Upon exciting the primary coil eddy currents are set up and die away in the cadmium which is detected by the secondary coil.

As the turns of copper wire were wound on the brass can a plastic spray was put on each layer. It is felt that after cooling and warming the plastic cracks causing open circuits in the coil. This particular wire is not good for coil winding. The problem was partially solved by separating the coils with paper. In fact, separating each layer with paper is better still.

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