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A study of some non-hydrated paramagnetic substances for cooling below $1^{o}K$.

by

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Abstract .

The desirable properties of the paramagnetic substances are discussed and the possibility of using some metallic alloys as well as dielectric crystals doped with proper substances capable of lowering the temperatures is illustrated . For this purpose some low temperature investigations of MgO:Mn and of Mg:Ce alloys is presented . The MgO:Mn doped with 0.0325 % Mn gives a final temperature of $0.04^{o}K$ when demagnetized from a field of 18 Kgauss and approximately $1.3^{o}K$. The specific heat measurements resulted in a value of $CT^2/R = 6 \times 10^{-3}$ for the "high temperature" tail of the specific heat .

The entropy determinations performed on the Mg:Ce alloy system on the other hand indicated that the magnetic entropy at about $1^{o}K$ is approximately of the same value as that of the conduction electrons . Therefore it seems that this particular alloy system is not suitable for appreciable lowering of the temperatures by adiabatic demagnetization .

The specific heat of a well behaved pure substance is proposed as a resonably sensitive thermometric standard . Its usefulness is illustrated by calibrating a secondary thermometer using the proposed method .

The difficulties encountered in low temperature calorimetry are described and our solution of them is given . A discussion is also included of the difficulties involved in using mechanical heat switches . A double mechanical heat switch is proposed and a design of it is included together with some illustrations of its usefulness .

Statement of originality.

In so far as the author is aware, the following parts of this work are original :

1., Calorimetric investigations of MgO:Mn .

2., Calorimetric study of Mg:Ce alloy system .

3., The use of the specific heat as a primary thermometer .

4., A systematic study of the difficulties encountered in using mechanical heat switches .

5., The double mechanical heat switch .

Acknowledgement .

I wish to express my sincere thanks to the entire Physics Deparment of this University , its academic and technical staff as well as its graduate students . I honestly feel that without the exciting atmosphere provided by this entire group this work would not have been possible . Due to the pleasent working atmosphere I derived great pleasure and personal satisfaction from the work presented in this thesis . For this I owe my deepest gratitude to all .

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Finally I am grateful to my ex-student colleague Mr.D.Walsh whose constructive influence on this work can not be overemphasized . I also thank him for his understanding encouragement during some of the very depressing stages of this work .

Foreword .

The work described in this thesis was begun at a time when there was some interest in this laboratory in the possibility of attaining low temperatures by adiabatic demagnetization of metallic alloys . A batch of Mg:Ce alloys was purchased and some preliminary demagnetization experiments were carried out on them . The cooling obtained however was disapointingly small . At best only a few hundredths of a degree Kelvin cooling was achieved .To find out the cause of the unsatisfactory cooling it was of interest to investigate in more detail the low temperature calorimetric properties of these alloys by measuring their heat capacities and thus determining the entropies available for adiabatic demagnetization at about $1^{o}K$.

It is also possible to dope dielectric crystals instead of metals with magnetic atoms .If the crystal selected has suitable thermal properties at low temperatures and the splitting of the energy levels of the doped atoms is favorable , a paramagnetic substance may be obtained suitable for attaining low temperatures with adiabatic demagnetization . In this case the loss of the heat conduction due to the absence of the conduction electrons may be more than compensated by the low magnetic ordering temperature and the relatively higher magnetic entropy available at low temperatures .

In line with these ideas a search for suitable dielectric crystals and doping materials was initiated by Walsh (1964) in

this laboratory . After considering several possibilities $MgO:Mn^{2+}$ was selected and the splitting of the energy levels of Mn^{2+} was studied using electron paramagnetic resonance , on a more concentrated specimen than that previously investigated by Low (1957) . The conclusions arrived at by Walsh (1964) were very favorable concerning the low temperature thermal and magnetic properties of this substance . It was therefore of interest to verify his conclusions experimentally and compare the experimentally observed behaviour of this class of paramagnetic substance with that of the metallic alloys represented by the system of Mg:Ce .

A calorimeter was therefore designed,then built . The first trial experiments indicated that the experimental problems normally encountered in low temperature calorimetry had not been eliminated . Since no one working in this laboratory had much experience in this field the choice had to be made between the following two alternatives . The detailed specifications of a low temperature calorimeter could be obtained from some research worker in this field or alternatively a general investigation of the difficulties involved in developing a reliable calorimeter could be made . The succesful completion of this work would open up the possibility of forming a low temperature calorimetric branch in this department . In this case the understanding of the technical problems of the field would be at least as important as the experimental results obtained . The second alternative was selected and a systematic study was begun of

all the possible heat leak phenomena into a specimen suspended in a calorimeter .

The first part of the opening chapter of this thesis gives a detailed description of the calorimeter together with the solutions adopted for the existing difficulties . A general discussion is also given of the problems encountered in using mechanical heat switches . After analysing the physical behaviour of the single mechanical heat switch , the idea of the double mechanical heat switch is proposed then its design described and its performance discussed .

The chapter is concluded with a comparison of the performance of this calorimeter apparatus with the performance of similar calorimeters in other laboratories . The comparison was made using the specific heat obtained for a pure Cu specimen .

The details of a series of experiments performed on $MgO:Mn^{2+}$ below $1^{o}K$ and a discussion of the results are presented in chapter two .

Chapter three describes further measurements with the calorimeter on the Mg:Ce alloy system and also on pure Mg . Details of the experimental results obtained are given .

In chapter four after giving a brief description of two of the conventional determination of the absolute temperatures below $1^{o}K$, the specific heat of a pure non magnetic substance is suggested as a primary thermometer for the purpose of calibrating secondary thermometers .

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CHAPTER I

Introduction .

The specific heat is defined dy

$$\lim_{T\to 0} C_v = \frac{\Delta Q}{\Delta T} \quad \text{at} \quad V = \text{const.} \quad \text{and} \quad \lim_{T\to 0} C_p = \frac{\Delta Q}{\Delta T} \quad \text{at} \quad P = \text{const.}$$

where C_v and C_p are the specific heats at constant volume and pressure respectively , ΔQ the heat supplied to the substance and ΔT the resulting temperature increase . At low temperatures $C_p = C_v$ within the accuracy of the measurements .

The calorimeter used for the determination of the specific heat is made up of a chamber that can be evacuated , placed inside a dewar vessel containing the cooling liquid . In this chamber the specimen is placed in a holder suspended or fastened by poor heat conducting supports . Also on the specimen or the holder , there is a heater and a thermometer .

Ideally the specimen should be perfectly isolated from its surroundings . In practice this condition is never achieved .

Assume that there is a temperature difference between the walls of the chamber and the specimen . The specimen can lose or gain heat by the following processes :

1. Thermal radiation .
2. Conduction through the gases present in the chamber .
3. Heat gained by vibrations .
4. Conduction through the supports .
5. In the case of metallic specimen any varying magnetic

field induces Eddy currents which produce some heating of the specimen .

These are the major sources of the thermal exchange , which have to be considered , and then minimized in order that the specimen should get heat energy only from its heater , at our will .

The other important function of the calorimeter is to bring the specimen to the desired temperature range . Hence the calorimeter must include a thermal switch between the specimen and the chamber walls . Its closed position corresponds to a large thermal exchange between the specimen and the surroundings and its open position in the case of a well designed calorimeter corresponds to little or no heat exchange between them .

Various schemes have been used to provide this thermal switch ;

Exchange gas : some gas that can be introduced and removed at will from the chamber .

Mechanical switch : mechanical contact introduced between the specimen and the chamber by remote action from outside .

Superconducting switch : a superconductor linking the chamber and the specimen is made normal or superconducting with an accompanying large change in its heat conductivity .

The choice of the proper switch depends on many considerations . In the next section we shall examine critically some design requirements for a good Nernst calorimeter and a proper thermal switching arrangement for the proposed measurements

described in this thesis . Following that we shall describe the actual calorimeter used , the circuitry , and the heat switch . Then we shall give details of the procedure applied to the various measurements reported and finally discuss their precision .

Design considerations .

Let us consider in turn the five heat transport processes mentioned in the previous section from the point of view of the design of our calorimeter .

I-1 Radiation .

The upper section of the pumping line is at room temperature and thus it represents a very hot source with respect to the specimen in the chamber at low temperatures . A simple numerical example will illustrate its importance . Let one mole of copper be at $2^{o}K$ in the chamber and let the pumping line be of 3/8" diameter . The heat capacity of the specimen is :

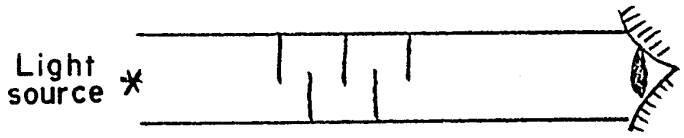
$$C = \gamma T + \beta T^3 = 0.7 \times 2 + 2 \times 10^3 \left(\frac{2}{340}\right)^3 \approx 1.8 \text{ mJ/}^{\circ}K$$

The energy per sec.channelled down by the pumping line into the chamber is : $\dot{Q} = \varepsilon \sigma T^4 = 0.1 \times 5.7 \times 10^{-12} \times 3^4 \times 10^8 \approx 2 \times 10^4$ ergs/sec cm^2

where $\dot{Q}$ is the rate of radiative heating in ergs/sec.cm^2, ε is the emissivity of the surface, σ the Stefan's constant , and T is the absolute temperature . This quantity is orders of magnitude higher than the heat leak of less than a few ergs/sec. tolerable in low temperature calorimetry . For instance , compare this heat leak with the heat capacity of the copper specimen .

To prevent this thermal radiation from reaching the specimen one needs to stop and dissipate it before it enters the calorimeter chamber . A simple and quite effective radiation trap is illustrated in fig. 1. A few (five is sufficient) plates covering more than half the cross section of the pumping line are soldered into slots made in the tube alternatively on one side and the other, properly spaced , matching the cross sectional area of the pumping line . Care must be taken to insure the good thermal contact with the bath and to use a good heat conducting material (copper for example) .

After the introduction of the radiation trap into the pumping line one can test its effectiveness by placing a light source at the end of the pumping line . If no light can be seen when the pipe is pressed against one's eye , the radiation trap will do its job . This is also illustrated by fig. 1.



Radiation trap

Fig. 1.

I-2 Gas conduction.

The problem of the heat leak through the He gas present in the calorimeter is just as severe in low temperature calorimetry as that of the radiation . The heat leak due to the different gases has been measured by Probert and Thomas (1964) and their results are reproduced in fig.2. The extrapolation for He gas indicates that in the case of a specimen of cylindrical shape having 2" height and 1" diameter , a few times 10^{-9} mmHg pressure would result in 1 erg/sec heat leak for one degree Kelvin temperature difference between the specimen and the chamber walls . This shows the necessity of having as good a vacuum as one can possibly get in order to minimize the heat leaks to the calorimeter . Two ways of achieving sufficiently low vacuum are considered :

A., Pumping for several hours at He temperatures with a high speed diffusion pump capable of low ultimate pressure until the necessary pressure is reached . The achievement and

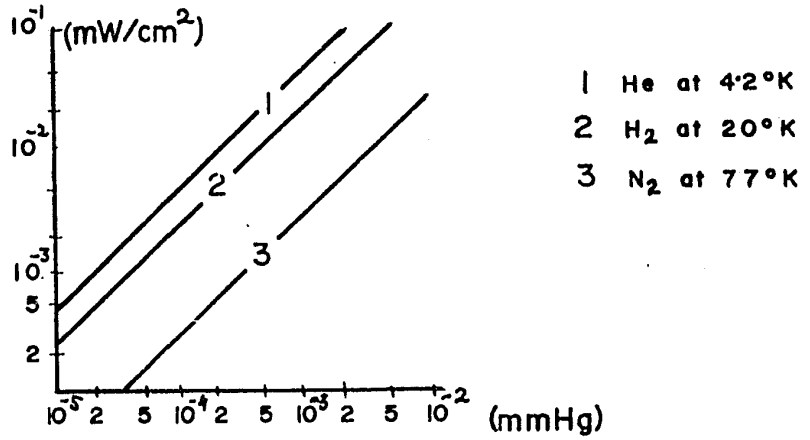


Fig. 2 . Heat conduction/cm^2 of various gases as a function of temperature for $\Delta T = 0.1^{\circ}K$ (Proberts and Thomas 1964)

measurement of high vacuum at these temperatures has been investigated by Garfunkel and Wexler (1954) . Their result on the time of pumping vs. pressure using a diffusion pump having pumping speed of 20 l/sec. connected to a calorimeter having a volume of 50 cm^3 is reproduced in fig. 3.

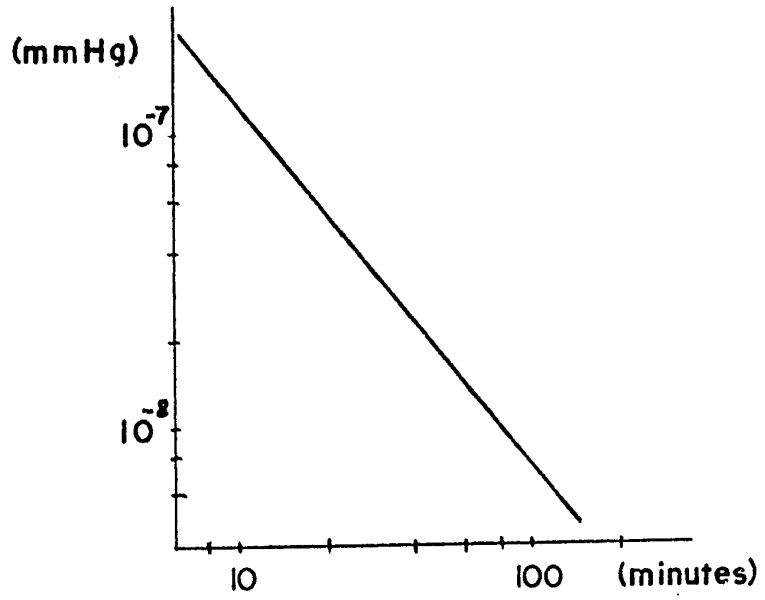


Fig. 3. Pressure in the calorimeter after the initiation of the pumping of the He exchange gas .(Garfunkel and Wexler 1954)

In order to optimise the pumping speed of a given diffusion pump one has to have minimum pumping resistance . In practice this means the following :

a., As few restrictions , elbows and valves in the high vacuum side of the pumping line, as possible.

b., The pumping distance from the pump to the vacuum chamber should be as short as possible .

c., The diameter of the pumping line should be as

large as possible matching the diffusion pump inlet. Due to the presence of the He gas there will be an unsaturated He film formed below the λ-point , covering everything within the chamber . This film moves toward the warmer parts of the system*, and thus in case of a temperature difference between the chamber walls and the specimen there will be a steady heat leak on the supports . Below about .4°K this effect and also the direct heat leak through the gas will give negligible contribution to the total heat leak experienced by the specimen due to the fact that the vapour pressure together with the heat conductivity becomes negligibly small . In the case of adiabatic demagnetization below one degree Kelvin this is a very helpful property as long as one does not want to raise the temperature of the specimen or of the salt to much beyond .4°K . If on the other hand one wants to perform heat capacity measurements to higher T than this , then the following situation will arise :

After the adiabatic demagnetization the surface of the cold specimen acts as a getter for the gases present , cryopumping the chamber to a very high vacuum . However during the measurement from .4°K up, the vapour pressure becomes appreciable and the specimen being warmed by the heater gradually begins to "bake out" the gases from its surface, thus reducing the vacuum in the chamber, resulting in a steadily increasing heat leak . The result of this is that the specimen warms up to the bath temperature in a few minutes i.e. the heat leak appears to be uncontrollable . This effect will be very pronoun-

* if the vacuum is not too high and the temperature not too low

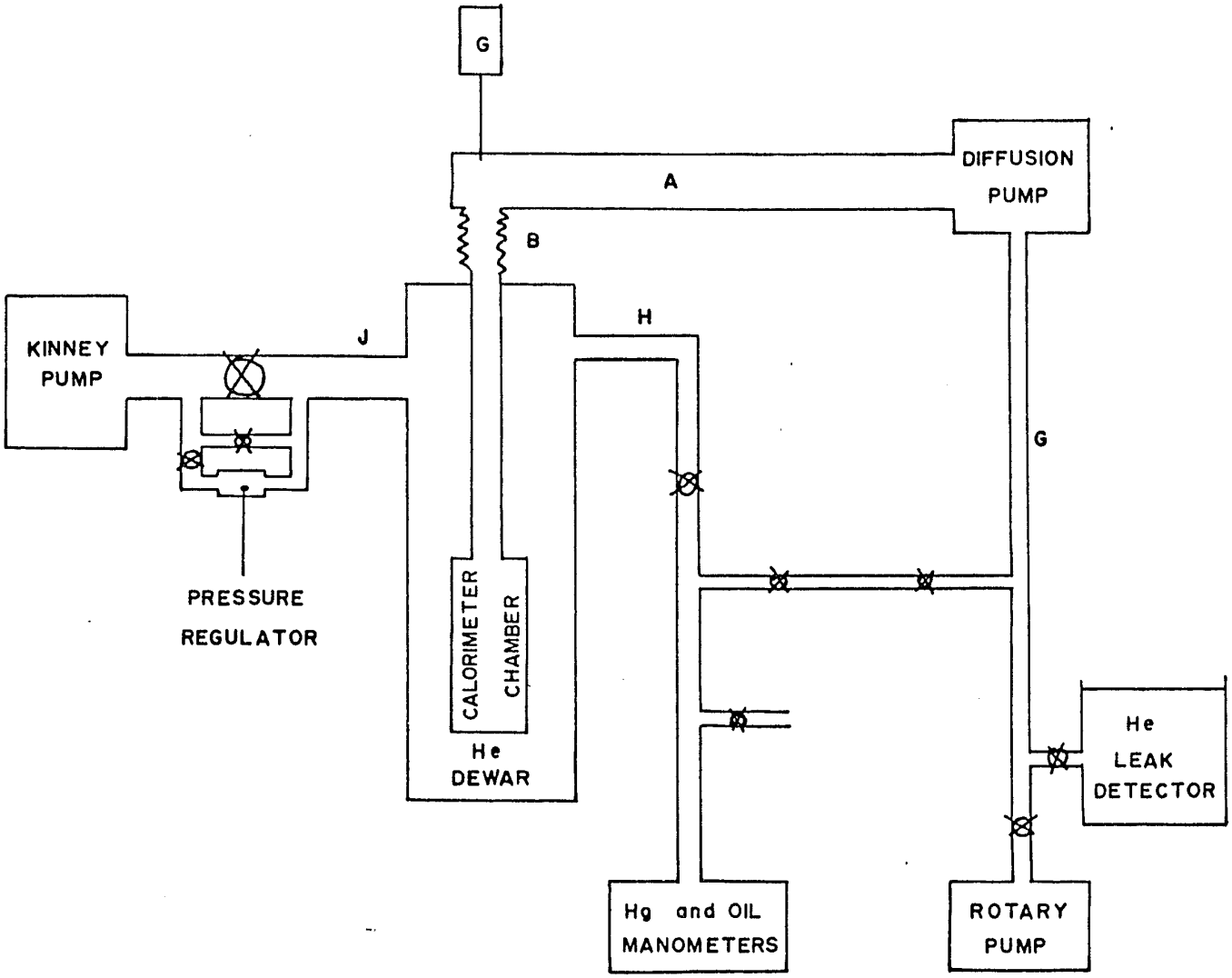
ced unless the pumping speed is very high .

B., The other way of achieving a satisfactory high vacuum is to prevent the He gas from ever entering the vacuum chamber . If the cooling of the specimen is done by other means then there is no need for letting He enter the chamber at all . In this case even moderately efficient pumping system can provide a very good vacuum since all the substances with the exception of He have negligibly small vapour pressures at liquid He temperatures .

Our pumping system connected to the calorimeter chamber is shown in fig. 4. In designing it the requirements for the maximum pumping speed described on page 6 were followed as closely as possible . The water cooled oil diffusion pump made by Balzer Co. has a pumping speed of 20 l/sec. with a pumping inlet diameter of 3.25" . This is matched with a 20" long and 3.25" diameter pumping line A . A Phillips gauge G used as a vacuum indicator was inserted in this line . The pumping line A was connected through a 1.5" long and 1.5" diameter flexible stainless steel vacuum coupling B to the 1/2" diameter stainless steel pumping line leading directly into the calorimeter chamber . Sections J,H, and G are also flexible vacuum couplings . Their purpose together with the 1.5" long flexible pipe will become clear when the problem of the vibrations will be discussed .

The diffusion pump was backed by a rotary pump .

The pumping system following the diffusion pump does



THE VACUUM SYSTEM

Fig. 4

not need to strictly satisfy the maximum pumping speed requirements . Its only purpose is to keep the pressure at the outlet of the diffusion pump at less than .5 mmHg .

A Veeco He leak detector was used in all the experiments as a vacuum gauge for the calorimeter chamber at liquid He temperatures . This is necessary because the pressure detected by the Phillips vacuum gauge is the sum of all the gases present in the room temperature section of the high vacuum pumping line . The actual pressure in the calorimeter chamber , however , will in general be orders of magnitude lower because, as mentioned before He is the only substance with non negligible vapour pressure at those temperatures . The He leak detector on the other hand will see only the He removed from the calorimeter chamber . Garfunkel (1954) has shown how to calculate the He pressure in the vacuum chamber from the rate of the amount of He detected knowing the pumping resistance between the diffusion pump and the calorimeter chamber (Garfunkel and Wexler(1954)).

All the necessary valves are installed in the low vacuum side of the system . They make the vacuum system quite versatile . To mention a few examples , exchange gas can be introduced either from outside or from the He dewar itself into the calorimeter chamber . Also the leak detector can be used to leak test either the calorimeter or the space of the He bath including the manometer section .

The pressure over the He bath could be reduced with the aid of 50 l/sec capacity rotary pump made by Kinney Co.

using a 2.5" diameter pumping line connecting the pump with the He dewar . The pressure can be kept constant at any value for $P > 1$ cm oil with the valves and a pressure regulator .

I-3 Conduction through the support .

For the evaluation of the heat leak resulting from the conduction along the suspension or support of the specimen one uses the well known equation of heat conduction :

$$Q = K(T)\, A \frac{\Delta T}{\Delta l}$$

Where $K(T)$ is the heat conductivity , A is the cross sectional area, Δl is the length of the suspension or support and ΔT is the temperature difference across the length of it .

Perhaps a few words should be mentioned at this point about our experiences with suspensions .

When using He exchange gas for cooling the specimen , in order to get a small heat leak through the suspension one follows the guidance of the equation of the heat conduction , i.e. one selects a poor heat conductor (say nylon or stainless steel) and makes the suspension as long as possible .

When the cooling of the specimen is done with a mechanical heat switch and hence no exchange gas , the equation of the heat conduction has new implications . It is true that after the specimen has been at low temperatures for sufficiently long time the above equation will control the heat leak in a clear manner . But before this condition is achieved the following phenomenon was observed :

On closing the heat switch the specimen would cool as expected . Once the equilibrium with the He bath was achieved and the heat switch was opened it was observed that the specimen would warm up gradually , asymptotically approaching a rather high temperature . This temperature in the case of a smaller specimen can be as high as several tens of degrees Kelvin . Closing the heat switch again to get back to $4.2^{o}K$ and then opening it, the same thing would happen with the only difference that the highest temperature reached will be lower than before . Eventually after a series of closing and opening of the heat switch the specimen will finally stay cold .

However we noticed that on shortening the length of the nylon thread used to suspend the specimen in the chamber the highest temperature reached after the first opening of the heat switch was lower and also the total time necessary for the complete cooling of the specimen was shorter .

This behaviour lead us to the following explanation :

When the heat switch is closed the specimen cools down to $4.2^{o}K$ together with the lower end of the suspending nylon thread holding the specimen . The middle region of the thread

however being a heat insulator stays warm , perhaps well over $100^{o}K$. On opening the heat switch this warm middle section heats the specimen slowly until after many cycles it too has cooled to the low temperature of the specimen .

This effect is unavoidable and can only be minimized by properly choosing the length and the diameter of the thread to optimize the heat leak after cooling the specimen and also to minimize the total time necessary for the complete cooling of the specimen .

When the exchange gas is present this effect is obviously not possible .

I-4 Vibration .

When the calorimeter is exposed to some mechanical vibrations , there will be some heat generated at the specimen and the specimen holder . The vibrational heating may be imagined as follows : A wire will warm by bending it back and forth or by hammering it . Similarly if an object is placed on a vibrating support it will experience warming by the hammering effect of its own weight . One could also say that the vibration excite a set of vibrational modes in the object i.e. raise its thermal energy .

The quantitative account of the vibrational heating is difficult and all sorts of conflicting experimental deductions can be found in the relevant scientific literature . To mention a few Cooke and Hull (1942) have investigated the problem of

the thermal isolation below 1°K . They obtained a heat leak of 1 erg/min. without having taken any care to avoid the vibrations of the specimen . Derby (1951) on the other hand mentioned a heat leak of about 300 ergs/min. on his specimen suspended by nylon threads due to the boiling of the oil in a small oil diffusion pump attached to the calorimeter . Malaker (1951) with a similarly suspended specimen reports a total of 3.6 ergs/min. heat leak with no mention of any vibrational disturbances . Wheatley et.al. (1956) made a systematic study of the problem of the vibrations by coupling mechanically a vibrator to their system whose frequency could be changed from 1 to 13 c/s . They found that the heating increases rapidly with increasing frequency , being about 10 ergs/min. with the vibrator off and about 235 ergs/min. at 13 c/s .

In spite of these conflicting reports it seems reasonable that in a well designed calorimeter assembly some attention should be given to prevent the specimen from excessive vibrations . The need for this is clearly illustrated by Manchester (1959) . He mentions that his low temperature measurements had to be performed on the quietest periods of the day when the street traffic and also the activities within the building were at their lowest level .

Let us consider the ways of eliminating most of the vibrational disturbances . One way is to mount the calorimeter on a pile reaching the bedrock , decoupled from the surrounding buildings and terrain . There may be circumstances where this is feasible . The other way which is perhaps more suitable

for smaller laboratories is to support or suspend the cryostat elastically from a rigid support clamped to the floor . Assume that the support of the cryostat vibrates in a vertical direction . The state of motion of the cryostat suspended on a spring can be described by the equation for forced harmonic oscillation:

$$m\ddot{X} + KX = F(t)$$

where m is the mass of the cryostat, K is the force constant of the spring, X is the displacement and F(t) is the exciting force.

with $F(t) = a_o \cos \omega t$

and $X = a \cos \omega t$

we get $$\frac{a}{a_o} = \left| \frac{1}{m(\omega^2 - \omega_o^2)} \right| \qquad \text{.....I-4-1}$$

where $\omega_o = \frac{k}{m}$ is the resonance frequency of the system . It is seen that at frequencies say $10\omega_o$, $\frac{a}{a_o} \doteq (1/100)(a/a_o)$ at $\omega = 0$, i.e. the amplitude is $1/100^{th}$ of the driving amplitude .

The resonance frequency of the system is ;

$$\omega_o = \sqrt{\frac{K}{m}} \qquad \text{but} \qquad K = \frac{W}{l}$$

where l is the extension of the spring caused by the weight W of the cryostat . So that

$$\omega_o = \sqrt{\frac{W}{lm}} = \sqrt{\frac{mg}{ml}} = \sqrt{\frac{g}{l}}$$

i.e. the resonance frequency is related simply to the extension. Using this relation the requirements can be evaluated in a straightforward simple manner . Let us calculate for example the extention necessary for getting a resonance frequency of 1c/s.

$$l = g/\omega_o^2 = 980/4\pi^2 \approx 25 \text{ cm}$$

i.e. the spring should be loaded such as to get about a foot extension .

This resonance frequency will be achieved with any spring as long as its elastic limit is not reached and the desired extension is obtained . However equation (I-4-1) shows that one must choose heavy loads i.e. springs with larger force constants .

The low resonance frequency of the system in itself is not sufficient for vibration free mounting of the calorimeter . It is also necessary that the system be damped .
Damping means dissipating the vibrational energy of a vibrating system . In the case of mechanical vibrations this can be done by friction . An example of it is illustrated in fig.5 A mass "A" oscillating on a spring rubs against the wall "B" . If the wall itself is in the state of small amplitude vibrations then in the case of large amplitude oscillations of "A" there will be some damping . For small amplitude oscillation of "A" however the friction at the vibrating wall will represent a force leading to the forced oscillations of "A" .

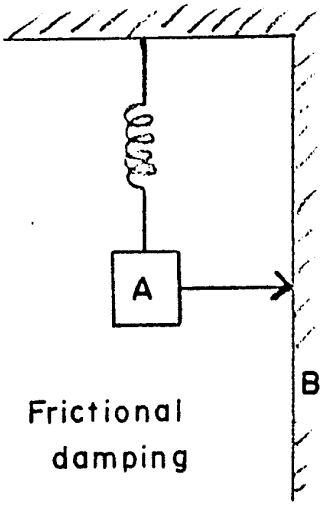
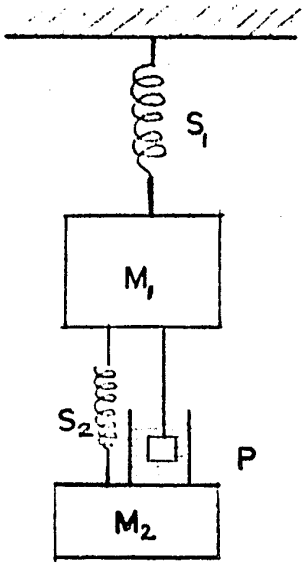


Fig. 5

A better way is to obtain the dissipation of the vibrational energy within the oscillating system itself . Fig. 6 illustrates how this can be done .
An auxiliary mass M_2 hangs on spring S_2



Viscous damping

Fig . 6

attached to the main mass M_1 which also hangs on a spring S_1 . There is a vessel on M_2 filled with viscous liquid . A plunger P attached to the main mass M_1 is immersed in the liquid . In the case of relative movement of M_1 with respect to M_2 the viscous force experienced by the plunger will dissipate the vibrational energy within the vibrating system . To achieve critical damping the proper choice of the force constant of the springs , the ratio of M_1/M_2 , the viscosity of the liquid , the optimal size of the plunger relative to the size and shape of the vessel is discussed by Haringx(1947) .

A different way of damping may be achieved by replacing the viscous unit by an other within which the vibrational energy would be dissipated by Eddy heating . A piece of metal may be held in a strong magnetic field produced either by a permanent or an electromagnet . The magnet should be attached to M_1 and the metal to M_2 . This way a rather powerful damping may be achieved . In this work however the viscous liquid damping was used .

Using the principles outlined in this section a cryostat support with much smaller vibrational level than the surroundings was made in the following way :

Six extension springs wound of piano wire having a force constant of about 3 lb./cm were suspended from two steel bars

mounted on concrete pillars . A 1/2" thick brass plate of 1.5' wide and 2' long was held by the spings and was loaded with several lead bricks to produce an extension of the springs of about 10 cms. This loaded brass plate corresponds to the main mass . An auxiliary mass in the form of a similar brass plate was attached to the main mass by four weaker springs having an extension about 8 cms .

Four rectangular damping pans made of 1/32" Cu sheet having a height of 8" and a base of 4" by 4" were mounted on the auxiliary mass . The four corresponding plungers made of similar Cu sheet having a height of 8" and a base of 3" by 3" were attached to the main mass . With the plungers put in place inside the damping pans #10 machine oil was introduced into the damping system , to provide the necessary viscous damping .

The calorimeter chamber was then mounted on the main mass together with the diffusion pump which was connected to the rotary pump with flexible tygon tubes to decouple the vibrations of the mechanical pump from the calorimeter chamber mounting . The cooling water for the diffusion pump was also carried with flexible tygon tubes . The vibrations of this system were projected with the aid of a mirror attached to the calorimeter chamber . A light source was held by a vibration free mounting at a distance of about 10' from the calorimeter chamber .

Vibrations were generated with an electric hand drill clamped to the steel bars from which the entire cryostat was hanging . A violent shaking of the steel bars could be produ-

ced by loading the drill chuck off center with a heavy object . These vibrations were also displayed on the screen with a mirror and light source arrangement similar to that of the calorimeter chamber . Thus both vibrations i.e. the vibrations of the chamber and the vibrations of its surroundings could be observed at the same time one beside the other .

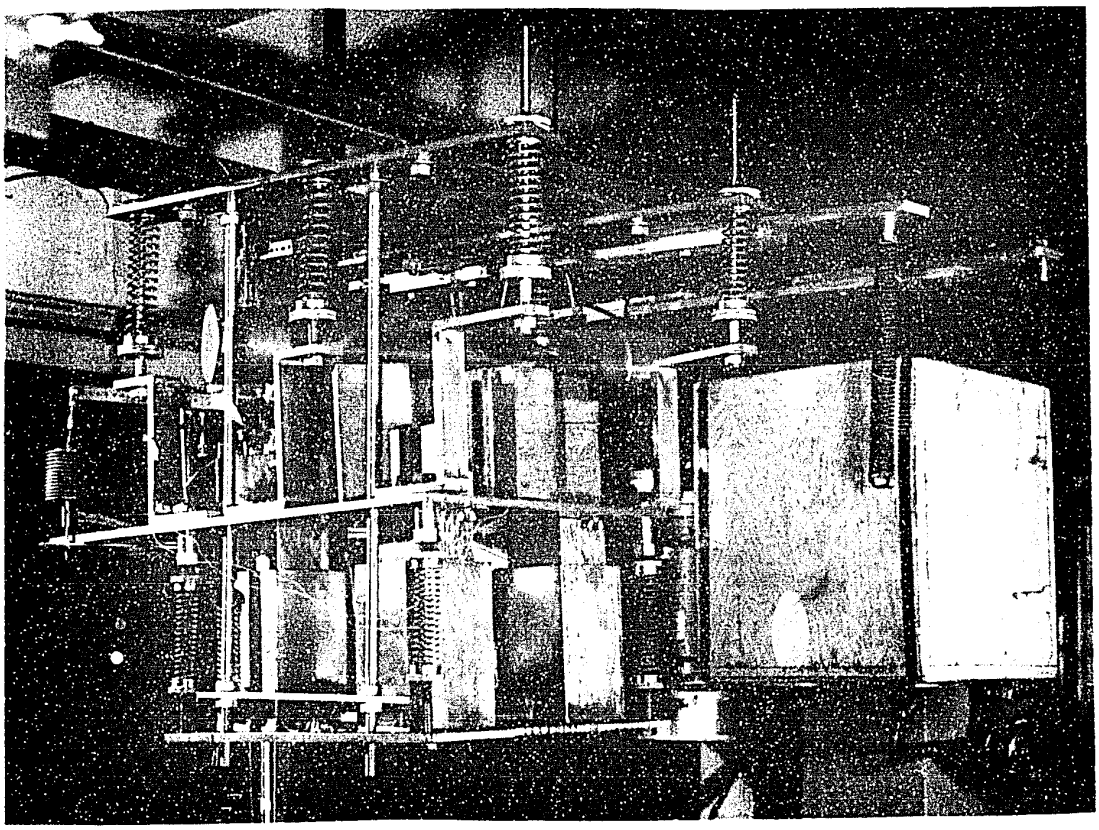
First with the pumps switched off the necessary adjustments were made for the damping oil height and the extension of the main springs so as to get optimal conditions . After optimizing the system , the vibrations of the calorimeter chamber were only a few mm in amplitude while the vibrations of the steel bars coresponded to several cm deflections of the light spot on the screen . Also , the damping was good enough because on stopping the drill , the vibrations stopped in a few cycles .

The effect of the vibrations of the pumping system was tried . As soon as the diffusion pump went on however the boiling of its oil (about 100 cm^3) set the calorimeter chamber in vigorous oscillations . It was therefore decided to build a separate vibration free mounting for the diffusion pump and couple the pump flexibly to the pumping line of the calorimeter chamber . For this purpose two rectangular shaped wooden boxes were made with dimensions of 1' by 1' by 1.5' . They were held rigidly with respect to one another with metal plates separated by a distance of 10" . These boxes were then suspended on four extension coil springs from the steel bars beside the cryostat with the diffusion pump mounted at the center of gravity of the

boxes . The boxes were then filled with sand and lead bricks to get an extension of about 10 cms for the springs . The vacuum connections were made the way described in section I-2 The diffusion pump was connected to the calorimeter mounting with flexible stainless steel pipe (B in fig. 4) . The backing pump line of the diffusion pump was a flexible tygon pipe (G of fig. 4) together with the tubes carrying the cooling water .

With this arrangement the vibrations of the calorimeter were undetectable during the pumping of the calorimeter chamber.

The effect of the vigorous slamming of the nearby door was also negligibly small .



I-5 Eddy heating .

Normally Eddy heating has a negligible effect in low temperature calorimetry because the measurements are done in the absence of or in a constant magnetic field . In either case , if the vibrations have been reduced to negligible level , this effect can be neglected .

It can be quite disturbing however when entropy determinations are performed on a paramagnetic substance . If it is either enclosed in a metal container or has metal wires distributed in it for the purpose of reducing the possible thermal gradients between different parts of it , then it is not possible to do strictly isentropic demagnetization . This is due to the fact that when the external magnetic field is reduced to zero there is a changing magnetic flux present producing Eddy heating in the metal parts of the paramagnetic cooling pill . The Eddy heating in turn will produce some entropy increase , depending on the speed of the demagnetization . Thus in the final calculation of the entropy some corrections will be necessary due to this effect which, depending on the circumstances, may not be negligible . We shall see an illustration when the measurements of the absolute temperatures below $1^{o}K$ will be discussed using MgO:Mn crystal .

I-6 Mechanical heat switches .

We shall now describe the ways the specimen can be cooled down from room temperature to the temperature of the liquid He . The following processes can be utilised in principle to conduct heat away from the specimen :

1., Radiation .

2., Convection .

3., Conduction .

Radiation . The rate of heat loss by the specimen can be described by the equation of radiation

$$\dot{Q} = \varepsilon \sigma (T^4 - T_o^4) \text{ ergs/sec cm}^2 .$$

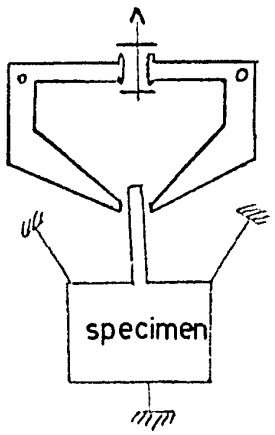
where ε is the emissivity , σ the Stefan's constant , T_o and T are temperatures of the specimen and the surroundings respectively . According to this equation it would take about 10 minutes for a specimen at 300^oK temperature with a surface area of 10 cm^2 to cool 1^oK if it is located in a calorimeter immersed in liquid He . This rate of cooling is much too slow for most practical purposes and for this reason it is not used in low temperature calorimetry .

Convection .This is the principle which is utilised when the specimen is cooled using exchange gas . The difficulties encountered at low temperatures when He gas is used has already been discussed.

Conduction . We have shown that several difficulties arise from the use of the exchange gas . Unfortunately other ways of providing thermal contact between the specimen and the chamber walls present new problems . One of the problems has already been discussed when the heat leak through the suspension was considered . The other major ones will best be appreciated by describing our

first series of experiments with the mechanical heat switches (H.S.) .

About 100 gms. of commercial Cu was used as specimen at the beginning and the H.S. constructed was similar to that used by Wilks and Webb (1955) and also by Manchester (1959) fig. 8 .



Heat switch of Wilks and Webb (1955)

Fig. 8

Its behaviour can be summarised as follows:

1., The specimen could not be cooled below about $6^{o}K$ even though the H.S. was well anchored at $4.2^{o}K$.

2., The rate of cooling of the specimen slowed down appreciably below about $15^{o}K$.

3., The opening of the H.S. warmed the specimen up by several degrees K .

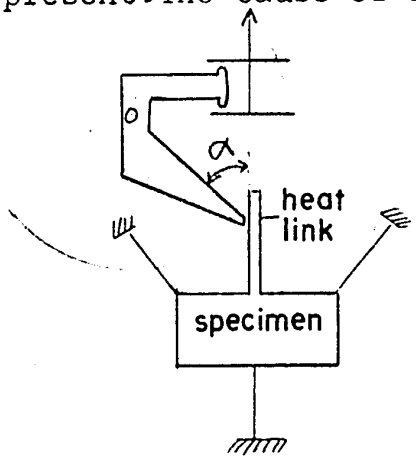
These disappointing results indicated that a great deal more thought should be put into the design of our H.S. Our first objective was making the H.S. cool the specimen to $4.2^{o}K$ from room temperature within reasonable time . The reason for the inability of the above described setup to provide effective cooling is not hard to understand.If the specimen were soldered to the chamber walls one would expect it to cool quite well . The fact that the specimen requires very long cooling time must have something to do with the contacts between the specimen and the H.S. If one were to magnify these contact surfaces they would appear to be rough , and therefore providing only point contacts at moderate pressures . On the other hand in making a solder joint one liquifies the solder thus making certain that every tiny irregularity of the contact surfaces is intimately filled up by the liquid . This state is simply frozen in on cooling the soldered

of obtaining better thermal contact between the H.S. and and the specimen .

1., By the increase of the pressure to the point of near cold welding .

2., By the coating of the surfaces with very soft material which at moderate pressures is pliable enough to shape itself to the irregularities of the other surface .

The first possibility would involve inconveniently high pressures and therefore we decided to use the second one . The coating substance selected was In because it is extremely soft and easy to solder . It has also been used by others for similar reasons . The coating of the H.S. claws did striking justification to the expectations . The specimen could be cooled within a few minutes with moderate pressures to $4.2^{\circ}K$ from $80^{\circ}K$. The problem of the warming of the specimen on opening the H.S. however was still present.The cause of it can be best understood by considering the movement of the H.S. during the opening process , illustrated in fig. 9 .



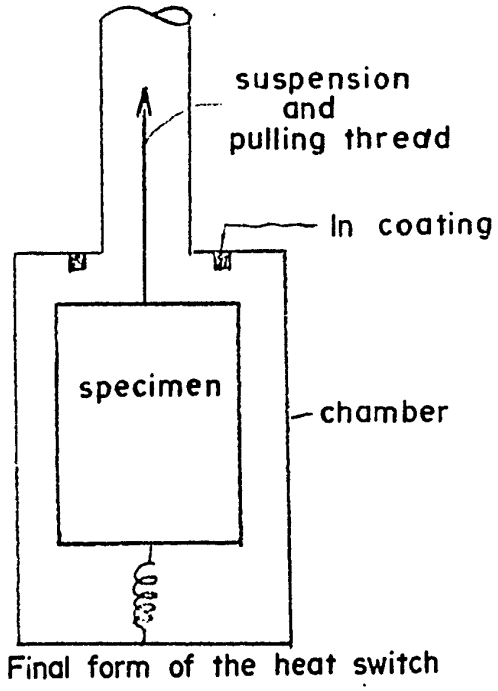
Movement of the heat switch

Fig. 9

When the H.S. is opened it moves along the drawn circle , as shown in fig. 9 . The H.S. will drag along the heat link , the extent of the drag will be proportional to sine α , which in turn will be proportional to the frictional work which heats the specimen .

Thus to get rid of the frictional heating produced by the opening of the H.S. it should be constructed such as to have $\alpha = 0$.

To test the feasibility of these considerations a series of experiments was performed with different heat switches constructed where α should have been zero . It would be pointless to describe all the variations tried . The final form of it which seems to give the best results is the one illustrated in fig. 10 .



Final form of the heat switch

Fig. 10

The specimen is suspended by means of a nylon thread and is pulled away from the contact by a spring . This thread serves also the purpose of pulling the specimen against the In coated cold chamber walls . With this arrangement it is possible to break the thermal contact at $1.3^{\circ}K$ using 4 gms of Cu as specimen with a few hundreths of a degree warm up . This is small enough for most practical purposes .

We can go a step further by noticing that the In coated surface against which the specimen is pulled can in principle be at any temperature . Thus if one wants to do measurements below $1^{\circ}K$ the surface can be the demagnetized paramagnetic

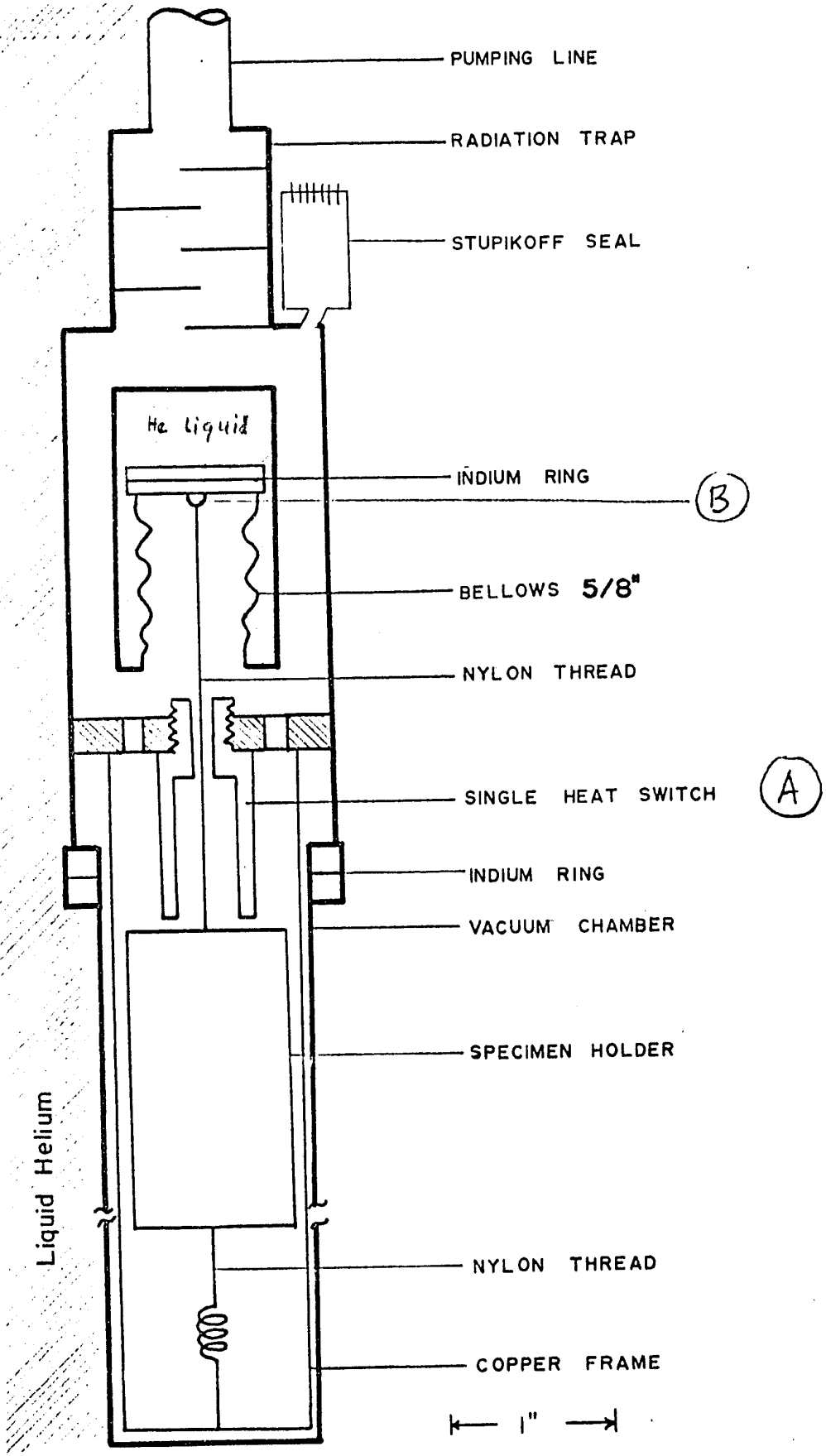
substance at very low temperatures . If an arrangement of this type would still provide sufficient thermal contact at those low temperatures then there would be no need for superconducting heat switches which are often used but are quite awkward to operate . Also their use is limited at high and low temperatures due to their heat conductivity behaviour .

This arrangement requires two heat switches in principle . One between the liquid bath and the paramagnetic substance and one between the paramagnetic substance and the specimen .

I-7 Behaviour of the heat switches .

The single heat switch arrangement of the specimen is illustrated in fig. 11 .

The bellows shown there can be pushed down or pulled up by stainless steel rods (for the sake of simplicity they are omitted from the figure) . The rods terminate in a larger 2" diameter bellows on top of the cryostat at room temperature . The mechanical motion of this arrangement is achieved with a rotary pump connected to the 2" bellows . With the aid of a 1/16" vacuum valve connected between the rotary pump and the bellows the speed of the displacement of the 5/8" bellows could be controlled very sensitively . The total force applicable in this way at the heat switch was about 40 lb. With this heat switch reasonably fast cooling times may be achieved depending on the pressures used . 1/2 mole of MgO with



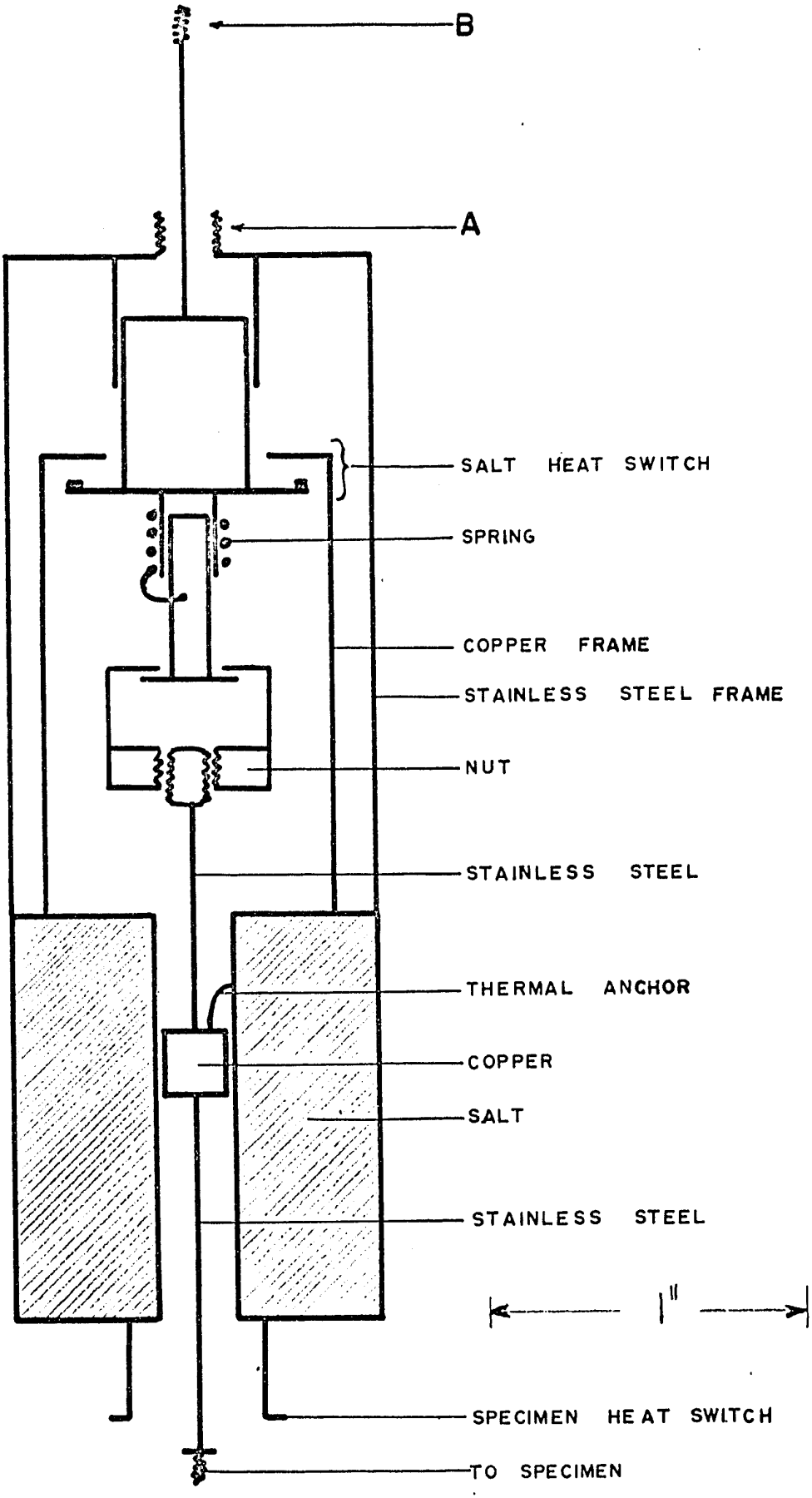
The vacuum chamber with the single heat switch

about 15 lbs. pulling force could be cooled in two hours from room to liquid air temperature . The further cooling from liquid air to liquid He temperature normally would take about twenty minutes . An additional two hours or so are necessary however to cool the suspending nylon thread sufficiently , for the reasons discussed in I-3 . The heat generated on opening the heat switch is of the order of 50 ergs .

The schematic diagram of the double heat switch assembly is seen in fig. 12 . The mounting of it into the calorimeter consists of simply replacing parts A and B of the single heat switch with the corresponding parts A and B of the double heat switch assembly .

With proper adjustment of the nut on the salt heat switch it is possible to close the specimen heat switch first with a given pulling force on the heat switch actuating rod . With the same nut the total pressure at the specimen heat switch could easily be changed for a given force constant of that spring . A further pull on the heat switch actuating rod would close the salt heat switch .

With this double heat switch assembly it takes longer to cool the specimen . During the experiments one atmosphere of N_2 exchange gas was used to precool the specimen and the salt to liquid air temperature . The time for this was about two hours . Using the heat switches the it took a further 2.5 to 3 hours to cool them to $4.2^{\circ}K$, with the calorimeter immersed in liquid He . The opening of the heat switches produced negli-



The double heat switch assembly

gible ammount of heat . The specimen and the salt suspensions in this case are made of stainless steel which being a better heat conductor than nylon gives much smaller initial warming after the first opening of the heat switches .

The procedure of cooling the specimen below $1^{o}K$ is as follows : The heat of magnetization and the Eddy heat in the case of metallic specimen are removed by keeping both heat switches closed . With proper pressure arrangements on the heat switches this takes about 1.5 hours . The salt heat switch is then opened keeping the specimen heat switch closed and then the magnetic field is reduced to zero . With the pressure on the specimen heat switch of a few lb. a Mg specimen of 1.8 moles was cooled to about $0.15^{o}K$ from $1.4^{o}K$ in about 35 minutes On opening of the specimen heat switch there was a sudden warming of the specimen of .02 - $.03^{o}K$ followed by a gentle steady warming toward $.3^{o}K$. The sudden temperature increase is attributed to the warming produced by the process of opening of the heat switch and the gentle warming to the heat leak from the still warm specimen suspension .

In this way with a single demagnetization of the paramagnetic salt it was possible to warm the specimen up to $1.3^{o}K$ and then to cool it to about .15 - $.25^{o}K$ several times .

The actual specific heat measurements on this specimen were repeated twice within about two hours . The first of the measurements yielded specific heat data for that specimen from $.4^{o}K$ to $1.3^{o}K$ and the second from $.2^{o}K$ to $1.3^{o}K$.

The salt itself in these experiments was expected to

be at about .08 - .09°K . The cause of the specimen not being able to cool lower than about .15°K may be as follows : The local warming at the specimen heat switch resulting from the steady transfer of heat from the warmer specimen to the colder salt pill may not be able to diffuse homogenously into the paramagnetic salt while the specimen heat switch is closed .

If this is the case then the specimen could be cooled to lower temperatures either by keeping the specimen heat switch closed much longer or by replacing the CrK alum with say MgO:Mn whose heat conductivity is orders of magnitude higher at these temperatures .

There is a very interesting possible application of this double heat switch arrangement . By putting a cage made of good heat conducting material around the specimen with a heater wound on it and linking it thermally to the salt pill , an adiabatic calorimeter is obtained at the same time thus being able to extend the range of usefulness of this calorimeter in principle from the lowest to the highest of temperatures .

I-8 Specimen holder .

The specimen holder used in the experiments described is a light Cu framework consisting of two thin circular plates forming the top and the bottom linked by two No.20 Cu wires soldered to the plates and thus leaving a cylindrical hollow space into which the specimen can be accomodated . As much material was removed from the plates as possible while maintaining a maximum rigidity by drilling holes into them . This was done for the purpose of decreasing the weight of the specimen holder . The top plate was arranged to be attached to the heat switch rod and the bottom plate was attached to the heater and the two resistance thermometers .

The two carbon resistance thermometers were respectively an Allen-Bradley , 10Ω, 1/2 watt and a Speer , 220Ω, 1/2 watt. Both had their outer bakelite core ground off and then were varnished , put into a Cu sleeve and baked at 140°C for several hours . The Cu sleeves containing the resistors were then soldered to the bottom plate of the specimen holder . A manganin wire of 300Ω was wound onto a 3/8" diameter , 1/2" high and .005" wall thickness coil former and was varnished and baked . This formed the heater . It was then soldered to the bottom plate of the specimen holder . The total weight of the holder with the heater and the thermometers was 4.84 gms .

I-9 Specimen mountings .

There were three different ways in which the specimen were mounted in this work .

MgO : The crystals (rectangular blocks) were soldered with In on a thin Cu plate which then was soldered with Wood's metal alloy to the specimen holder Cu wires.

Mg:Ce : Three #4-40 tapped holes were made in the sides of the cylindrical specimen , into which a few mgs of In was dropped . Then tight fitting short Cu bolts were screwed into the holes squeezing the In at the bottom of the holes for lasting thermal contact . The Cu bolts were then soldered with Wood's metal to the Cu wires of the specimen holder .

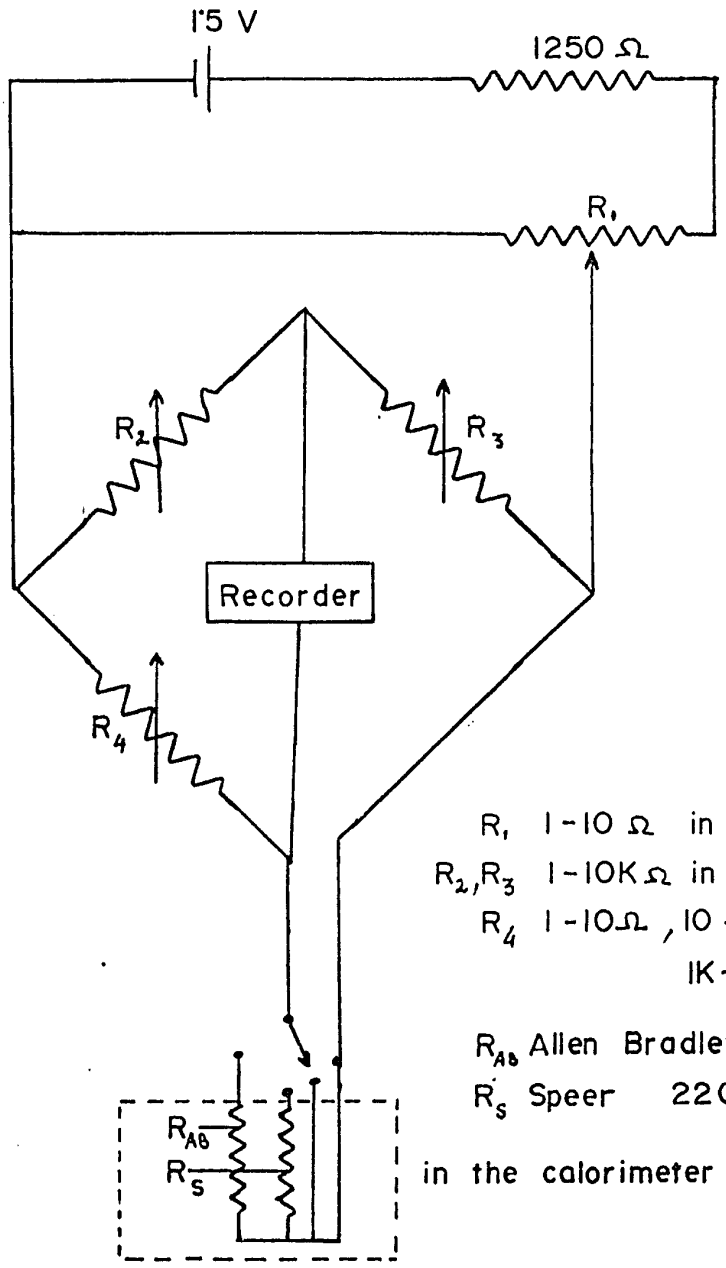
Pure Cu : The cylindrical specimen was stuck to the bottom plate of the specimen holder using a small amount of Silicone vacuum grease .

In all cases the thermal contact between the specimen and the heater and the thermometer was sufficiently good even at the lowest of temperatures .

I-10 Electrical circuits .

There are two circuits necessary for the measurements : one to read the resistance of the carbon thermometers and one to provide known amount of heat to the specimen . To measure the resistance,a three wire Wheastone bridge was used .

The two carbon resistance thermometers on the specimen holder were connected such that either one of them could be made part of the Wheastone bridge . The circuit of the bridge is shown in fig. 13 .



R_1 1 - 10 Ω in 1 Ω steps

R_2, R_3 1 - 10K Ω in 1K Ω steps

R_4 1 - 10 Ω , 10 - 100 Ω , 100 - 1K Ω
1K - 10K Ω in unit steps

R_{AB} Allen Bradley 20 Ω , 1/2 W

R_S Speer 220 Ω , 1/2 W

in the calorimeter

THE WHEATSTONE BRIDGE

Fig. 13

The variable resistors were General Radio decade resistor units of .05% accuracy . All parts of the bridge with the exception of the two thermometers and the recorder were in a shielded metal box . This was found necessary for the reliable operation of the recorder . The electrical leads between the thermometers and the bridge and also between the recorder and the bridge were all shielded cables .

The sensitivity of the recorder used during the measurements was 40 μv/cm . Thus an off balance voltage across the bridge of about 2 μv could be detected . With the thermometers used this corresponded to a temperature change of the order of 10^{-3} ^{o}K at the measuring power dissipation of $2 > P > 10^{-3}$ ergs/sec. , depending on the temperature .

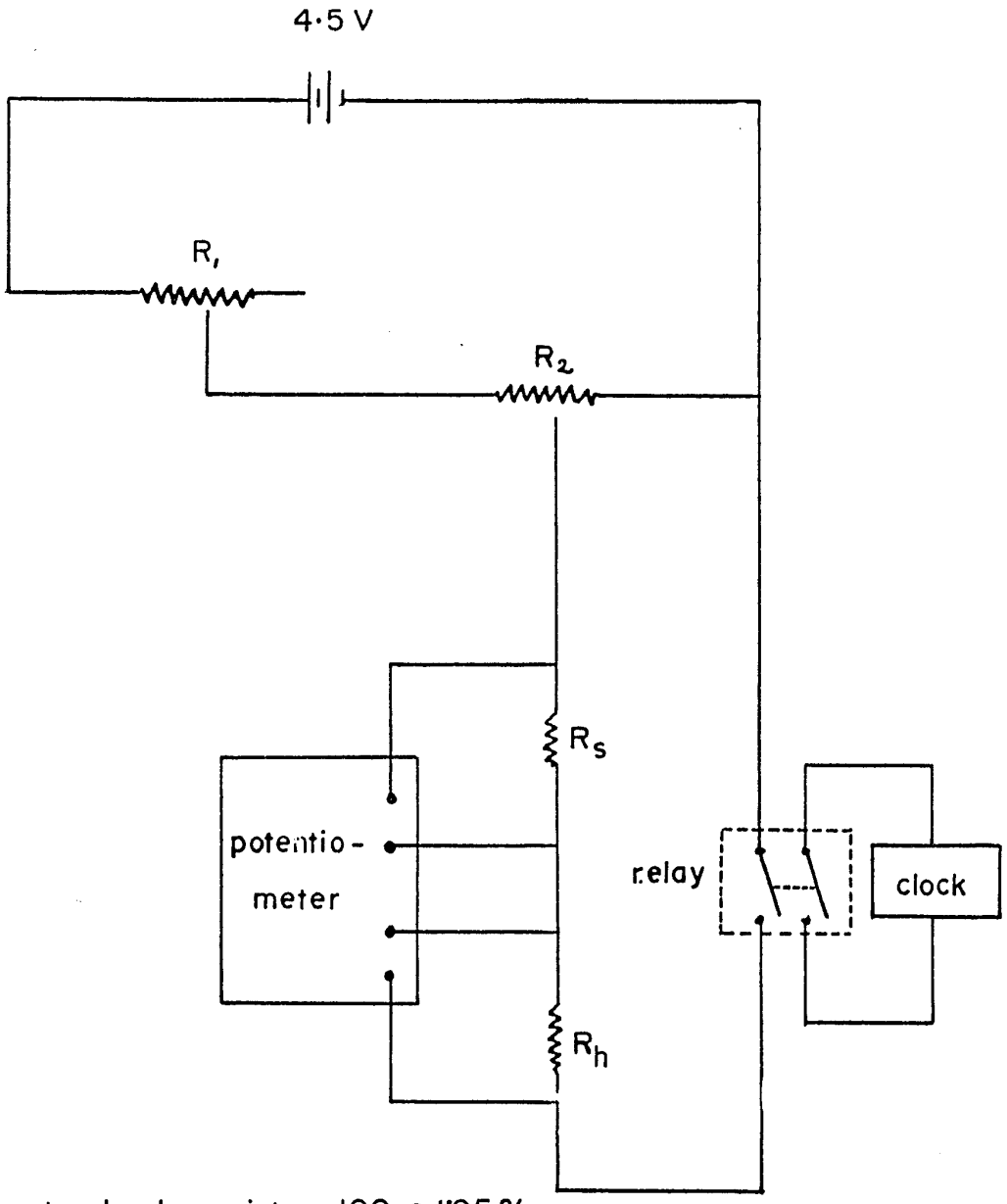
The heater circuit is shown in fig. 14.

I-11 Calibration procedure for the liquid He^4 range .

The carbon thermometers are calibrated against the vapour pressure of He^4 using the 1958 He^4 scale .

At the conclusion of the specific heat measurements the pump evacuating the calorimeter chamber is stopped and about .5 mmHg He exchange gas is introduced into the chamber .

The calibration of the resistance thermometers consists of the measurements of their resistances at different vapour pressures of the liquid He . Below about 1.8^{o}K the different pressures are obtained by setting different pumping speeds over the He bath with vacuum valves . Above this temperature the manostat controls the vapour pressure . The vapour pressures are determined with a Hg and an oil manometers .



R_s standard resistor 100 Ω±05 %

R_h Manganin heater (300 Ω)

R_1 decade resistor in 10 Ω steps

R_2 —— " —— 1 Ω —" —

THE HEATER CIRCUIT

Fig. 14

The height of the liquids in the manometers is measured with a Cathetometer ($\pm$ .01 mm.) .

The readings of the manometer and the resistances are taken when there is no resistance change detectable on the potential recorder due to temperature drift .

The calibration below the λ -point is a simple matter since the heat conductivity of the liquid He is very good . Above the λ -point however it suddenly becomes a very poor heat conductor , thus considerable temperature gradients are possible within the liquid .

If a dewar vessel containing a certain volume of liquid He is allowed to warm up naturally from below the λ-point to $4.2^{o}K$, then up to the λ -point there is no detectable temperature gradient present at any point of the liquid . On passing through the λ -point however the top layer of the liquid will continuously warm up to $4.2^{o}K$ while the lower parts of the liquid column will stay at a temperature just above the λ -point for a long time . This is the result of the poor heat conductivity enhanced by the sensitive dependence of the density on the temperature . (There is about 18% density change between $2.2^{o}K$ and $4.2^{o}K$, with the maximum of density located at the λ-point .) The light warm liquid will tend to float in the uppermost region . This density vs. temperature dependence can be utilised on the other hand to homogenize the temperature within the liquid . If a heater is placed at the bottom of the liquid column , producing light density liquid then due to the

convection currents it will be possible with the matching of the pumping speed over the liquid to produce reasonably homogenous temperature distribution within the entire liquid . By switching the heater off at a given pumping speed the temperature will drop continuously toward lower temperatures . In this case however the density vs. temperature relationship will help homogenizing the temperature of the liquid He .

On the basis of these considerations the calibration above the λ-point was carried out as follows :

First a given pressure was set on the manostat and then a sizable current was passed through the heater located at the very bottom of the He dewar . Afterwards the heater current was switched off and the readings of the carbon resistance thermometers together with the manometer reading were recorded when the temperature change of the liquid was no longer detectable by the carbon resistors .

With this procedure a calibration involving more than 15-points was performed in all the experiments between about $1.2^{\circ}K$ and $4.2^{\circ}K$.

The data so obtained were least square fitted to either

$$\log R + \frac{Z}{\log R} = X + \frac{Y}{T}$$

for the Allen-Bradley resistor , or to

$$R = \frac{A}{T} + B$$

for the Speer resistor .

The scatter of the experimental points over the entire

range of the calibration was within 1/4% in either case .

It was noticed that the constants of the calibration equations were different at different experiments . These constants are displayed in table I .

The Speer resistor used for the measurements of the MgO specimen was accidentally broken at the end of those measurements and therefore a similar resistor was made in a similar way called #2 in the table .

In order to see the reproducability of the thermal behaviour of the carbon resistances , the temperatures corresponding to 1KΩ resistance was calculated for each set of the calibration constants .

The maximum differs from the minimum value of the temperature by 1.25 % in the case of the Allen-Bradley resistor over a period of four months . In the case of the Speer resistor #1 there is a 4.2 % deviation over three months whereas in the case of Speer resistor #2 there is a 5.1 % deviation between the minimum and maximum values of the temperatures , over a similar period .

I-12 The calibration of the carbon resistance thermometer below 1°K .

Temperature measurements below 1°K are not as straightforward as in the 1-4°K range . This is because there does not exist a conventional primary thermometer against which the secondary thermometer could be calibrated . For this reason

		Speer		Allen-Bradley			
		A	B	X	Y	Z	
November	3	438.8	669.5				
	10	435.0	660.0				
	19	430.2	650.3				
	24	432.9	663.6				#1
December	1	434.5	672.2				
	8	435.7	671.6				
February	4	435.0	673.0				
	27	404.7	626.2	2.354	1.460	1.526	
March	3			2.263	1.495	1.327	
	24			2.281	1.509	1.413	
	29	393.1	606.9				
	31	394.4	608.4	2.269	1.507	1.386	
April	6			2.253	1.538	1.380	
	14			2.256	1.518	1.372	#2
	20			2.279	1.514	1.413	
	23			2.273	1.508	1.397	
	29			2.346	1.458	1.515	
May	3			2.275	1.503	1.398	
	20			2.275	1.505	1.389	
June	14	390.5	581.4	2.208	1.545	1.279	
July	2	394.2	592.0				

Table I

in doing the calibration we utilised the second law of thermodynamics .

$$T = \frac{\Delta Q}{\Delta S} = \frac{\Delta Q / \Delta T^*}{\Delta S / \Delta T^*} = \frac{C^*}{\Delta S / \Delta T^*}$$

where T^* is a parameter which is a single valued function of the absolute temperature in the proper temperature range . In our case the parameter chosen is the temperature obtained by the extrapolation of the calibration equation for the Speer resistance thermometer obtained in the range of $1.2^{\circ}K < T < 4.2^{\circ}K$. C^* is the "specific heat" of the substance as determined by the thermometer to be calibrated , and $\frac{\Delta S}{\Delta T^*}$ is the slope of the entropy vs. T^* curve . It can be obtained by doing a series of demagnetizations with a paramagnetic substance from a set of known initial magnetic fields and temperatures .

If one were to determine $\frac{\Delta S}{\Delta T^*}$ graphically from the measured S vs. T^* curve the experimental errors would be very large . For this reason Bleaney (1951) has derived an equation which reduces the error in calculating the values of $\frac{\Delta S}{\Delta T^*}$. Let us apply his derivation to our case :

Let $X = g\beta \frac{H_i}{T_i}$ and $\alpha = X T^*$ then with $g = 2{\cdot}00$

$$X = 0{\cdot}134 \frac{H_i}{T_i}$$ where H_i is in Kgauss .

Then
$$\frac{\partial S}{\partial T^*} = \frac{\partial S}{\partial X} \frac{\partial X}{\partial T^*}$$
$$= \frac{\partial S}{\partial X} \frac{\partial}{\partial T^*}\left[\frac{\alpha}{T^*}\right]$$
$$= \frac{\partial S}{\partial X}\left[\frac{1}{T^*} \frac{\partial \alpha}{\partial T^*} - \frac{\alpha}{T^{*2}}\right]$$

$$\frac{\partial S}{\partial T^*} = \frac{\partial S}{\partial X}\left[\frac{1}{T^*}\frac{\partial \alpha}{\partial T^*} - \frac{X}{T^*}\right]$$

$$= -\frac{X}{T^*}\frac{\partial S}{\partial X}\left[1 - \frac{1}{X}\frac{\partial \alpha}{\partial T^*}\right]$$

Finally

$$\frac{T}{T^*} = \frac{C^*}{-X\frac{\partial S}{\partial X}\left[1 - \frac{1}{X}\frac{\partial \alpha}{\partial T^*}\right]} \qquad \text{.....I-12-1}$$

For a given X , $-X\frac{\partial S}{\partial X}$ can be obtained from the tables of Hull and Hull (1941) . $\frac{\partial \alpha}{\partial T^*}$ on the other hand is the slope of α vs. T^* curve .

The situation is further complicated in our case because it is not possible to perform a strictly adiabatic demagnetization on the paramagnetic substance . Due to the presence of metal in the mounting of the paramagnetic substance there will be a gradual increase of the entropy during the process of demagnetization for the following reasons :

1., Heat leak .

2., Eddy heating of the Cu addenda .

3., Change of the enthalpy and of the lattice of the paramagnetic substance .

The entropy S_f then at the end of the demagnetization will have the following value :

$$S_f = S_i + \Delta S(\text{Eddy}) + \Delta S(\text{Enthalpy}) + \Delta S(\text{Heat leak})$$

where S_i is the initial entropy obtained from the tables of Hull and Hull (1941) for a given X .

In what follows we assumed that the corrected entropy S_f is the value for which the demagnetization can be considered as adiabatic .

With this assumption in mind the procedure of the calculation of the absolute temperatures is then as follows :

For a given X the corresponding S_i is obtained from the tables . After calculating S_f the corresponding X_f is obtained together with $-X_f \frac{\partial S_f}{\partial X_f}$. Finally from the plot of α vs. T^* the slope $\frac{\partial \alpha}{\partial T^*}$ is calculated . With these quantities available the necessary T vs. T^* relationship can be plotted .

We shall now indicate the way of calculating S_f .

Calculation of $\Delta S(\text{Eddy})$.

If there is varying magnetic flux present then in a conductor the voltage induced is given by :

$$V = -\frac{\Delta \phi}{\Delta t} = K \dot{H}(t)$$

where $\frac{\Delta \phi}{\Delta t}$ and $\dot{H}(t)$ are the rate of change of the magnetic flux and magnetic fields respectively , and K is a constant .

The Eddy heating produced is given by :

$$\Delta Q = V I \Delta t = \frac{V^2}{R} \Delta t = K' \dot{H}^2(t) \Delta t$$

$$\therefore \quad K' = \frac{\int dQ}{\int \dot{H}^2(t)\, dt} \qquad \text{.....I-12-2}$$

i.e. the constant K' is independent of the temperature .

Finally from the second law of thermodynamics

$$\Delta S(Eddy) = \int \frac{dQ}{T} = K' \int \frac{\dot{H}^2(t)}{T} dt$$

Calculation of ΔS(Enthalpy) :

Assuming that the lattice entropy of the paramagnetic substance can be neglected the only contribution to the entropy increase will be that due to the enthalpy of the addenda . At low temperatures it will be given by :

$$\Delta Q = (\gamma T + \beta T^3)\Delta T$$

so that

$$\Delta S(Enthalpy) = \int_{T_f^*}^{T_i} \frac{\gamma T + \beta T^3}{T} dT$$

$$= \gamma(T_i - T_f) + \frac{\beta}{3}(T_i^3 - T_f^3)$$

Calculation of ΔS(Heat leak) :

The contribution of the heat leak to the entropy increase can be calculated as follows :

$$S(Heat\ leak) = \int \frac{dQ}{T} = \int_0^t \frac{\dot{Q}}{T} dt$$

where $\dot{Q}$ is the measured heat leak .

I-13 Procedure for the calculation of the specific heats .

During the specific heat measurements the resistance of the carbon resistance thermometer (Allen-Bradley for $T > 1.2^{\circ}K$ and Speer for $T < 1.2^{\circ}K$) was constantly recorded on the chart recorder , at chart speed of $1/v = 12$ sec/cm . There were usually 5 or more resistance null values taken during the "no heating" periods on the chart . These were used for calculating the heat leak to the specimen before and after the heating period . The heating duration was in general less than about $1/5^{th}$ of the "cooling" period and was never shorter than 30 sec. The heating power was usually arranged such as to give a temperature rise of more than 9-times* the temperature change due to the heat leaks . The time of heating was measured with an electric clock ($\pm .1$ sec.) . The clock and the heater were connected across a relay thus making certain that the switching on and off of the timing and the heating would happen simultaneously . The resistance values read on the chart were then tabulated and the corresponding temperatures were calculated with an I.B.M. 1620 electronic computer , using the values of the constants of the R vs. T equations obtained from the calibration data at the end of each experiment . There were normally about 120 such values for each experiment . In order to calculate the specific heat of the specimen from the temperature values available the effect of the heat leak has to be considered .

The heat capacity of the sample can be calculated from its definition equation :

$$C = \frac{\Delta Q}{\Delta T}$$

where ΔQ is the heat supplied by the heater , C the heat capacity and ΔT is the temperature increase . This equation is valid only if the thermal isolation of the sample is perfect . If it is warmer than the surroundings , however , there will be some heat leaks present resulting in a steady cooling of the specimen which will continue during the heating period . Thus the heat supplied by the heater will result in a smaller net temperature increase of the specimen than it would have in the absence of the heat leak . There are two ways of accounting for this :

1., Extrapolating the cooling lines to the middle of the heating period as indicated in fig. 15 by $\Delta T(true)$.

2., The other way is to obtain the slopes of the cooling lines $\dot{T}_c$ together with $\dot{T}_w = \Delta T(net)/\Delta t$ where $\Delta T(net)$ is the net increase of the temperature of the specimen and Δt is the heating duration . See fig.15 .By plotting $\dot{T}_c$ vs. T for the entire experiment and drawing a smooth curve through the points one can obtain $\dot{T}_c$ for the middle of the heating period .

The heat capacity of the specimen then can be obtained by

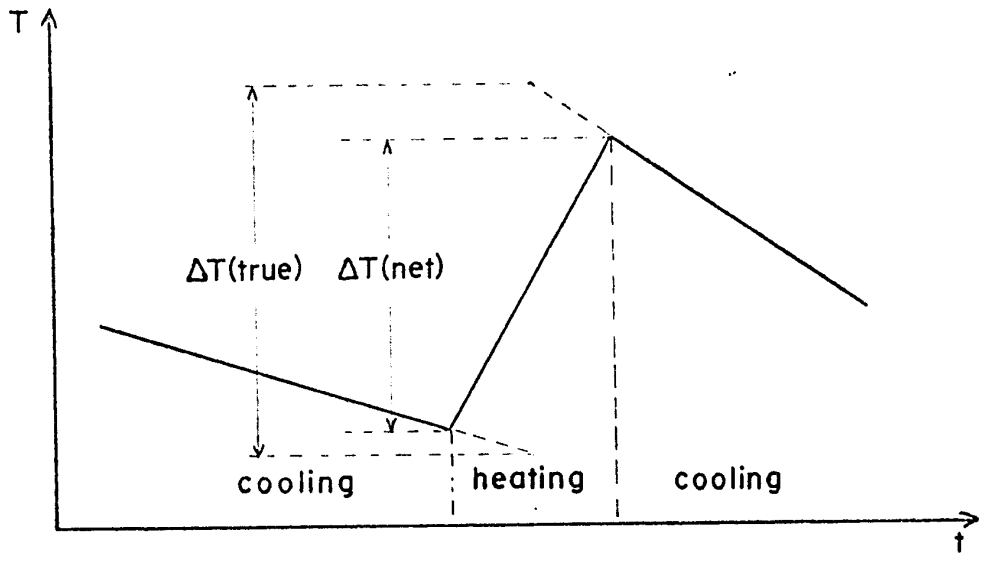
$$C = \frac{\dot{Q}\ \Delta t}{\Delta T(true)}$$

using the first way , and by

$$C = \frac{\dot{Q}}{\dot{T}_W + \dot{T}_C}$$

using the second way . Here $\dot{Q} = VI$ where I is the heater current and V is the voltage drop across the heater .

Finally the specific heat of the specimen can be calculated after subtracting the heat capacity of the addenda obtained in a similar way .



Estimation of the heat leaks

Fig. 15

I-14 Specific heat of Copper .

The purpose of this measurement was to see how the reliability of our experimental techniques compare with that of other workers in this field .

Cu is the substance which has been measured by several experimenters and now it is becoming a common practice to use it as a specific heat standard from $4.2^{o}K$ to the lowest of temperatures . It is a convenient substance because below $4.2^{o}K$ its specific heat is of the form

$$C = \gamma T + \beta T^3$$

i.e. the Debye Θ is constant in this temperature range . Plotting C/T vs. T^2, one gets a straight line the slope being $(1947/\Theta)^3$, (when the specific heat is in mJ/mole deg.) and the intercept being γ .

Description of the Cu specimen .

The specimen in the form of a cylinder of 1" diameter and about 7/8" height having a weight of 119.425 gms was obtained from Dr.D Martin of N.R.C. It was vacuum cast in graphite crucible . The chemical analysis indicated the following impurities : Fe = .25 ppm

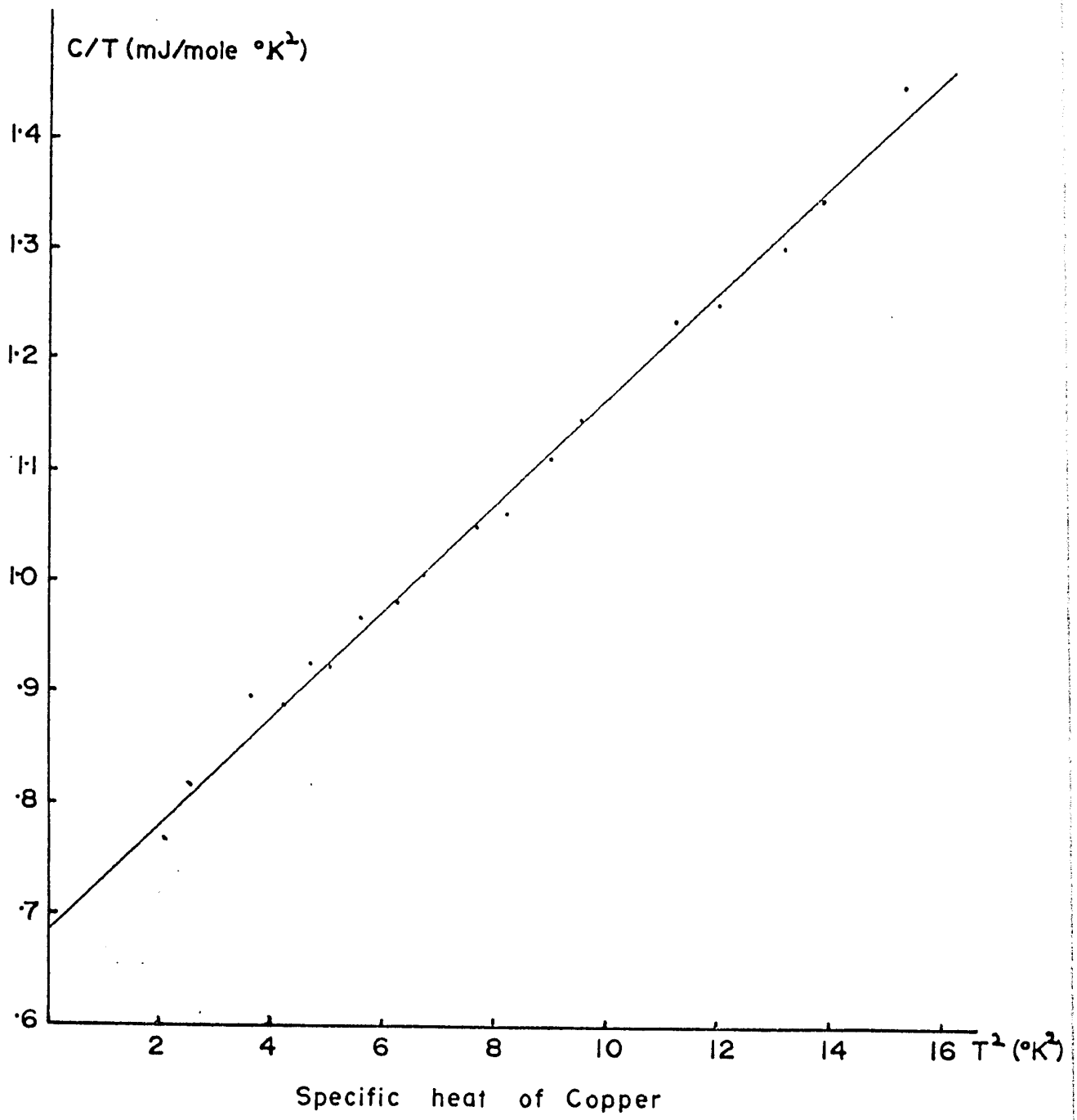
Mg $< 10^{-3}$ %

Si $< 10^{-2}$ %

Ca $< 10^{-3}$ %

Results .

Our experimental values are displayed in fig.16 . The slope of the line is .0481 mJ/mole deg.^{3} corresponding to the Debye



Specific heat of Copper

Fig·16

theta of $\Theta = 343.0 \pm 2.4^{\circ}K$. The intercept gives a value of $\gamma = .682 \pm .011$ mJ/mole deg.^{2}. These values are in good agreement with those found by others in this temperature region . See Table II.

The results obtained for this Cu specimen indicate that our calorimetric apparatus and the experimental technique used are sufficiently reliable .

γ mJ/mole deg^2	Slope mJ/mole deg^4	Debye Θ (°K)	Reference
.694	.0480	343	Phillips (1964)
.688	.0478	344	Corac et.al.(1955)
.686 ± .012	.0473	344.5 ± 3	Rayne (1956)
.691 ± .006	.0486	342 ± 2	Griffel et.al.(1957)
.720	.0523	334	Ramanathan (1957)
.696 ± .021	.0478	344 ± 7	Manchester (1959)
.721	.0500	339	du Chantenier (1962)
.698	.0482	343	Kneip (private com.)
.682 ± .011	.0481	343.0 ± 2.4	This work

Table II

Errors .

The specific heat data in the measured temperature range are described in terms of γ and Θ . Therefore it is convenient to assign standard errors to these quantities . The standard error can be calculated from the scatter of the experimental points with respect to the least square fitted $C = \gamma T + \beta T^3$ curve . The details of the calculations will not be discussed here because they can be found in any of the standard texts dealing with errors and probability calculations (See eg. Smart (1958) p.45) This is the error which is quoted in this work whenever necessary .

CHAPTER II

II-1 Calorimetric measurements of $MgO:Mn^{2+}$ below $1^{o}K$.

In a search for non-hydrated paramagnetic substances suitable for achieving low temperatures by adiabatic demagnetization Walsh(1964) has suggested the use of MgO doped with small quantity of Mn^{2+} ions . This substance should be capable of attaining fairly low temperatures from the usual $\frac{H_i}{T_i}$ =15 Kg/^{o}K value , and should also have a suitable heat capacity . It was therefore of interest to verify experimentally these two points . This chapter then describes both the cooling and the calorimetric experiments using $MgO:Mn^{2+}$ To evaluate these properties of the substance it was necessary to use a secondary thermometer (in this case a Speer carbon resistor) . As the thermometer could not be extrapolated with certainty below .4^{o}K or so,an effort was made to establish the true thermodynamic scale of temperature from first principles . The way in which this can be done has already been discussed in I-12 and in this chapter its practical details will be given . From the point of view of cooling below $1^{o}K$ MgO doped with Mn^{2+} has very attractive properties . Let us summarise them :

The substance should have high Debye characteristic temperature Θ which will guarantee that the lattice entropy at $1^{o}K$ and below will be negligible compared to the magnetic entropy . The energy level splitting ΔE should be much smaller than kT at $1^{o}K$. This will make possible a low final temperature on demagnetization . The specific heat maximum should be as high as

possible at $T = E/k$ if it is to be useful to cool other substances with it and give long useful experimental time below $1^{o}K$. It should also have good heat conductivity in the low temperature range and have both chemical and physical stability under high vacuum and repeated cycles from room temperature to the lowest temperature . Finally it is a definite advantage if it can be soldered or bound to metal to insure the maximum heat contact at low temperatures .

II-2 Physical properties of $MgO:Mn^{2+}$

MgO has a high Debye θ approximately $950^{o}K$ (de Launay, 1956) and reasonably good heat conductivity at low temperatures ($K = .1$ watts/cm deg. at $T = 2^{o}K$, Slack, 1962) . Its crystal structure is simple cubic .

Low(1957) and Walsh(1964) have investigated $MgO:Mn^{2+}$ using E.P.R. technique and found that the cubic crystal field splits the 6-fold spin degeneracy of the Mn ions into a 2-fold and a 4-fold degenerate levels with a separation of $a = .006\ cm^{-1}$. (This corresponds to about $.0086^{o}K$ temperature) A further splitting of these lines is caused by the nuclear spin of 5/2 through the so called hyperfine interaction . From the measured resonance spectra they derived a hyperfine structure coupling constant of $A = .0081\ cm^{-1}$.

On the basis of these splittings they predicted a low temperature specific heat of

$$CT^2/R = (hc/k)^2 \left\{ 2a + 1/3\ S(S+1)I(I+1)A^2 \right\} = 3.66 \times 10^{-3}$$

with the maximum of the specific heat located at about .035°K .

II-3 Experimental procedure .

The specimen of MgO were In soldered into the addenda as described in I-9 . The addenda was then mounted into the vacuum chamber . This consisted of attaching it to a 10 lb. tensile strength nylon thread hanging from the bellows on top of the vacuum chamber (see fig12, B). By pulling on the bellows the addenda could be pulled against an In coated surface in good thermal contact with the walls of the vacuum chamber . Releasing the tension from the bellows , the contact between the addenda and the In coated surface could be broken . This arrangement served as mechanical heat switch . After mounting the addenda in this way the electrical leads for the heater and the carbon resistance thermometer were connected . They were made of #42 Manganin wires coated with lead which in turn was varnished to provide electrical isolation . These leads terminated in Stupakoff vacuum seals located on top of the vacuum chamber as seen in fig. 11 . From the Stupakoff seals thin Cu wires were carried out of the He dewar into the heater and the Wheatstone bridge circuits .

Afterwards the vacuum chamber was sealed off using In ring and the liquid He and liquid air dewars were put in place .

With closed heat switch the vacuum chamber was cooled to liquid air temperature through the soft He dewar by filling the outer dewar vessel with liquid air . At this stage of the experiment the pumping on the vacuum chamber has also begun . When the specimen cooled to about 80°K,liquid He was introduced into the

He dewar . The specimen was then cooled to 4.2°K with the aid of the heat switch . The pumping on the He bath then began thus the specimen was cooled to about 1.3°K .

The specimen at this temperature was magnetized in about 18 Kg magnetic field with closed heat switch to remove the heat of magnetization . When the magnetized specimen cooled back to about 1.3°K the heat switch was opened and the magnetic field was reduced to zero . In this way the specimen cooled to well below 1°K .

On the demagnetized specimen heat capacity measurements were performed as described in I-13 .

In a different set of experiments a number of demagnetizations were performed from approximately 1.3°K but from various initial magnetic fields in order to establish the absolute temperature scale as discussed in detail in the next section .

II-4 Results .

In fig.17 the experimental heat capacity of $MgO:Mn^{2+}$ is displayed as a function of T* . This temperature is obtained as explained before by extrapolating below 1°K the calibration equation obtained in the range of $1.2 < T < 4.2$°K for the Speer resistance thermometer . T* thus coincides with T the absolute temperature above 1.3°K and probably down to about .4 or .5°K according to several workers (cf. for instance Scurlock and Wray, 1965)

The heat capacity displayed is that of the $MgO:Mn^{2+}$ alone after subtracting from the raw data the contribution of the specimen holder assembly . The experimental points from five separate series of measurements have been assembled to

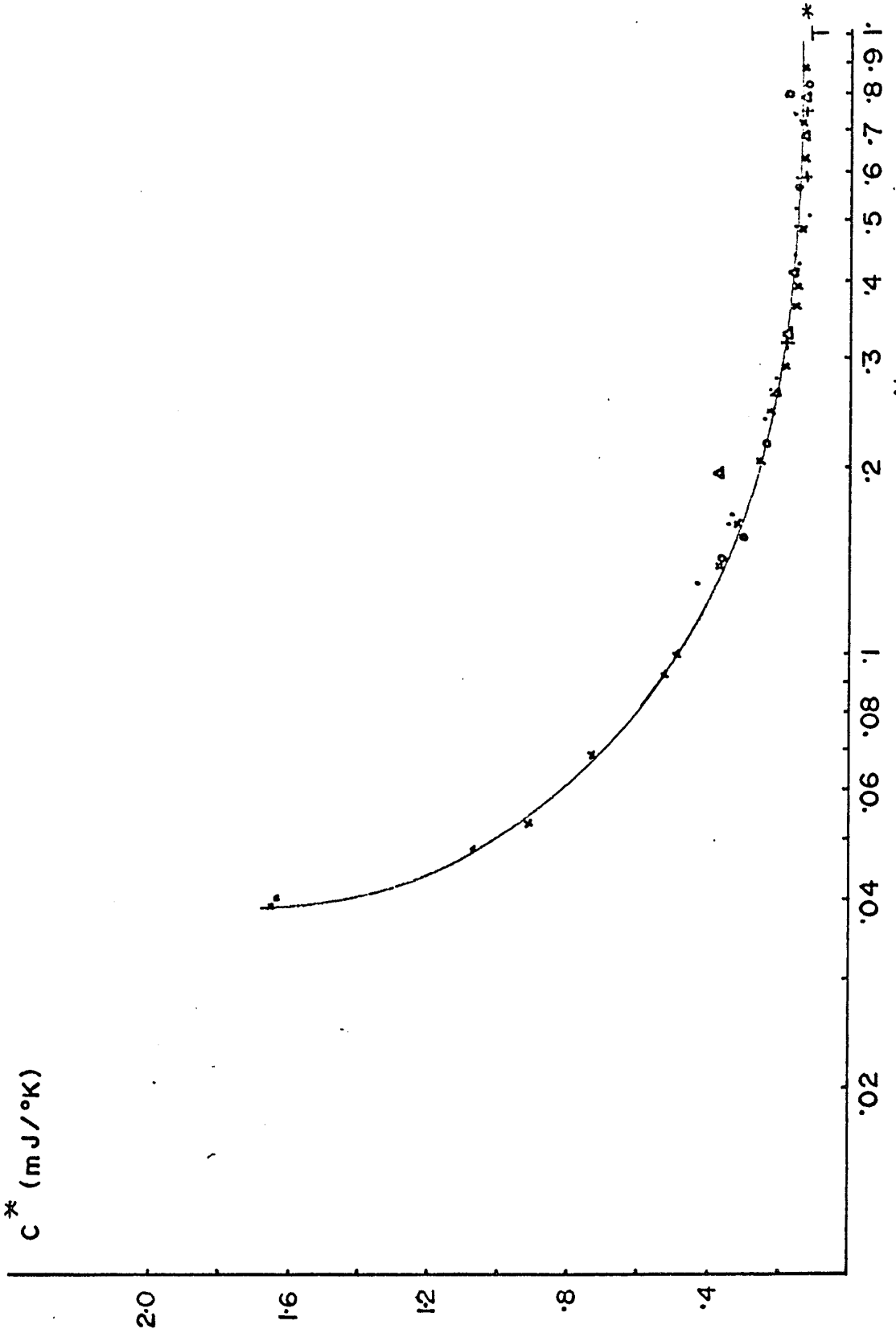


Fig.17. Heat capacity of MgO:Mn^{2+} below 1°K obtained in 5 experiments

show the extent of the reproducibility of the results . It is seen that very few points need to be rejected . The lowest temperature T_f^* obtained from the initial conditions of $H_i = 18$ Kg and $T_i = 1.35^oK$ is $T_f^* = .08^oK$, while the highest heat capacity C^* measured is $C^* = .6$ mJ/mole deg.K

It should be mentioned that on one occasion 2.5 gms of Ce Mg nitrate crystal was added to the MgO specimen and a final temperature of $T^* = .04^oK$ was obtained from approximately the same initial conditions . This is understandable however because the Ce nitrate is expected to cool to a few $10^{-3o}K$ and this would account for the further cooling of the MgO .

Fig. 18a shows the corrected final entropy (S_f/R) vs. T_f^* . To obtain this curve fifteen demagnetization experiments were performed from approximately the same initial temperature of $T_i = 1.35^oK$ but from various initial magnetic fields , in the range of $4 < H < 18$ Kg . For H_i vs. T_f^* obtained from these experiments see fig. 19 .

To obtain fig. 18 first the quantity $X = .134\ H_i/T_i$ was calculated for the set of H_i and T_i values then the corresponding entropy S_i was obtained from the Hull and Hull(1941) tables .

In order to account for the increase of the entropy S_i during the process of the demagnetizations a calculation of the corrections was necessary as explained in I-12. Let us now consider them in turn :

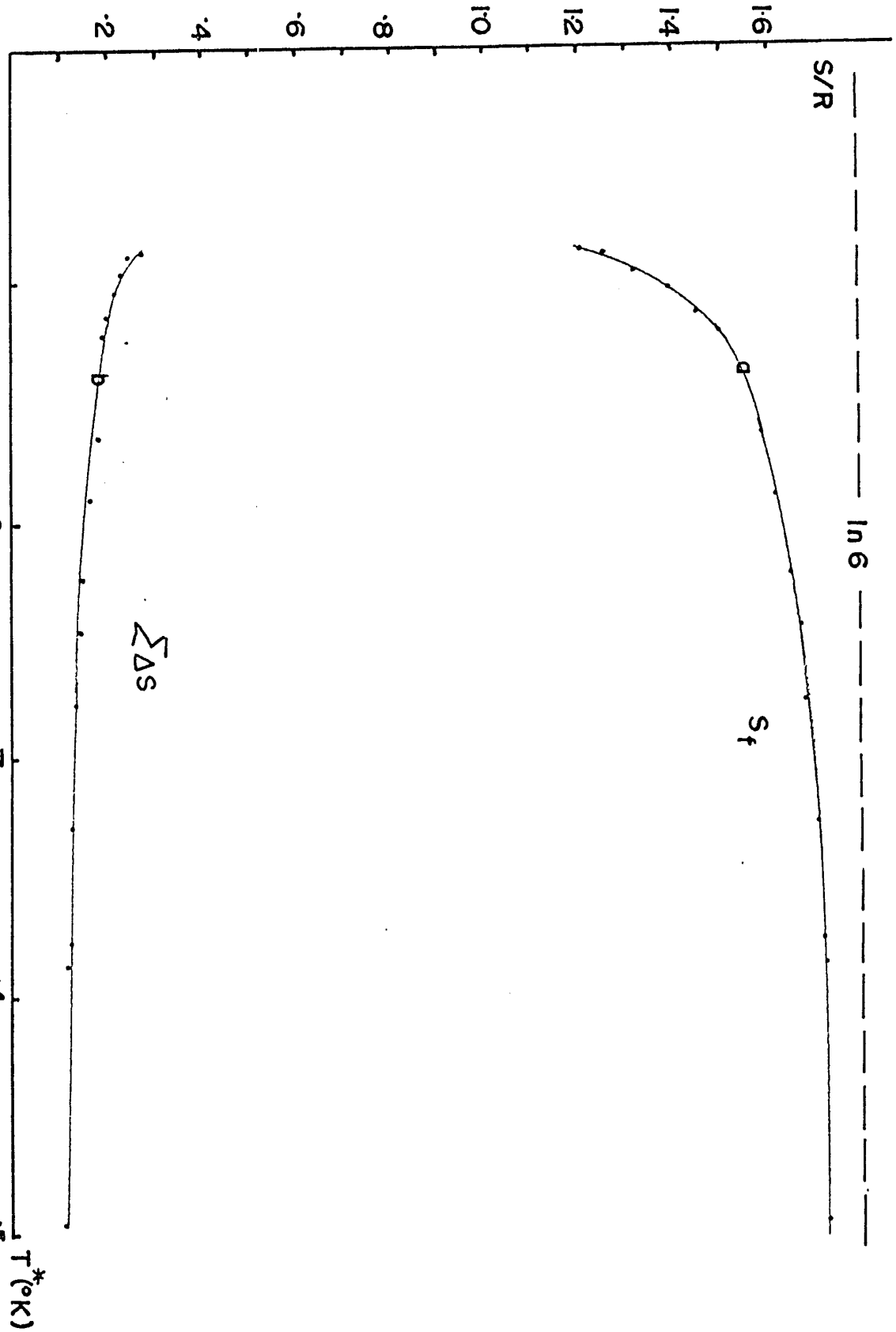


Fig. 18 a ; Entropy of $MgO:Mn^{2+}$ with corrections
b ; Entropy corrections

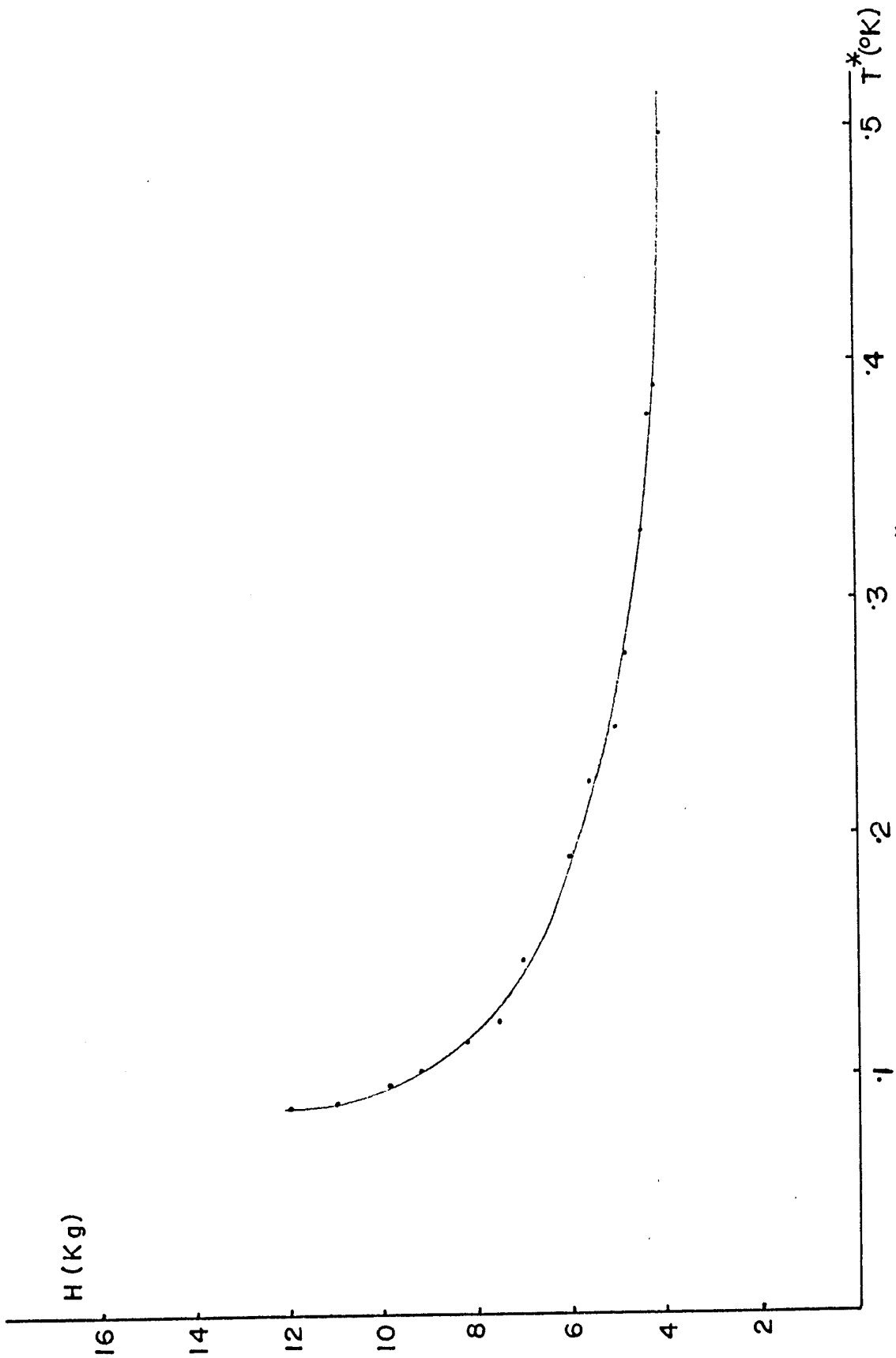


Fig.19 H vs. T*

ΔS (Eddy).

Fig. 20 shows the change of the magnetic field as a function of time . This speed of demagnetization was used during all the measurements made in connection with the MgO crystals . By the numerical differentiation of this curve $\dot{H}$ vs. t was obtained , and it is seen in fig. 21 . Fig. 22 shows $\dot{H}^2$ vs. t obtained from fig 21 . The temperature of the specimen as a function of time during the demagnetization for the different initial magnetic fields used is shown in fig. 23 . The instantenous temperature of the specimen as seen by the carbon resistance thermometer was steadily displayed on the potential recorder . In this way the process of the cooling of the specimen during the demagnetization could be observed as a function of time . This was possible because the calibration relation for the Speer carbon resistor is independent of the magnetic field as observed from the results of a separate calibration experiment performed in 5 Kg magnetic field . Fig. 24 shows $\dot{H}^2 / T$ vs. t obtained from figures 22 and 23 .

There was also an experiment to measure the Eddy heating of the empty addenda . For this experiment the MgO crystal was removed from the addenda and its temperature rise was measured in the liquid He range when subjected to the same rate of change of the magnetic field as shown in fig. 20 . Using the temperature rise obtained and knowing the heat capacity, the Eddy heating $\int \Delta Q$ was calculated . The constant K' (I-12-2) was then obtained by dividing $\int \Delta Q$ with the numerically integrated value of the curve shown in fig. 20 . I.e.

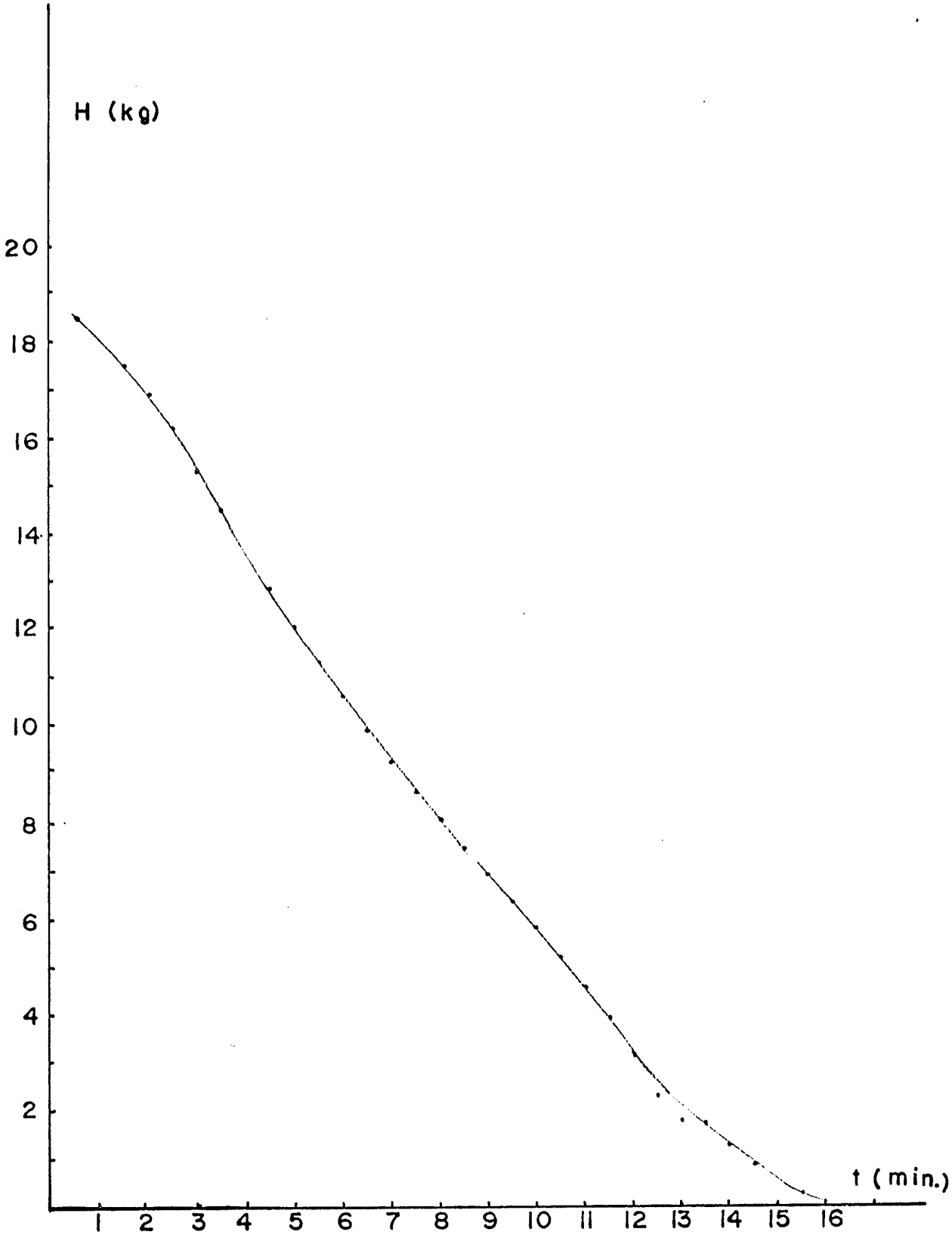


Fig.20 Magnetic field vs. time

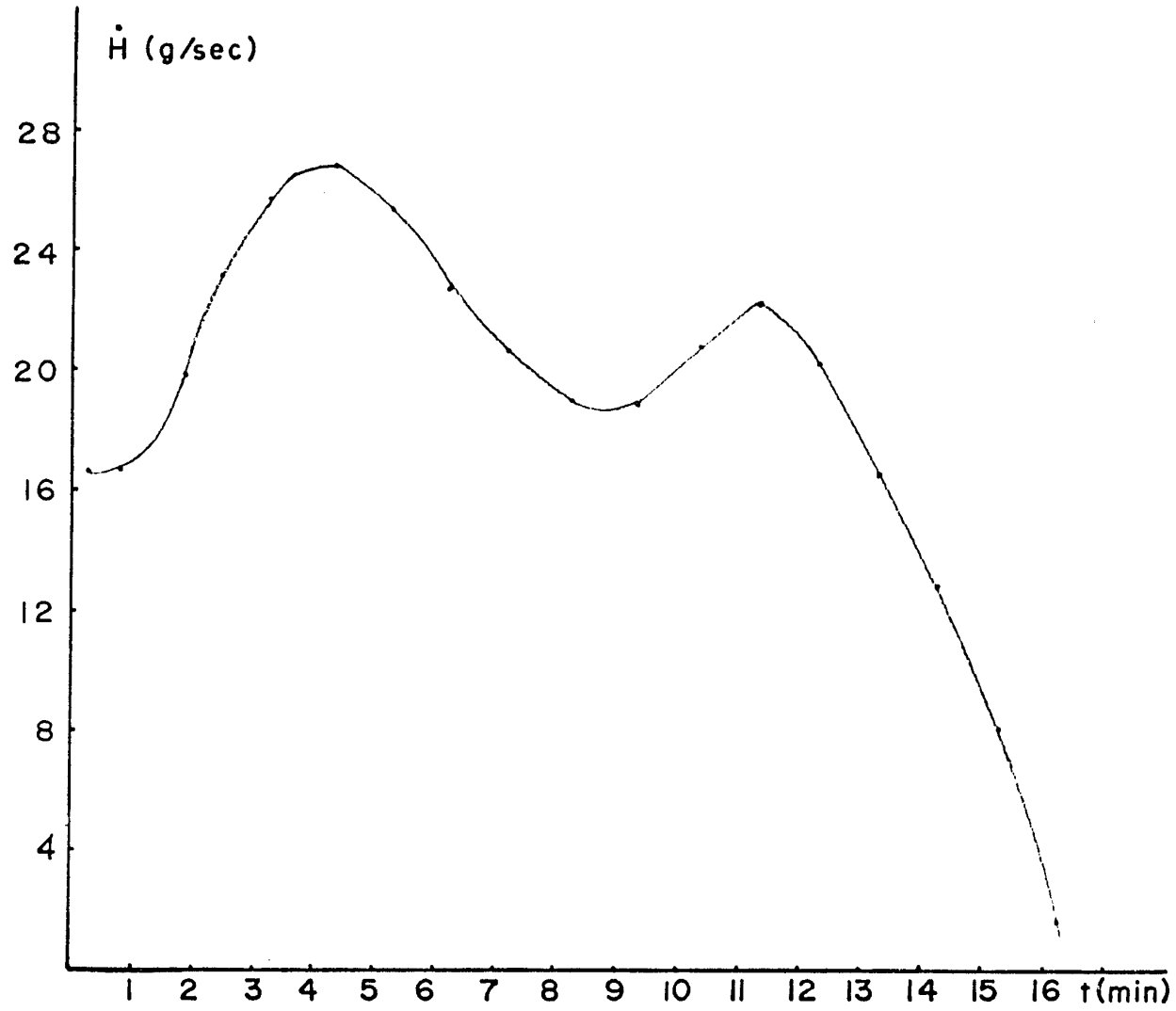


Fig.21 $\dot{H}$ vs. t

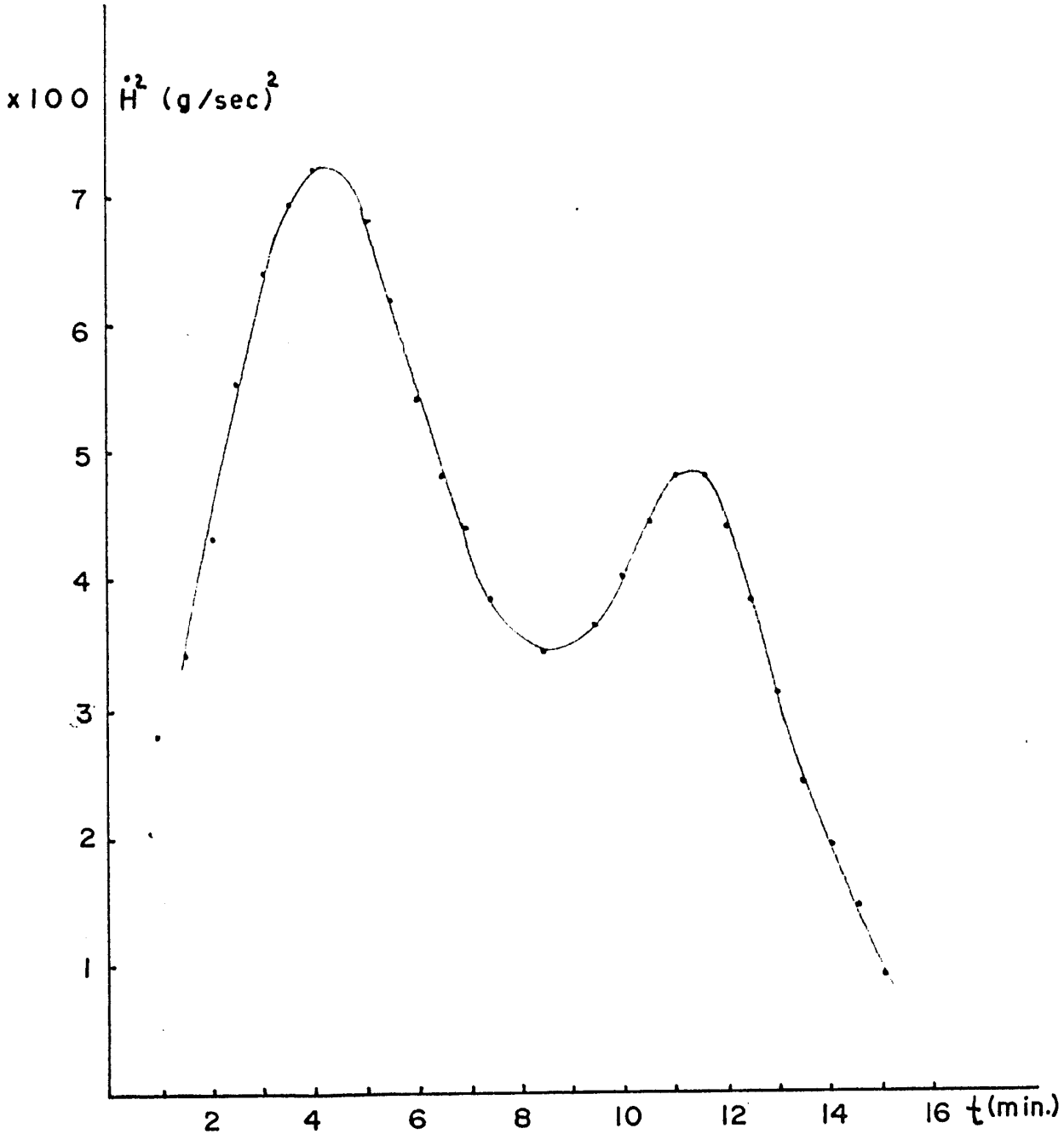


Fig. 22 $\dot{H}^2$ vs. t

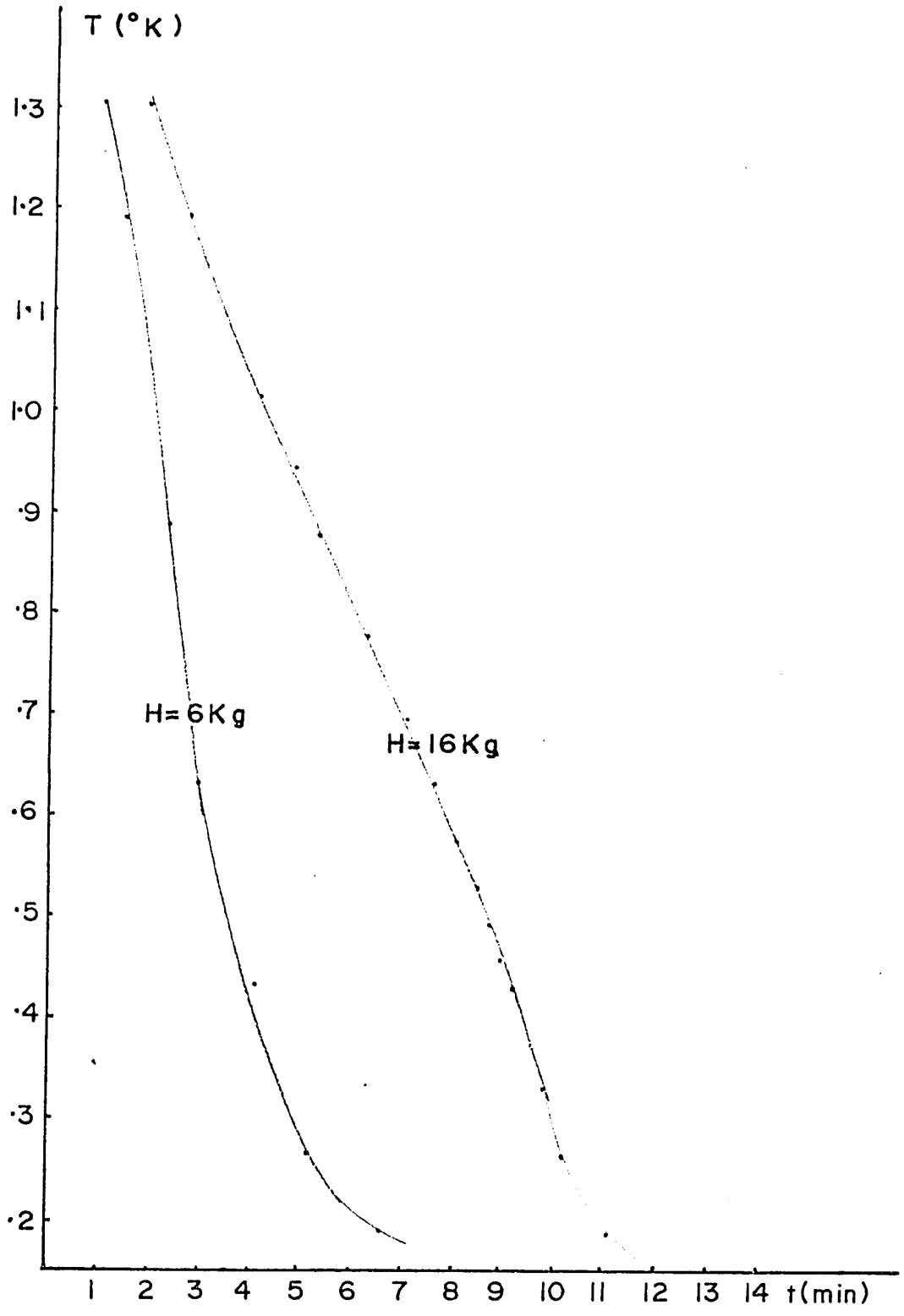
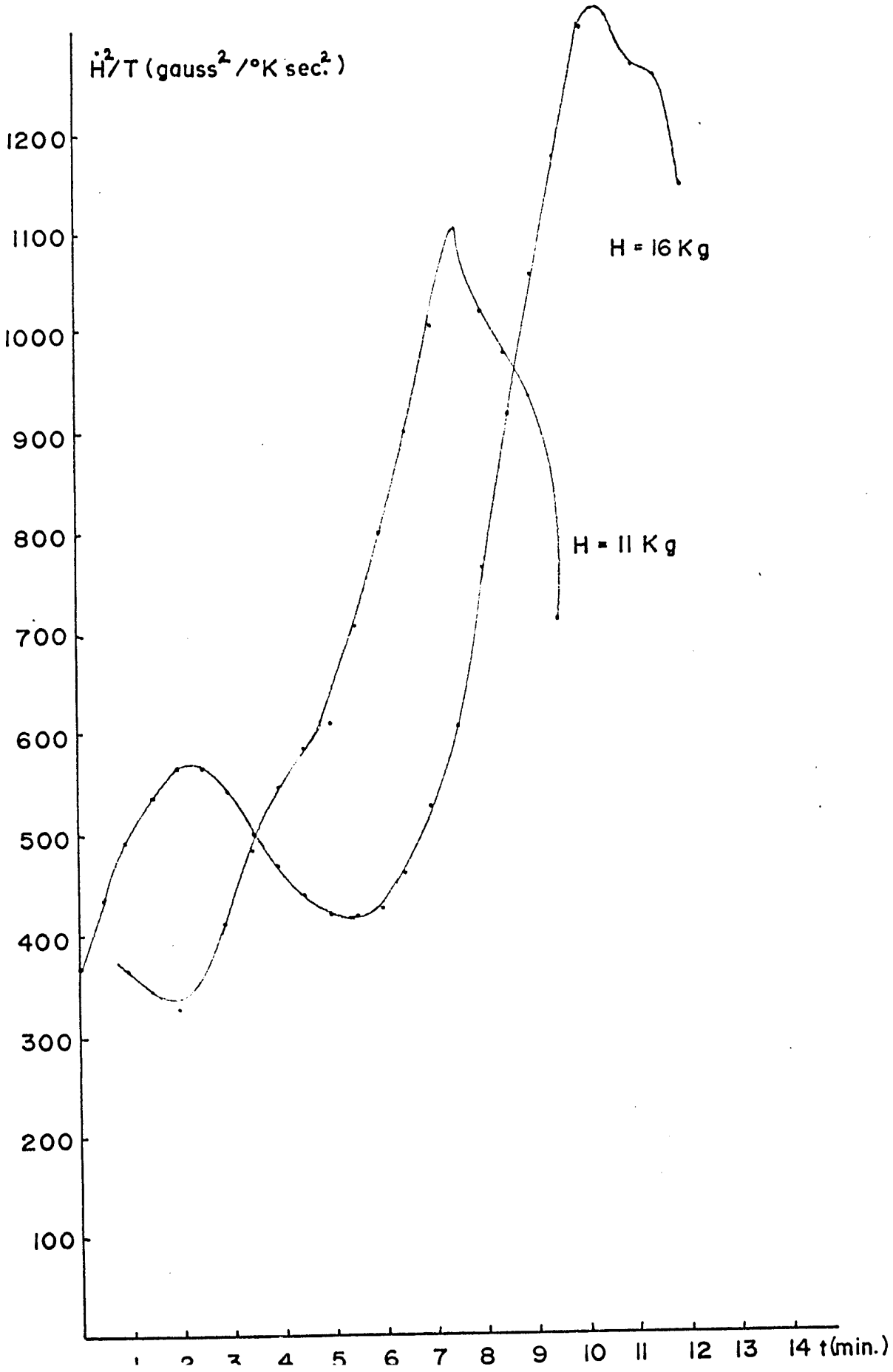


Fig.23 Temperature vs. time during the demagnetization


$\dot{H}^2/T$ (gauss^2 /°K sec^2)
1200
1100
1000
900
800
700
600
500
400
300
200
100
H = 16 Kg
H = 11 Kg
1
2
3
4
5
6
7
8
9
10
11
12
13
14 t(min.)

$$K' = \frac{\int dQ}{\int H\, dt}$$

Finally ΔS (Eddy) was obtained as

$$\Delta S(\text{Eddy}) = K' \int \frac{\dot{H}^2}{T} dt$$

where the value of the integral is the result of the numerical integration of the curve in fig. 24 .

Δ S (Enthapy):

As shown in I-12

$$S\ (\text{Enthalpy}) = \gamma (T_i - T_f) + \beta/3\, (T_i^3 - T_f^3)$$

In order to calculate this quantity the constants γ and β are needed . For obtaining them a heat capacity measurement was performed on the empty addenda in the liquid He region . These experimental results are displayed in fig. 25 . Plotting them as C/T vs. T^2 a straight line was obtained yielding an intercept of $\gamma = .08$ mJ/^oK and a slope of $\beta = .019$ mJ/ $^oK^4$, for $T < 2.5^oK$.

ΔS (Enthalpy) was then calculated for all fifteen demagnetization experiments , using the initial and final temperatures obtained .

Δ S (Heat leak):

To calculate this quantity , the heat leaks were measured after the demagnetization of the specimen . The measurement consisted of recording the temperature as a function of time resulting from the natural warming of the specimen toward the

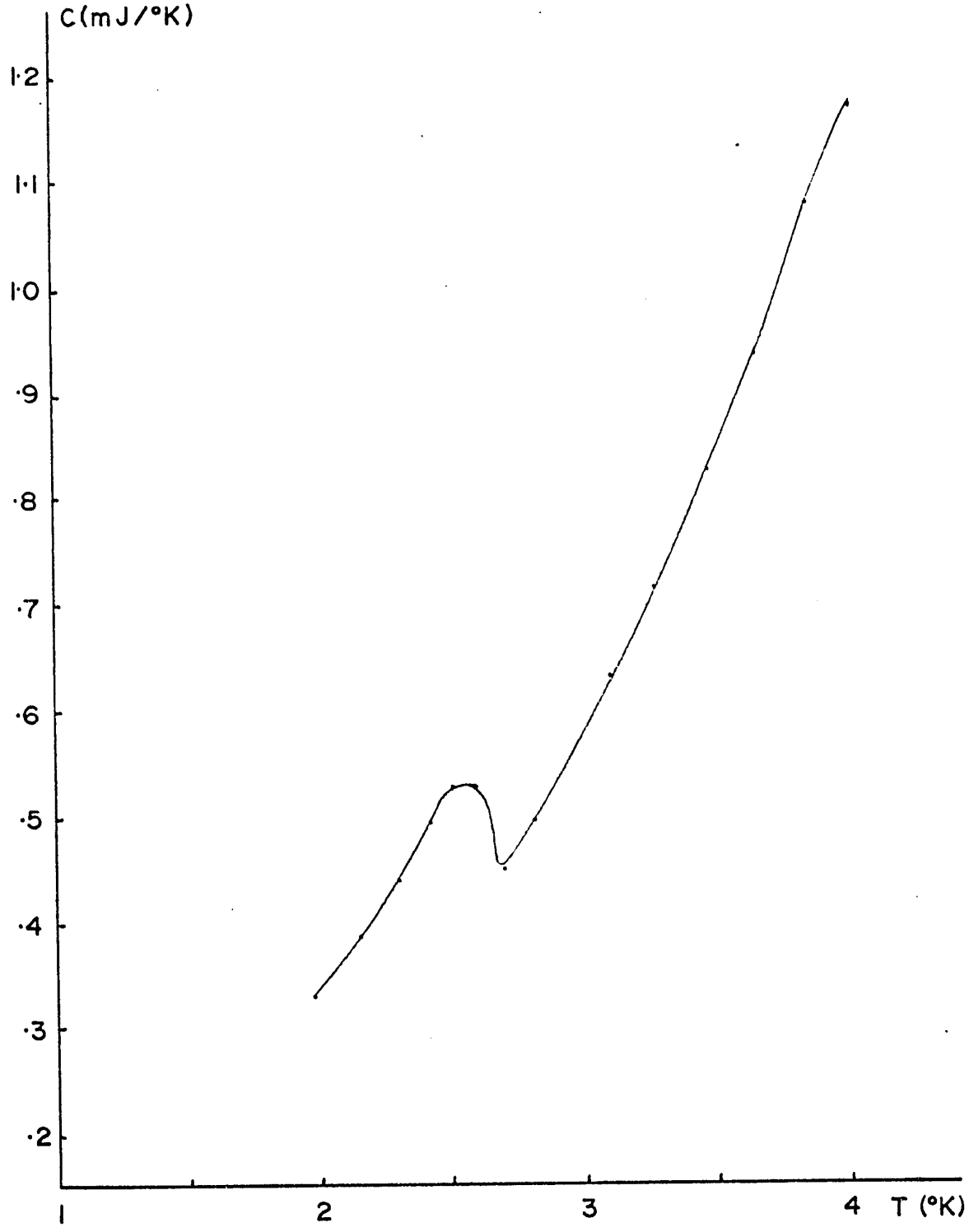


Fig. 25 Heat capacity of the addenda

temperature of its surroundings . Using the total heat capacity previously measured the heat leak per sec. $\dot{Q}$ was calculated . Dividing $\dot{Q}$ with the appropriate temperature from fig.23 the values of $\dot{Q}/T$ were obtained and they are displayed in fig. 26 Integrating this curve numerically

$$\Delta S \text{ (Heat leak)} = \int (\dot{Q}/T)\,dt$$

is obtained .

Finally

$$\sum(\Delta S/R) = 1/R \left\{ \Delta S(\text{Eddy}) + \Delta S(\text{Enthalpy}) + \Delta S(\text{Heat leaks}) \right\}$$

is plotted in fig. 26 .

For calculating the absolute temperatures the equation (I-12-1) is used :

$$(T/T^*) = \frac{C^*}{-x\frac{\partial S}{\partial x}\left[1 - \frac{1}{x_f}\frac{\partial \alpha}{\partial T^*}\right]}$$

Using S_f the corresponding values of x_f are obtained from the Hull and Hull (1941) tables together with $(-x\frac{\partial S}{\partial x})$.

For calculating $\frac{\partial \alpha}{\partial T^*}$, $\alpha - x_f T^*$ was plotted as a function of T^* (see fig. 27) and from this curve the necessary slopes were calculated .

Using $C^*(T^*)$, $(-x\frac{\partial S}{\partial x})$, x_f and $\frac{\partial \alpha(T^*)}{\partial T^*}$ the calibration relation for T^* was plotted in fig. 28

For converting the $C^*(T^*)$ values into $C(T)$ the relation $C = C^*/(T/T^*)$ was utilised , and the results are shown in fig. 29 .

For the purpose of comparing the measured value of CT^2/R with that predicted by Low (1957) and also by Walsh(1964)

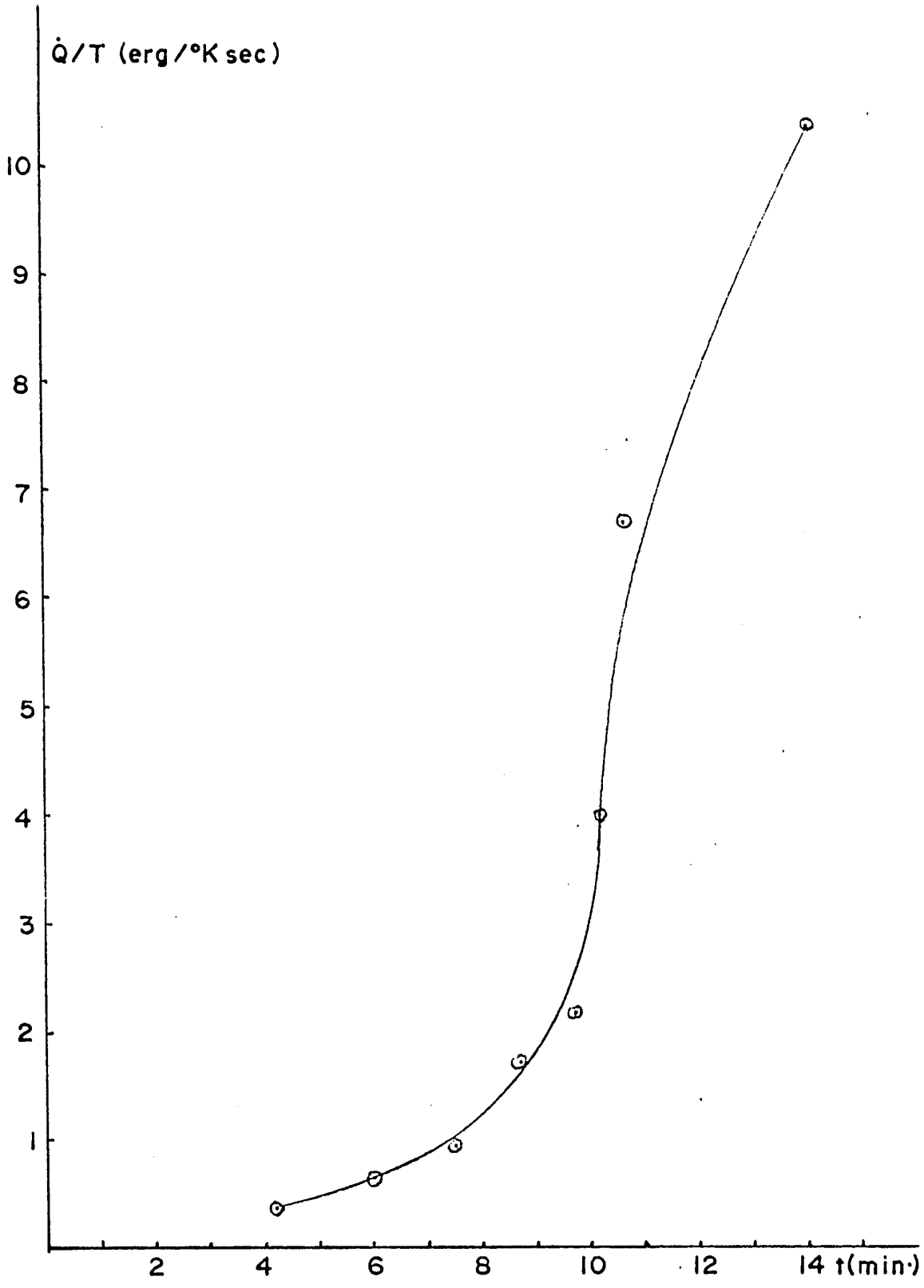


Fig. 26 $\dot{Q}/T$ vs. t

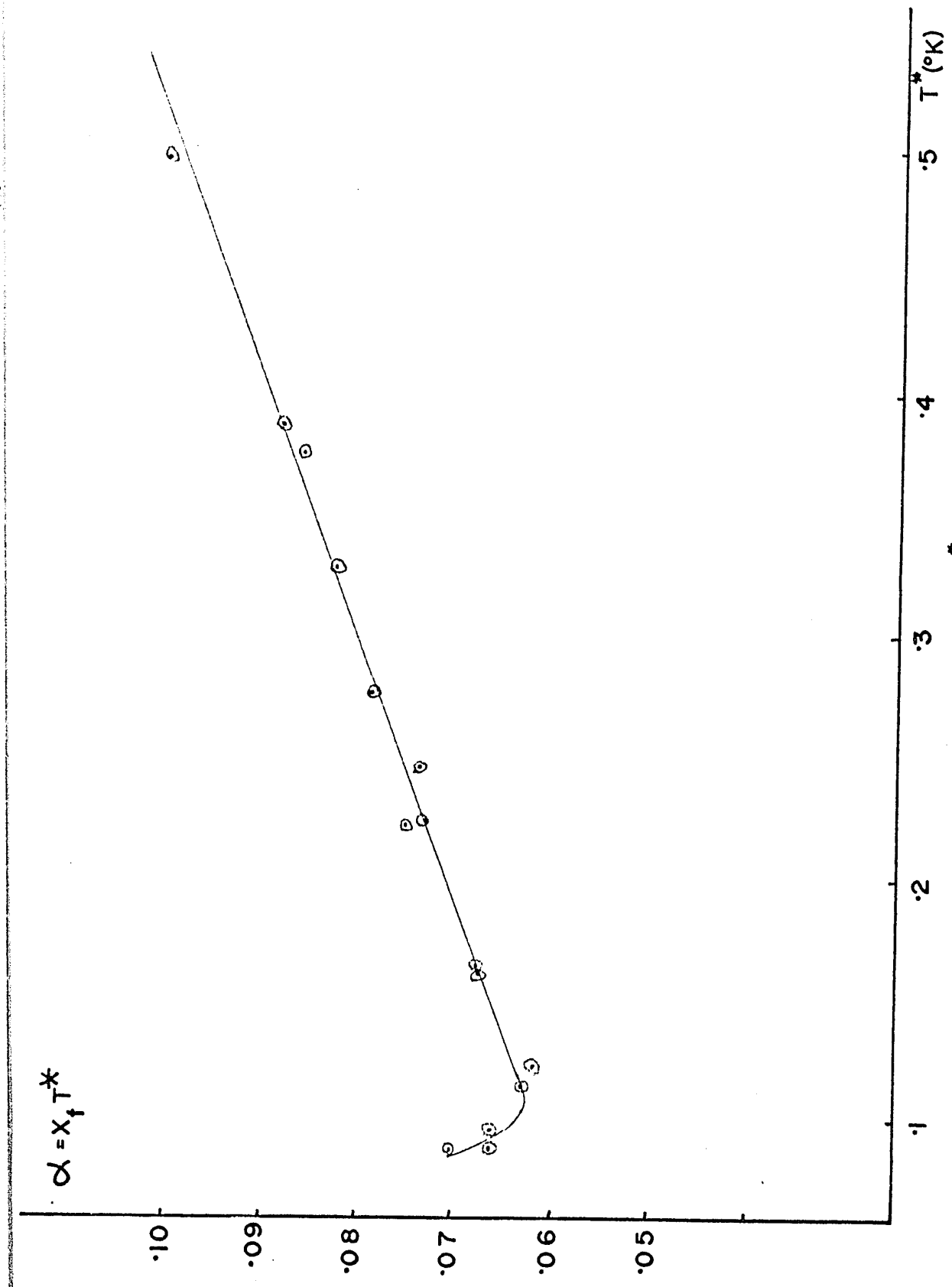


Fig.27 α vs T*

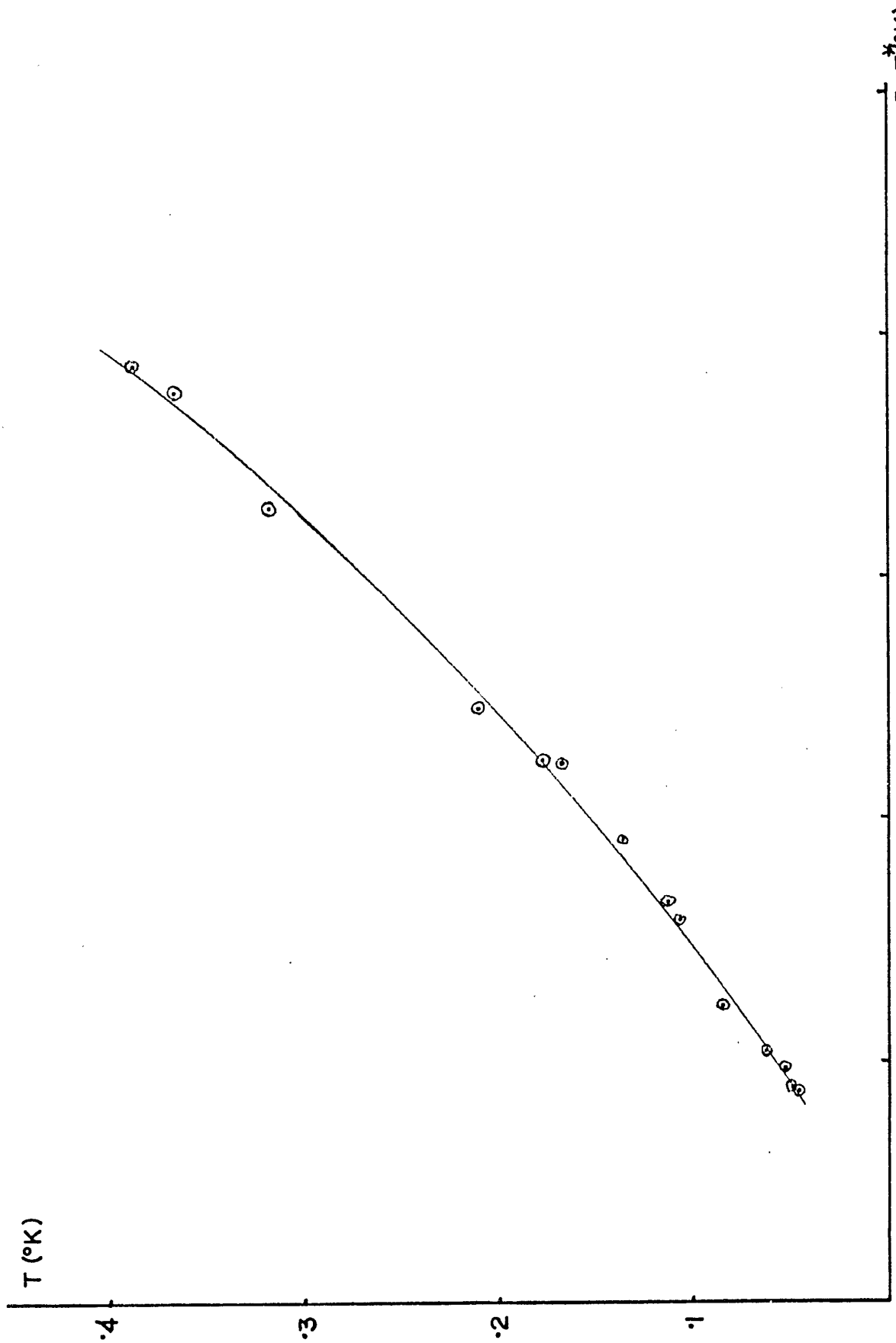


Fig.28 T vs T*

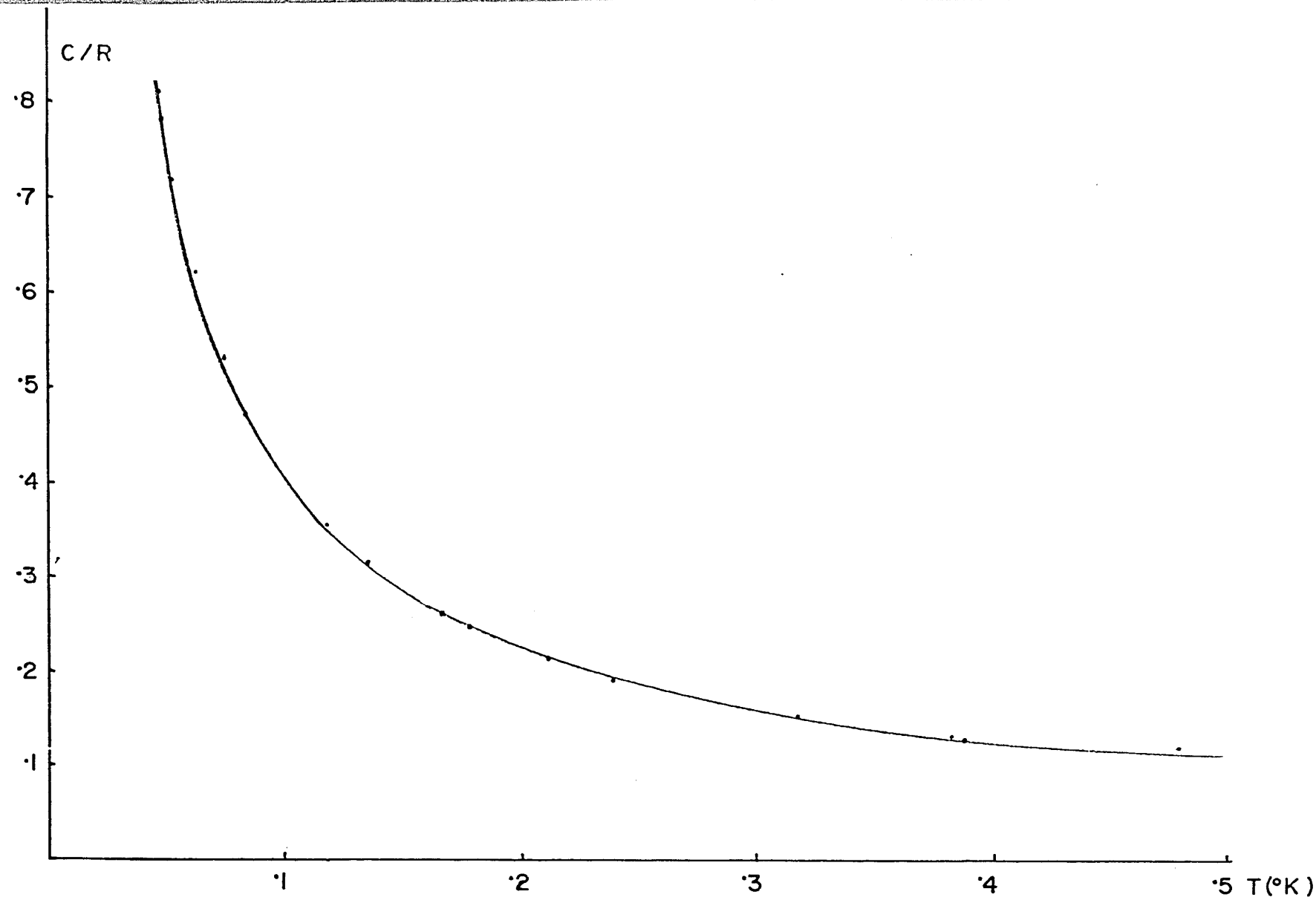


Fig.29 C/R vs. T for MgO:Mn

C/R was plotted as a function of $1/T^2$ (see fig. 30). The initial slope gives $CT^2/R = 6 \times 10^{-3}$ as compared with the predicted value of 3.66×10^{-3} .

The cause of this disagreement may lie in the fact that in the temperature region where the specific heat should be $1/T^2$ dependent the heat capacity of the addenda is of the same order of magnitude as that of the MgO specimen . Consequently in subtracting the heat capacity of the addenda fairly large systematic errors could be introduced into the calculations of the specific heat of the paramagnetic substance . These errors will become insignificant at lower temperatures where the heat capacity of the addenda will be very much smaller than the specific heat of the MgO specimen .

An additional explanation is necessary to the foregoing discussion .

When calculating the entropy corrections and also (T/T^*) it was assumed that $\sum \Delta S$ and C^* were the quantities per one mole of Mn^{2+} ions . Thus for converting them into values per mole , a certain concentration of Mn in MgO had to be assumed . If the concentration as given by the manufacturer of this specimen of .182% was used , unreasonable values of (T/T^*) were obtained . For this reason all the calculations leading to the value of (T/T^*) at $T^* = .5\ ^{o}K$ were repeated for different assumed concentrations in the range of .182% to .025% , and the results are plotted in fig. 31 . It is seen that a concentration of .0325% gives the expected value of $T/T^* \simeq 1$ at $T^* = .5^{o}K$. This is about 5.5-times less than the nominal concentration .

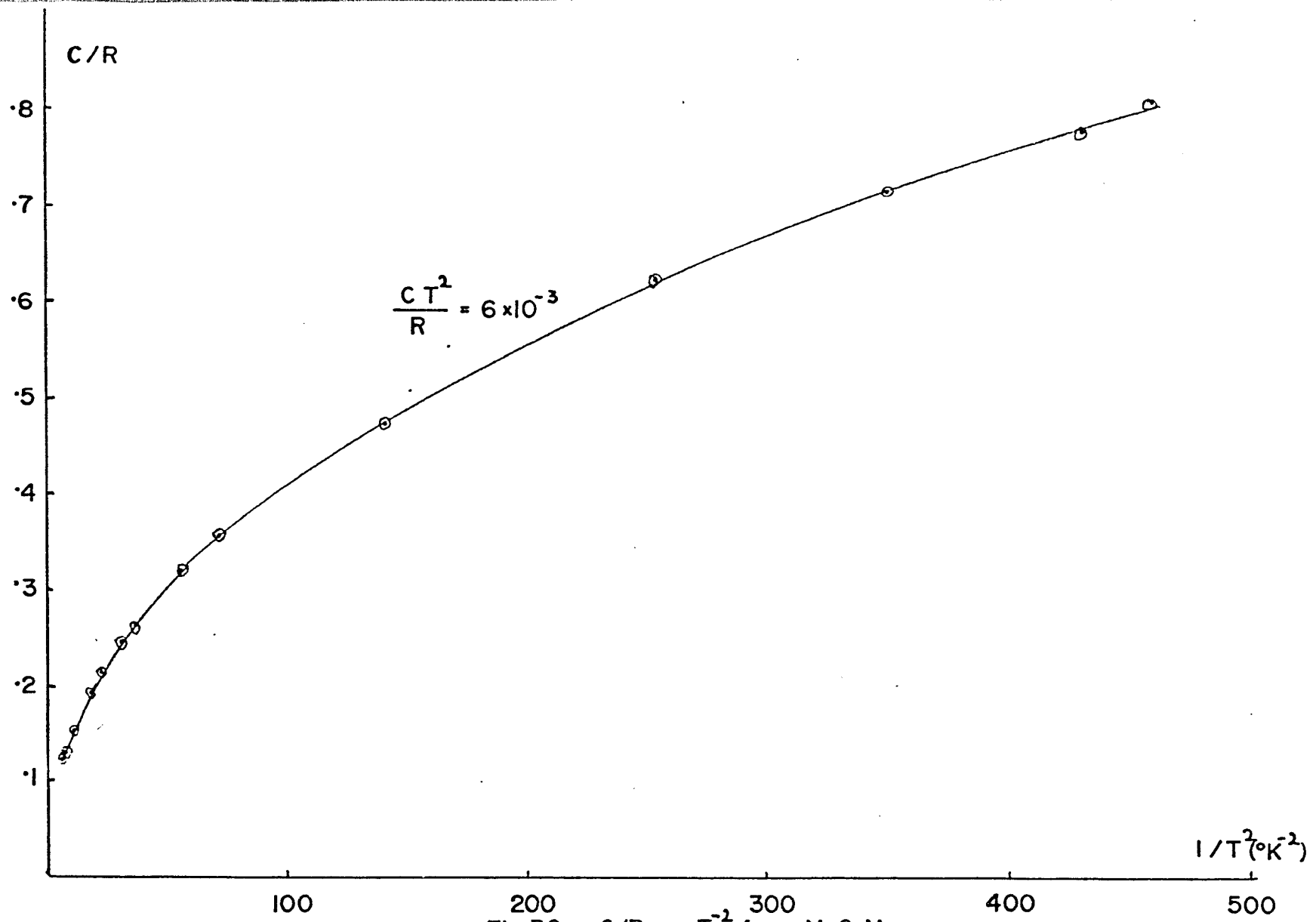


Fig.30 C/R vs. T^{-2} for MgO:Mn

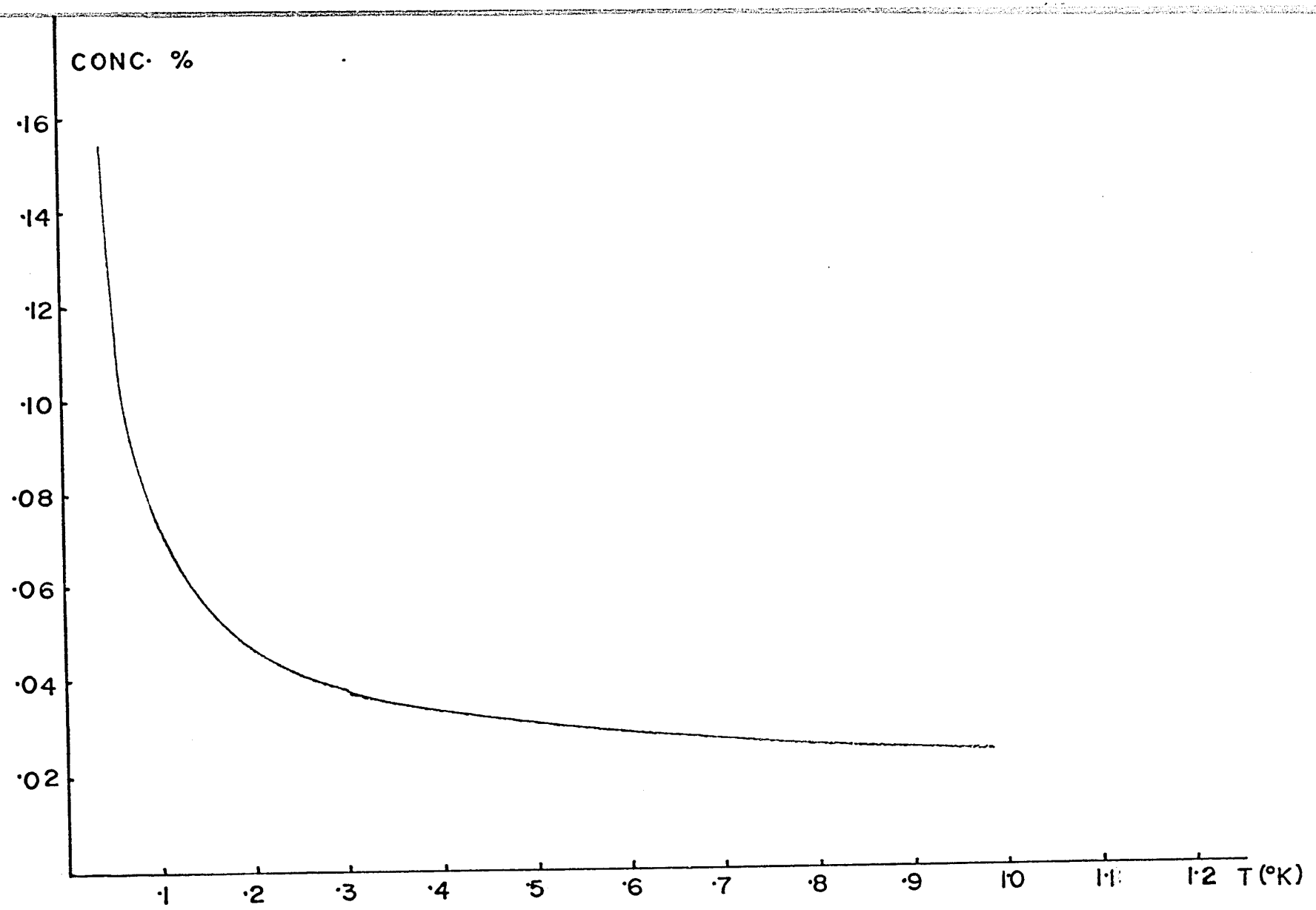


Fig.31 Concentration % vs. T

Discussion .

The experimental results indicate that the carbon resistor is a useful secondary thermometer down to at least 10^{-2} ^{o}K. In a way it is more convenient than the susceptibility because of the ease of measuring its resistance , its independence of the magnetic field , its negligible heat capacity and the relative ease of making good thermal contact between it and the specimen . Also at very low temperatures for determining temperatures by measuring susceptibility it is necessary to shape the paramagnetic substance into sphere or ellipsoid to be able to account for the demagnetizing field , whereas when carbon resistor is used the shape of the specimen is immaterial..

The MgO crystal proved to be a good medium for housing magnetic atoms . The speed of thermal exchange between the metallic heater and the crystal (less than about 1.5 - 2 secs even at $T^{*} \simeq .04^{o}K$) and also the straightness of the cooling lines indicate a good thermal conductivity of the interface , good lattice heat conductivity and also short spin-lattice relaxation time i.e. good coupling between the lattice vibrations of the MgO and the spins of the unfilled electron shell of the Mn ions . The lattice entropy of the MgO specimen at $1^{o}K$ is about $1/3\ 10^{-6}$ mJ/mole deg. and the entropy of the Mn ions is about 2.5 mJ/mole deg. of MgO . This is more than six orders of magnitude larger than the lattice entropy , and is very much better than the values found at any of the conventional paramagnetic substances .

CHAPTER III .

III-1 Specific heat of pure Mg and of Mg:Ce alloys below 4.2°K .

In chapter II the desirable properties of the paramagnetic substances capable of attaining temperatures below 1°K were discussed . Of these properties , the relatively good heat conductivity at low temperatures , the ease of making thermal contact , and the physical and chemical stability are readily met in most metals . Therefore it is worth conidering the possibility of producing paramagnetic alloys , i.e. non-magnetic metals doped with magnetic atoms , for cooling purposes .

It is well known that appreciable lowering of the temperature can be achieved by adiabatic demagnetization if there is a large magnetic entropy present which can be reduced with an external magnetic field .

In many paramagnetic salts the lattice entropy left at 1°K (for most salts used $\Theta \sim 100^{\circ}K$) is

$$\frac{S}{R} \approx \int_0^1 \frac{1}{T} 240 \left(\frac{T}{\Theta}\right)^3 dT \approx 10^{-4}$$

In the case of metals the Debye Θ is higher in general , thus representing a lower entropy . It is however supplemented by the entropy of the conduction electrons ($S/R = \gamma T/R \sim 10^{-4}$) . The magnetic entropy , on the other hand , for one mole of paramagnetic salt of $J = 1/2$ amounts to

$$\frac{S}{R} = \ln(2J+1) \approx .7$$

which is several orders of magnitude larger than the lattice entropy .

Thus , in making alloys suitable for cooling purposes , one must introduce sufficient number of magnetic atoms into the metal in order to make the magnetic entropy ,

$$\frac{S}{R} = \text{Concentration} \times \ln (2J + 1)$$

very much larger than the entropy of the conduction electrons and the lattice at about $1^{o}K$.

An other point needs to be emphasized . The equations quoted above for the magnetic entropy represent the total entropy of a completly disordered system of dipoles . The lowering of the temperature , however , will result in a progressive ordering of these dipoles due to the mutual interaction energy between them , and also between the dipoles and the surroundings . The ordering on the other hand will result in a reduction of the entropy (with an associated increase in the specific heat) . The ordering for most paramagnetic salts used for cooling begins at liquid He temperatures or below .

In the case of paramagnetic alloys , however , the magnetic ordering is expected to commence at much higher temperatures because in addition to the interaction energy of dipoles present in non-metallic paramagnetic substances , there will be a further , indirect exchange interaction between the dipoles via the conduction electrons , as explained by Ruderman and Kittel (1954) . Also , as shown by several experimenters (see eg. Crane and Zimmerman (1961) , Zimmerman and Hoare (1960))

the temperature at which the ordering of the dipoles will begin , will be higher for higher concentrations .

When the magnetic atom belongs to the iron group , the magnetic electron shell (3d) being nearly directly exposed to the sea of the conduction electrons , the ordering temperature is expected to be high .

When on the other hand the magnetic atoms belong to the rare earth group the indirect exchange interaction is expected to be much smaller the magnetic shell being well screened from the conduction electrons . Liu (1961) and de Gennes (1958) have shown that T_c (temperature at which magnetic ordering occurs) varies as $N(JS)^2/J(J+1)$ for the rare earth elements . Here N is the number of the magnetic dipoles per cm^3 , J is the angular momentum of the magnetic shell , and S the spin of the conduction electrons . According to Parks and Little (1961) the smallest T_c should occur for Ce , Yb and Er .

A rather successful attempt at cooling with rare earth alloys has been reported by them using Thorium - Erbium alloys . At approximately the same time our laboratory has obtained 10 specimens of Mg doped with various concentrations of Ce for similar purposes .

In this chapter , then , the calorimetric measurements performed on these specimens for $T < 4.2^{\circ}K$ will be discussed . The results obtained will be analysed primarily for the pur-

pose of estimating the entropy loss in the measured temperature interval , together with some estimate of the temperature at which the magnetic ordering begins . Also as one of the samples is relatively free of magnetic impurities it was convenient to measure its specific heat and compare the values obtained for γ and Θ with the previously published values of Mg .

III-2 Description of the Mg:Ce specimens .

All the specimens were in the form of cylinders of 1" diameter and 1.3/4" long . They were prepared for us by the Dominion Magnesium Co. with nominal concentrations of Ce as shown in table III .

Specimen	Concentration Wt. %
#1	0.90 % Ce
#2	0.70 % Ce
#3	0.47 % Ce
#4	0.36 % Ce
#5	0.26 % Ce
#6	0.19 % Ce
#7	0.15 % Ce
#8	0.06 % Ce
#9	0.02 % Ce
#10	less than 0.007% magnetic impurities

Table III

X-ray pictures taken of these samples indicated a definite clustering of the Ce atoms in specimens #1 and #2 . For this reason these samples were excluded from the analysis what follows . The rest of the photographs displayed different states of annealing of the specimens .

III-3 Results .

Fig.32 and table IV shows the specific heat of the Mg:Ce specimens measured in the range of $T < 4.2^{\circ}K$. For the sake of clarity only the data for specimens #1 , #2 , #4 , and #10 are plotted . It is seen that the specific heat in this temperature interval, at any temperature increases with increasing concentration of the magnetic impurities . In fig. 33 C/T vs. T^2 is plotted . Here also for similar reason only the data for specimens #1 , #2 , #4 , #9 , and #10 are displayed . This is a conventional way of analysing the low temperature specific heat data of metallic substances . The least square fitting of the data obtained for the purest specimen according to the equation $C = \gamma T + \beta T^3$ gives $\gamma = 1.12 \pm .01$ mJ/mole$^{\circ}$K and $\theta = 337.9 \pm 2.1^{\circ}K$. The value of γ obtained does not agree with any of the previously published values . (See table V) The cause of this disagreement may be due to the possible magnetic impurities present in the specimens used by these workers . Martin (1961) has measured the specific heats of two specimens of Mg doped with 0.025% and 0.15% Mn respectively . His results indicate that the specific heat is a very sensitive function of the Mn concentration . At $1^{\circ}K$ the specimen having the concentration of 0.025% has about 20% higher heat capacity than a pure Mg specimen would have . Our results confirm this . If the specific heat data for specimens #8 and #9 are least square fitted simply as $C = \gamma T + \beta T^3$, we obtain the apparent value of

Table IV. Specific heats C(mJ/mole deg.) of the Mg:Ce specimens as a function of the temperature T(^{o}K) . The temperatures for T<1.2^{o}K were obtained by extrapolation of the Speer resistor . For concentrations see table III.

T	C	T	C	T	C	T	C
#1							
.216	1.062	2.238	6.293	4.822	9.506	1.210	2.288
.242	1.208	2.524	6.691	4.285	10.637	1.466	2.711
.270	1.135	2.669	7.170	#3		1.664	3.026
.299	1.307	2.868	7.602			1.863	3.280
.330	1.426	3.077	8.002	1.360	3.269	2.084	3.601
.368	1.475	3.329	8.938	1.480	3.408	2.297	3.954
.415	1.624	3.592	9.280	1.593	3.676	2.594	4.486
.433	1.603	3.863	10.102	1.697	3.971	2.931	5.196
.468	1.766	4.144	11.750	1.814	4.117	3.145	5.693
.491	1.775	#2		1.958	4.474	3.253	5.874
.524	1.962	1.397	3.736	2.139	4.793	3.424	6.503
.545	1.851	1.517	3.941	2.320	5.137	3.566	6.806
.582	2.190	1.641	4.056	2.320	5.127	3.742	7.301
.593	2.125	1.757	4.257	2.447	5.377	3.816	7.418
.638	2.143	1.870	4.505	2.481	5.452	4.073	8.235
.690	2.588	2.007	4.712	2.629	5.757	4.108	8.627
.754	2.574	2.169	4.881	2.685	5.931		
.838	2.979	2.315	5.034	2.838	6.169	#5	
.921	3.422	2.451	5.300	3.098	6.773	1.393	2.245
.997	3.632	2.588	5.646	3.139	6.843	1.501	2.412
1.071	4.177	2.787	5.951	3.354	7.376	1.622	2.592
1.148	4.642	2.393	5.248	3.369	7.481	1.770	2.756
1.224	4.654	2.536	5.453	3.589	8.119	1.956	3.075
1.347	4.335	2.676	5.918	3.607	8.084	2.150	3.420
1.425	4.782	3.033	6.558	3.836	8.538	2.368	3.805
1.486	5.125	3.077	6.442	3.884	8.771	2.586	4.216
1.558	5.200	3.278	7.000	4.063	9.408	2.596	4.062
1.629	5.360	3.306	7.037	4.195	9.973	2.784	4.481
1.702	5.436	3.549	7.680	4.240	10.294	2.991	4.953
1.767	5.524	3.578	7.791	#5		3.119	5.533
1.966	5.724	3.828	8.504			3.256	5.860
2.100	5.945	3.852	8.587			3.550	6.570

Table IV cont'd

T	C	T	C	T	C	T	C
3.865	7.481	4.154	8.796	2.427	3.754	.633	.774
4.188	8.824	#8		2.556	4.263	.645	.763
#6		1.322	1.942	2.576	3.803	.698	.818
1.433	2.138	1.427	1.992	2.685	4.152	.692	.814
1.580	2.301	1.530	2.132	2.791	4.347	.748	.874
1.718	2.576	1.624	2.524	3.001	4.899	.743	.884
1.871	2.773	1.767	2.536	3.062	5.008	.796	.942
2.014	3.040	1.952	2.828	3.266	5.594	.830	.984
2.144	3.228	2.165	3.191	3.268	5.436	.850	1.013
2.295	3.577	2.432	3.676	3.496	6.093	.913	1.075
2.461	3.859	2.457	3.703	3.586	6.299	.930	1.104
2.636	4.228	2.641	4.072	3.762	6.799	.986	1.169
2.657	4.252	2.684	4.163	3.833	6.819	1.004	1.206
2.794	4.562	2.839	4.556	4.010	7.714	1.071	1.292
2.873	4.670	3.072	5.132	4.104	7.965	1.076	1.250
3.103	5.290	3.104	5.165	4.289	8.523	1.180	1.402
3.149	5.258	3.332	5.670	#10		1.180	1.378
3.315	5.774	3.425	6.003			1.247	1.476
3.446	6.204	3.583	6.578	.206	.337	1.261	1.515
3.581	6.408	3.728	6.812	.233	.345	1.286	1.597
3.744	7.245	3.859	7.328	.264	.387	1.332	1.629
3.869	7.221	4.146	8.221	.304	.418	1.346	1.667
4.004	7.911	4.160	8.488	.345	.466	1.390	1.714
4.224	8.745	#9		.354	.468	1.392	1.730
#7		1.399	1.914	.392	.526	1.443	1.807
2.500	4.080	1.527	2.071	.414	.528	1.455	1.808
2.703	4.493	1.637	2.272	.424	.516	1.467	1.828
3.061	5.425	1.740	2.465	.456	.576	1.490	1.846
3.252	5.887	1.868	2.653	.492	.604	1.518	1.916
3.458	6.510	2.204	3.181	.528	.640	1.537	1.870
3.710	7.202	2.222	2.822	.528	.669	1.561	1.993
3.928	7.936	2.387	3.478	.563	.687	1.591	2.076
				.600	.733	1.647	2.091

Table IV cont'd

T	C
1.664	2.245
1.723	2.184
1.802	2.294
1.877	2.408
1.985	2.585
2.137	2.827
2.288	3.100
2.428	3.377
2.622	3.692
2.859	4.280
3.082	4.872
3.299	5.493
3.563	6.231
3.876	7.280
4.137	8.300

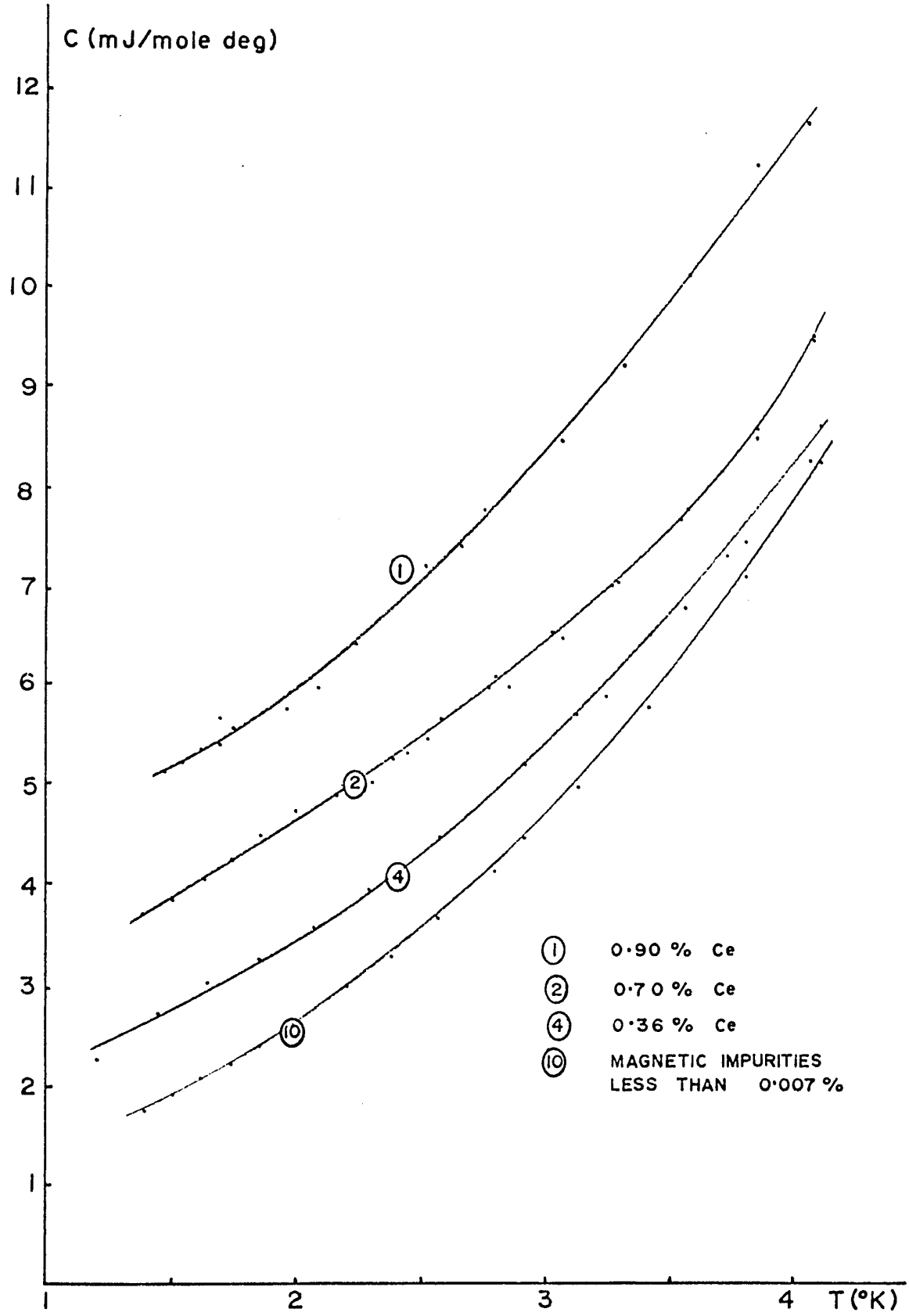


Fig.32. Specific heat of Mg and of Mg:Ce alloys

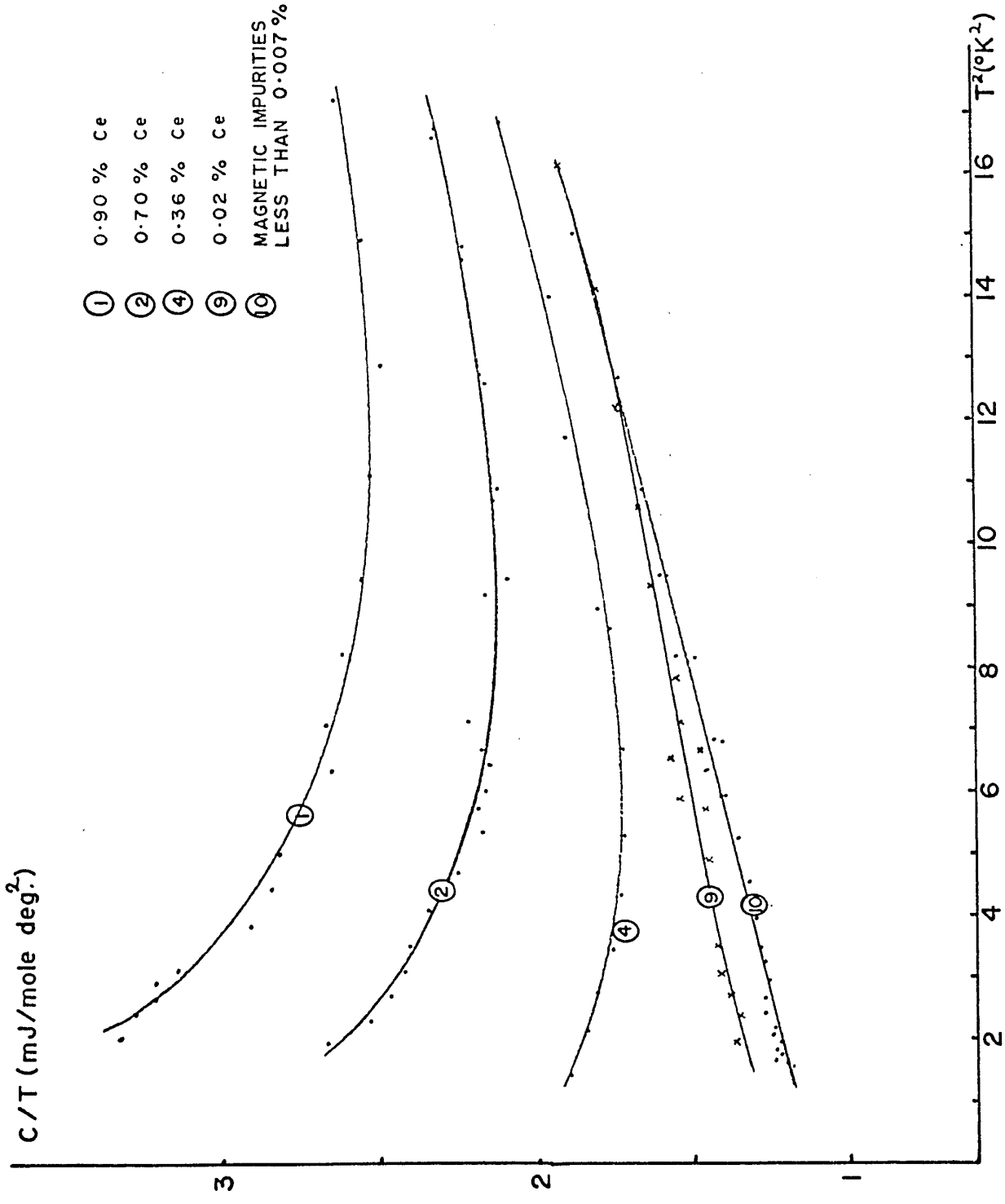


Fig.33 C/T vs. T^2 for Mg and of Mg:Ce alloys

γ	Θ	Purity	Reference
1.36	342	99.96%	Esterman et.al.(1952)
1.32	406	?	Smith (1955)
1.28	390	0.013%Fe 0.043%Mn	Logan et.al. (1957)
1.12 ± .01	337.9±2.1	0.007% total magnetic	This work
1.26 ± .02	367.3±6.8	0.02%Ce	
1.26 ± .02	356.7±3.6	0.06%Ce	

Table V

γ as quoted in the table V , in agreement with the first three values in that table .

For specimens of higher concentration of Ce there is a definite minimum , followed by an increase of C/T with decreasing temperature . The temperature at which the minimum occurs T_m as a function of the Ce concentration is displayed in fig. 34 Specimen #7 is not included in this figure because its heat capacity was not measured at sufficiently low temperatures .

We can estimate the entropy associated with the excess specific heat in the measured temperature interval .

Let us assume that the Ce atoms representing the magnetic dipoles are randomly distributed throughout the lattice of the Mg . The total entropy required to disorder C moles of magnetic moments associated with spin 1/2 is given by

$$S = RC \ln 2$$

Assuming further that the spin of the Ce atoms in the lattice of Mg is 1/2 (this assumption may not hold strictly because

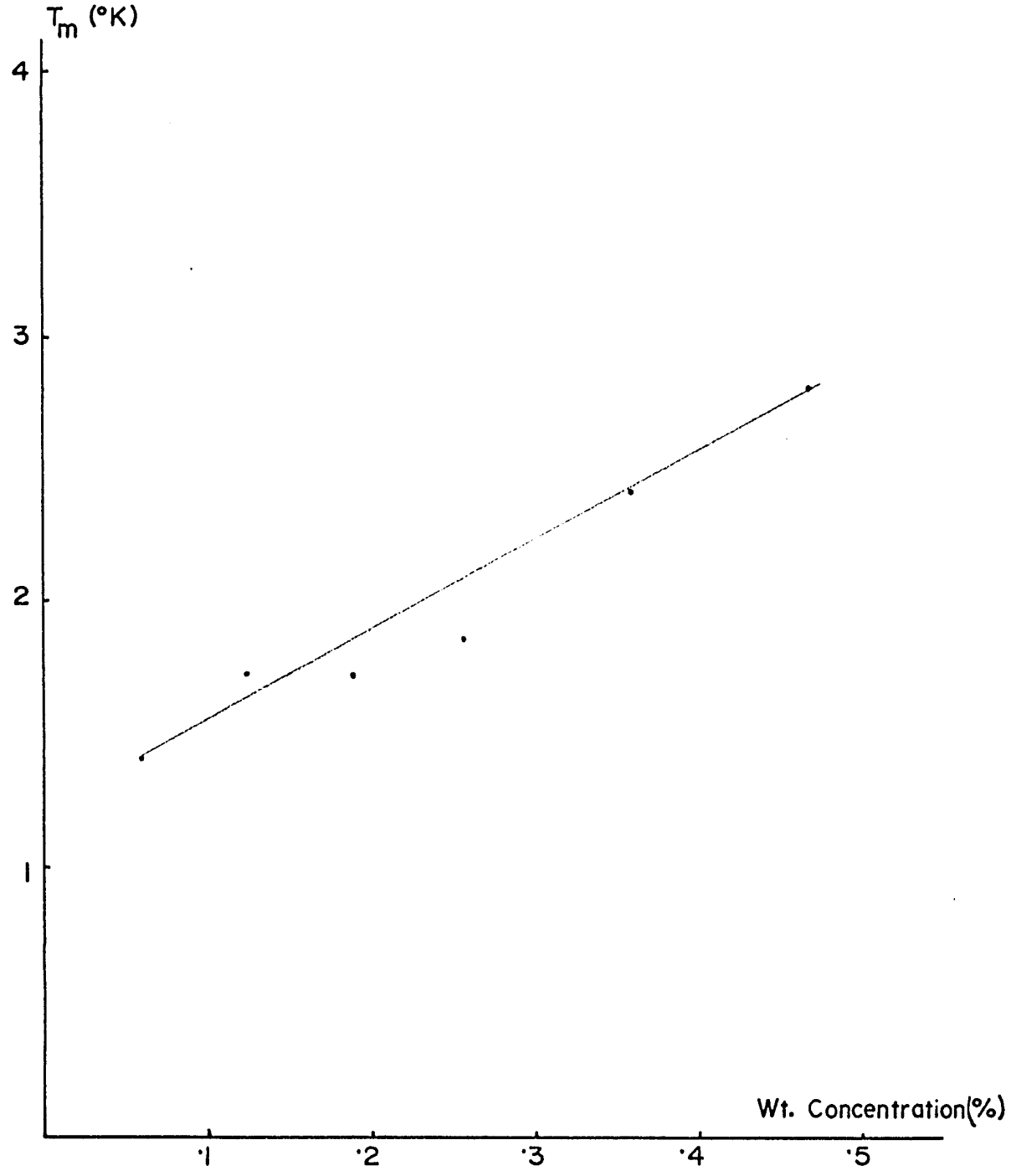


Fig.34 T_m vs. Wt. concentration

it may happen that the 4f electron is partially promoted to the 5d shell as noticed by Matthias et.al.(1958)) , then the calculated entropy can be plotted as a function of the Ce concentration as shown in fig.35a .

In order to determine the entropy from the measured specific heat excess , the quantity $\Delta C/T$ is plotted against T . This is shown in fig.36 . The entropy then , using its definition equation

$$\Delta S = \int \frac{\Delta C}{T} dT \quad \text{where } \Delta C = C(\text{alloy}) - C(\text{Mg})$$

can be calculated in the measured temperature range by performing a numerical integration of the curves in figs. 36a, and b. The resulting ΔS thus obtained are also displayed in fig. 35b .

According to fig.35 if the spin of Ce is 1/2 then , for most specimens between 1.2 and 4.2°K the excess specific heat accounts for the ordering of a large portion of the available Ce spins .

The curves in fig.36 on the other hand indicate that most of the remaining spin disorder will be removed below 1.2°K and only a small fraction of it above 4.2°K .

The temperature at which the magnetic ordering begins can also be estimated from the curves of fig. 36. The extrapolation yields values between 3.8 and 5.5°K .

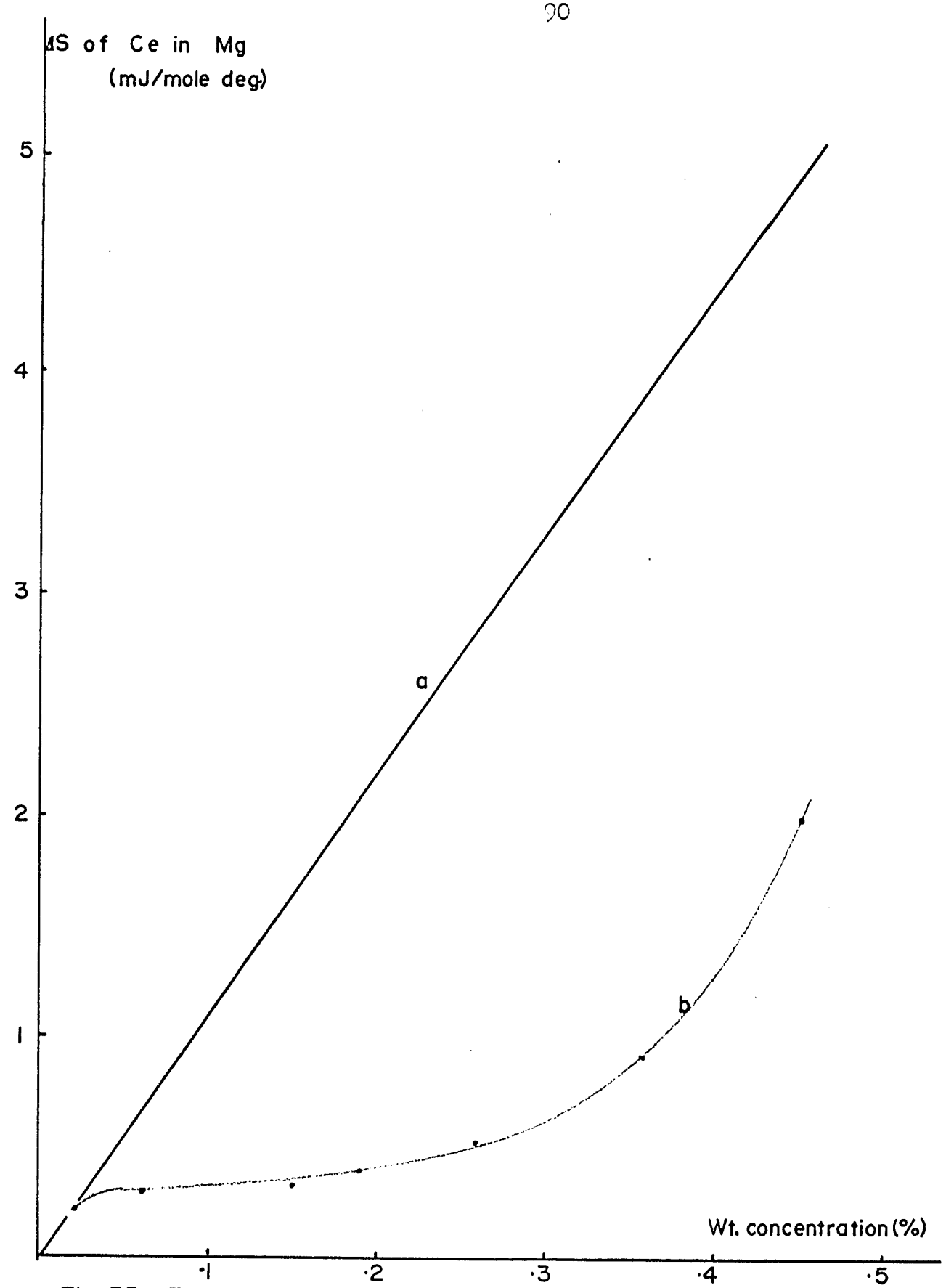


Fig. 35 Entropy vs. concentration for Mg Ce alloys
a : Total entropy due to the Ce
b : Entropy loss between 1·2 and 4·2° K

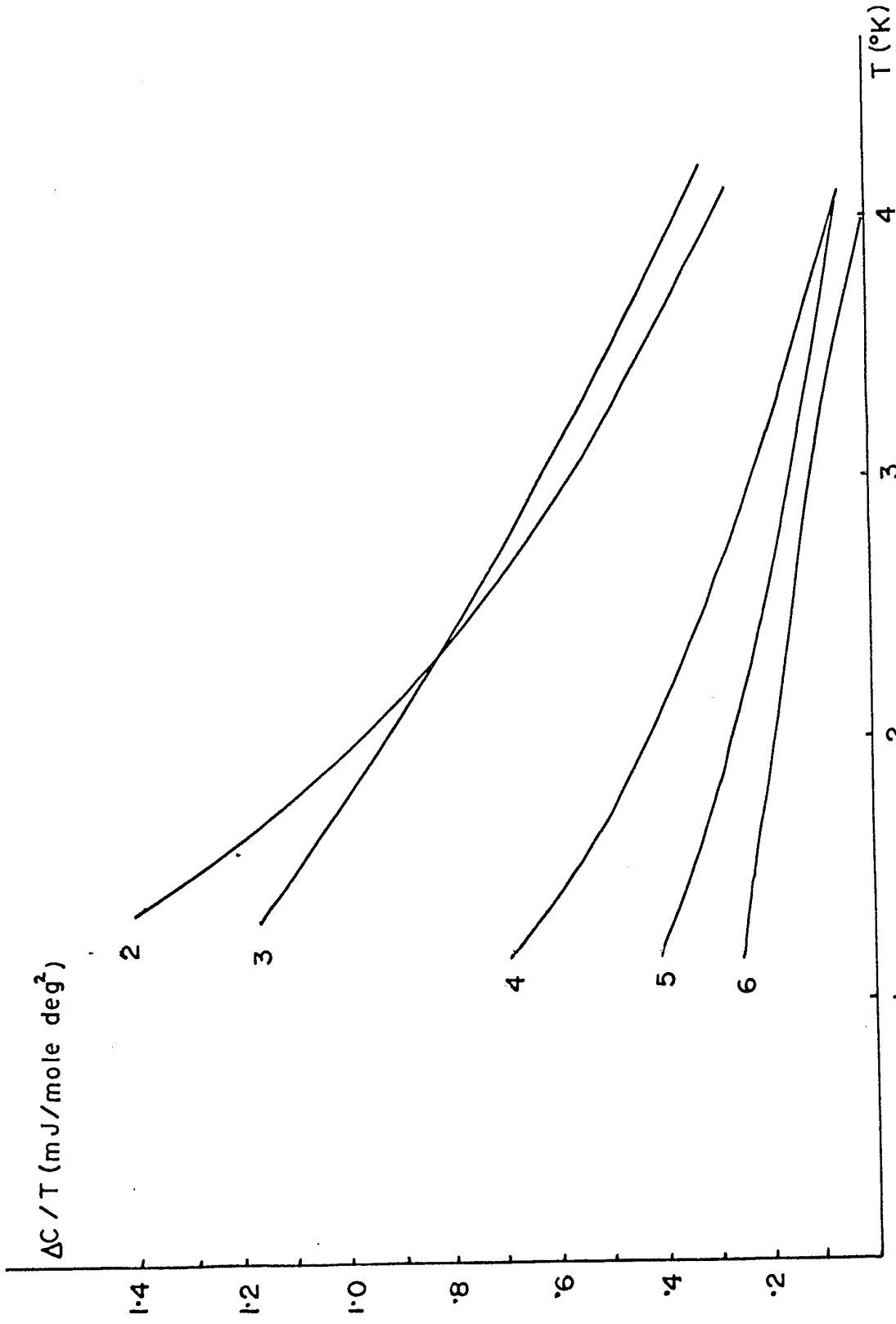


Fig.36a ΔC/T vs. T for Mg:Ce alloys

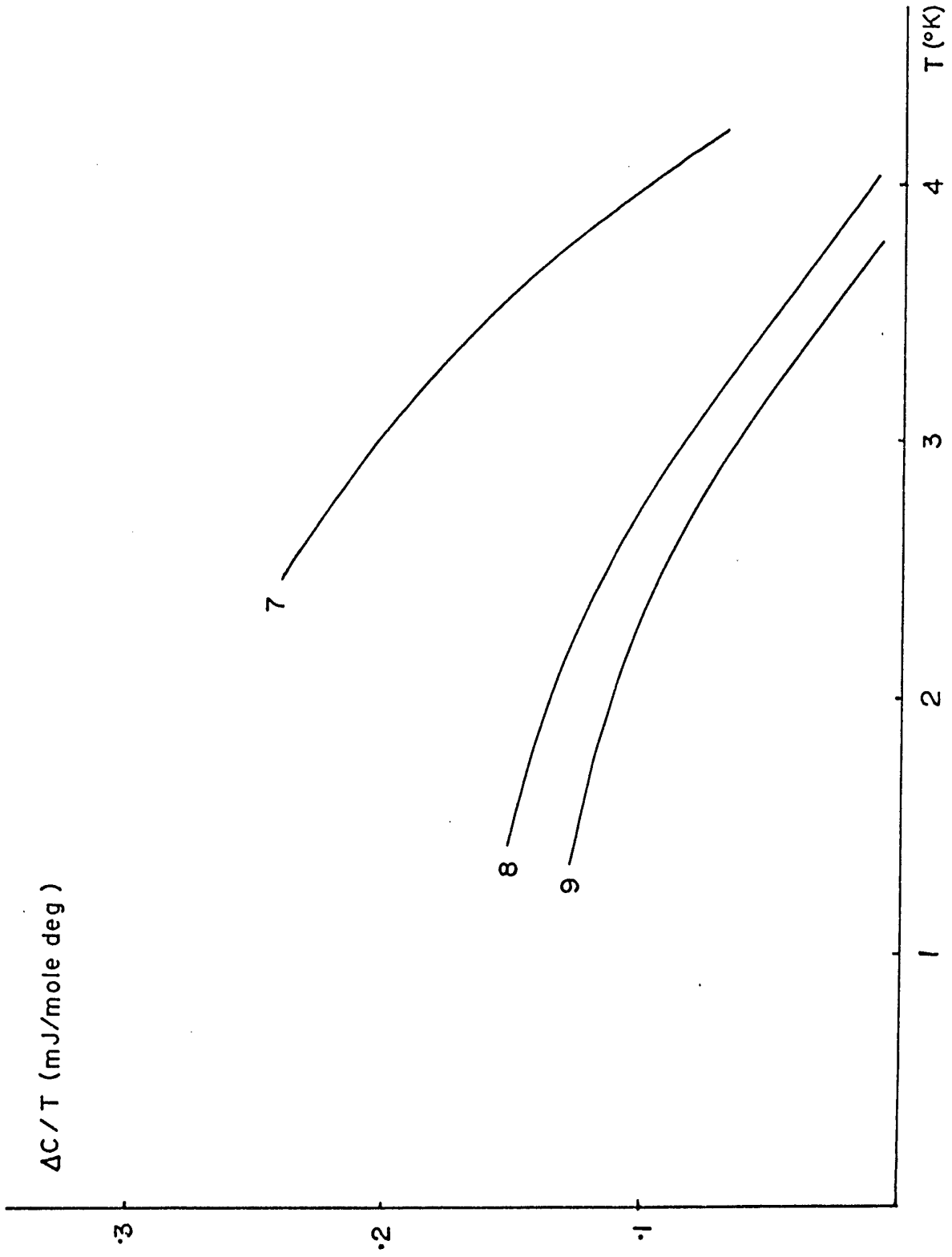


Fig.36b ΔC/T vs. T for Mg : Ce alloys

III-4 Discussion .

The entropy left at 1.2°K due to the still disordered Ce dipoles for the most concentrated specimens is between one and two mJ/mole deg. of Mg. The lattice and the electronic entropies on the other hand are 10^{-2} and 1.3 mJ/mole deg. respectively . I.e. the magnetic entropy due to the Ce is approximately the same as the thermal entropy due to the Mg.

One could argue that by going to lower temperatures the entropy due to the conduction electrons might drop faster than the magnetic entropy and thus at lower temperatures the magnetic entropy may become very much larger than that due to the conduction electrons . This would mean that this alloy system might become a useful paramagnetic substance for the lowering of the temperature by adiabatically demagnetizing it from that temperature region . This however is very unlikely to happen . Overhauser (1959) and also Marshall (1960) have investigated theoretically the specific heat behaviour of alloys of this types . They conclude that the expression for the specific heat excess for low temperatures should be proportional to the absolute temperature , in agreement with the measurements of Zimmerman and Hoare (1960) , performed on Cu:Co alloys .

It seems then that the Mg:Ce alloy system investigated in this work does not meet the requirements necessary for paramagnetic substances useful for attaining low temperatures .

CHAPTER IV .

IV-1 Establishment of the absolute temperature scale at low temperatures . A proposed method .

Absolute temperatures (for $1 < T < 4^{o}K$) in practice are measured using secondary thermometers calibrated against the vapour pressure of liquid He^4 . Between $3.5^{o}K$ and about $.3^{o}K$ the vapour pressure of liquid He^3 can similarly be used .

Below about $1^{o}K$ and $.3^{o}K$ for the liquid He^4 and He^3 respectively the vapour pressures are so small that it is difficult to do precise measurements with conventional manometers . For this reason and also due to the difficulty of attaining still lower pressures , other temperature sensitive properties are desirable for the determination of the absolute temperatures .

In a widely used method paramagnetic substances obeying Curie's law are utilised in the temperature region $T \gg T_c$ where T_c is the paramagnetic Curie temperature . As T approaches T_c however the Curie law will no longer give a good description of the susceptibility of the paramagnetic substance . Fortunately the 2^{nd} law of thermodynamics can be utilised .

$$T = \frac{dQ}{dS} = \frac{dQ/dT^*}{dS/dT^*}$$

where T^* is a parametric temperature . In this case it can be the temperature obtained from the Curie-Weiss law . In order to calculate T a series of adiabatic demagnetizations can be performed thus obtaining S vs. T^* relationship , together with dQ/dT^* , the parametric specific heat . According to the 2^{nd} law then , by forming the ratios of $\frac{dQ/dT^*}{dS/dT^*}$, the absolute tem-

peratues can be obtained . In practice this involves a long series of experiments . A similar procedure was followed in Chapter II , using a carbon resistance thermometer instead of the susceptibility as a secondary thermometer .

There are other possibilities . Nuclear radiation for instance is an other probe for the determination of the absolute temperatures below $1^{o}K$. In this case the fact is used that the angular distribution of the emitted γ- rays is a function of the nuclear orientation which in turn depends on the temperature .

Our proposal is that the specific heat of a pure non-magnetic substance can also be used as a primary thermometer for the determination of the absolute temperatures . It is well known from the theory of the specific heats that at sufficiently low temperatures for metals and insulators the specific heats are of the form :

$$C = aT + bT^3$$

and $$C = cT^3$$ respectively .

Here aT is the specific heat due to the conduction electrons and bT^3 is the lattice contribution to the specific heat . At any temperature T the heat supplied ΔQ to the specimen can be written as :

$$\Delta Q = \frac{\Delta Q}{\Delta T}^{*} \Delta T^{*} = C^{*} \Delta T^{*}$$

$$= \frac{\Delta Q}{\Delta T} \Delta T = C \Delta T$$

where C^* and ΔT^* are the measured specific heat and temperature differences determined by the thermometer to be calibrated and C and ΔT are the absolute specific heat and absolute temperatures respectively . Integrating these expressions :

$$\int_{T_i}^{T_f} C\, dT = \int_{T_i^*}^{T_f^*} C^*\, dT^*$$

where T_i and T_f are the initial and final absolute temperatures respectively , T_i^* and T_f^* are the corresponding temperatures as determined by the thermometers used . If T_f^* or T_i^* are taken in the temperature interval where there exists a calibration of the secondary thermometer , the only unknown T_i^* or T_f^* can be calculated .

This method in principle does not seem to have a lower limit of applicability for pure substances with no nuclear spin .

IV-2 Application .

In order to illustrate an application of the above described proposed method, we have selected the measured specific heat for pure Mg (Chapter III) . At the same time the data illustrate the usefulness of the double heat switch .

The procedure of the measurements together with the purity of the sample has already been discussed (see III-2 and I-7) . The results of the measurements for $1.2^{\circ} < T < 4.2^{\circ}K$ gave $a = 1.12$ mJ/mole deg.^{2} and $b = .0505$ mJ/mole deg.^{4} . The details of the calibration for the Speer resistor #2

(see Table II) for temperatures $T < 1.2^{o}K$ is as follows :

$$\int_{T_i^*}^{T_f^*} C^* dT^* = \int_{T_i}^{T_f} (aT + bT^3)\, dT$$

Let $$A = \int_{T_i}^{T_f} C^* dT^*$$

and $$B = (a/2)T_f^2 + (b/4)T_f^4$$

then $$A = B - (a/2)T_i^2 - (b/4)T_i^4$$

$$(b/4)T^4 + (a/2)T^2 + (A - B) = 0$$

finally $$T_i = \sqrt{\frac{-(a/2) + \sqrt{(a/2)^2 - b[A - B]}}{(b/2)}} \quad \text{.....IV-2-1}$$

Here A can be obtained by numerical integration of the curve in fig. 39 .

It turns out that if the numerical integration is carried out in such a way that T_f^* is kept constant say at $1.2^{o}K$ and the lower limit of the integration T_i^* changes from T_f^* on then the error in T_i will be large for the lowest temperatures . In order to increase the accuracy of the calculations , the upper limit T_f is taken to be the lower limit of the previous interval . (See fig.37)

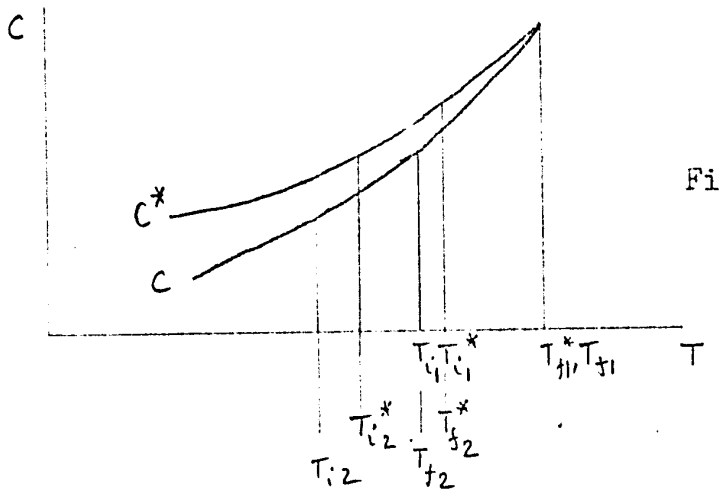


Fig.37 Illustration for taking the upper limit of calculations .

The calibration relation for the Speer resistor #2 obtained from the data displayed in fig. 39 is shown in fig. 38 .

IV-3 Discussion .

Unfortunately the calibration can not be carried much below .4°K . The reason may be the following :
Referring to the work of Martin(1961) on Mg:Mn alloy of .025 % Mn concentration a noticable deviation in the specific heat begins from a nearly straight line at about .7°K . From then on the deviation of the specific heat from the value of pure Mg increases with decreasing temperature . Our specimen contains about 1/3rd or less of the magnetic impurities Martin's specimen had . The rise in the specific heat is therefore expected to begin at lower temperature and to a lesser degree . This rise is sufficiently large however to make the square bracket in equation IV-2-1 positive , and thus the resulting T_i imaginary , below .3°K .

This does not indicate a shortcoming of our calibration proposal , because it is caused by the impurity of the specimen for which we made no allowance in the derivation of the calibration equation . If the specific heat of a substance is known in the desired temperature interval , whatever its temperature dependence may be our calibration procedure can be applied .

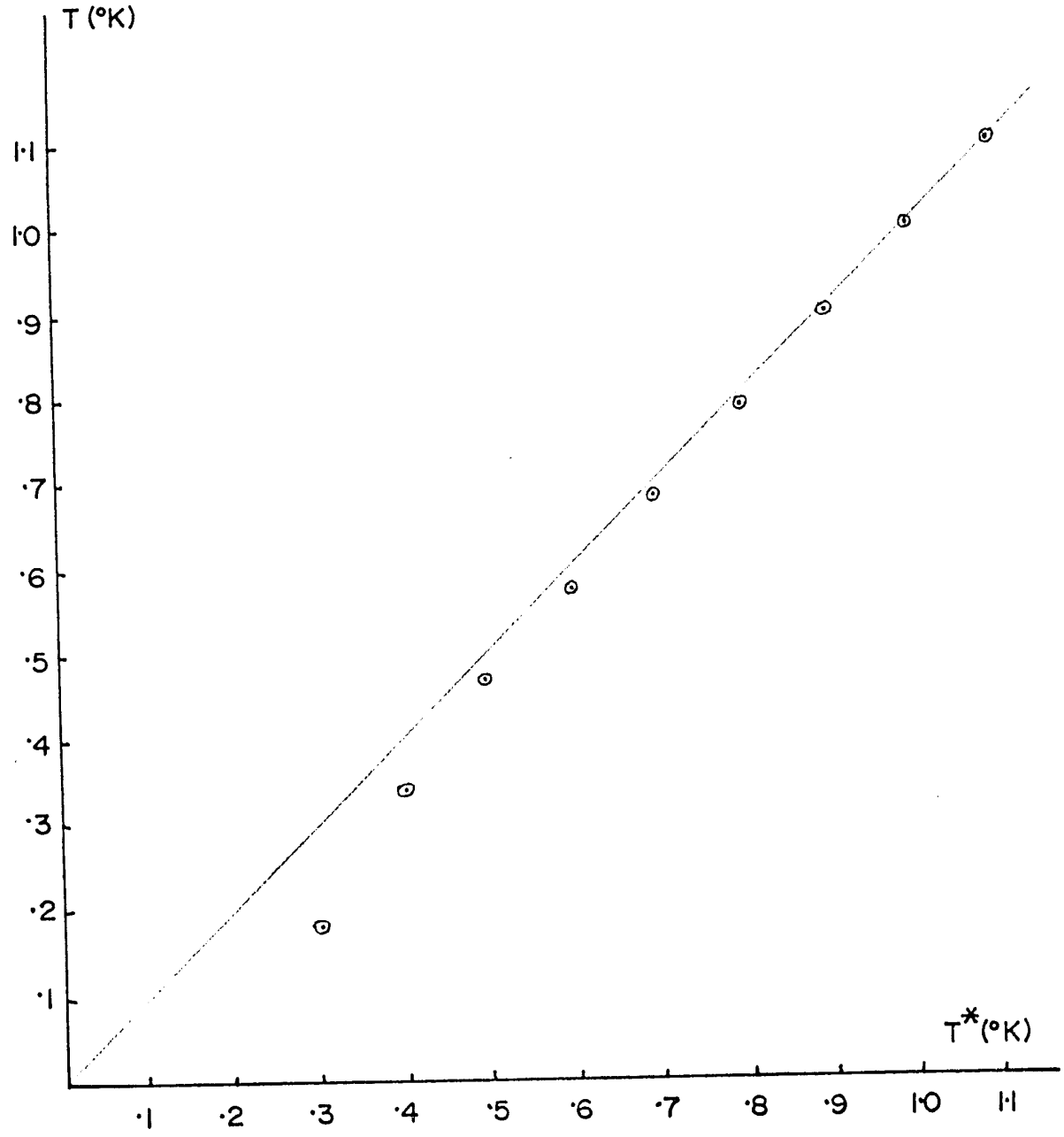


Fig. 38 Calibration relation of Speer resistor no.2 obtained using equation (4-2-1)
dots : calculated points
solid line : $T = T^*$

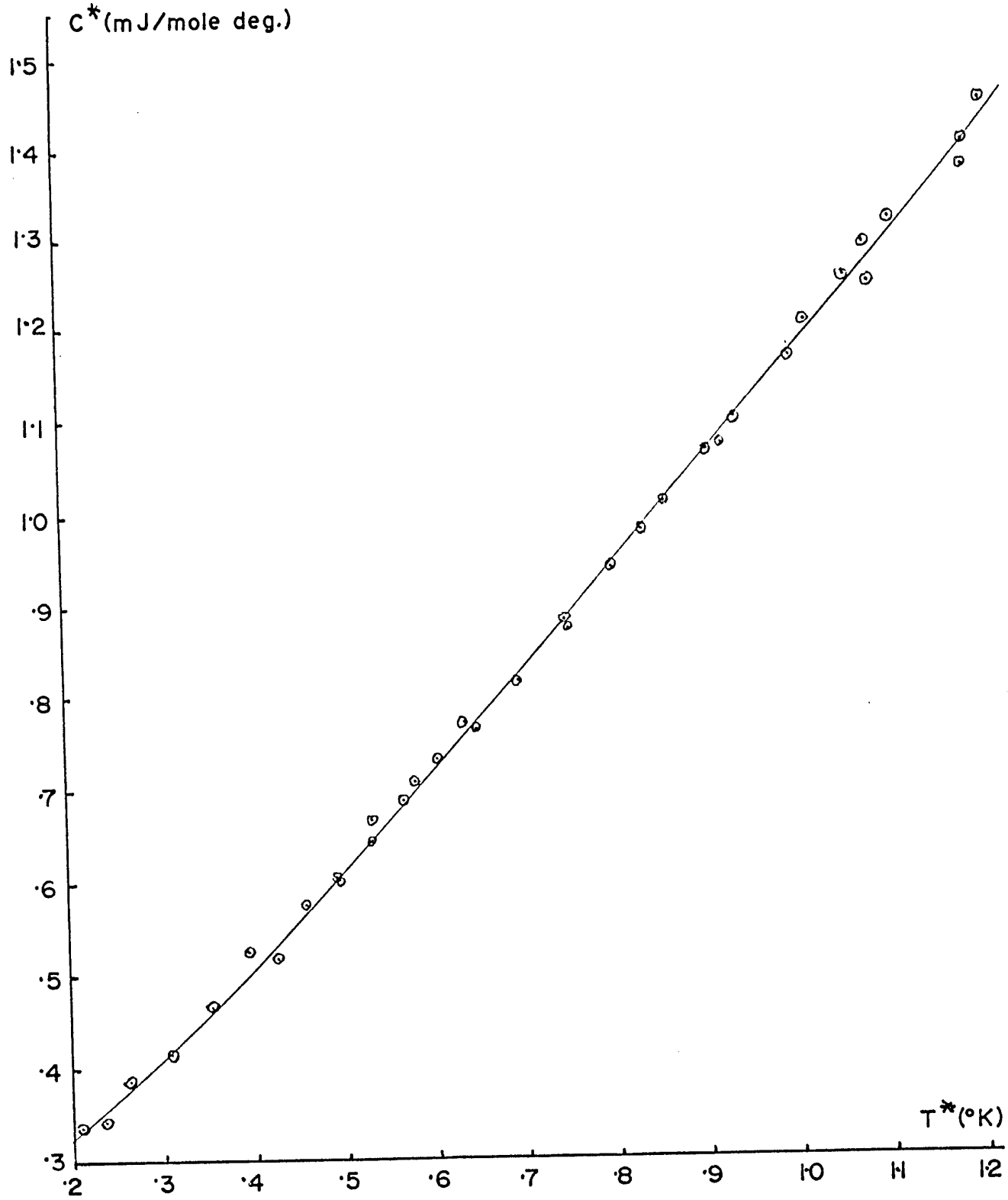


Fig. 39 C^* vs T^* for "pure" Magnesium

Conclusions .

A., Analysing the data in the light of the desirable properties of the paramagnetic substances suitable for appreciable lowering of the temperatures below $1^{o}K$ it was found that the crystal of MgO:Mn is well suited for this purpose .Its magnetic ordering temperature is below $.04^{o}K$ for the concentration of .0325 % where it has a specific heat maximum of $C(max.)/R \geq .7$. This quantity compares favourably with the conventional salts used for cooling other substances .

Several further investigations are possible along this line: The temperature at which the magnetic ordering occurs as a function of the concentration might be of some practical use . It would also shed some light on the strength of the dipole dipole interaction .

It would also be of interest to try other doping materials in MgO in order to see if the heat capacity per cm^3 of MgO can be raised appreciably without shifting too much the peak of the specific heat .

Spin lattice relaxation time measurements would also be of importance in order to learn more about the speed of the energy transfer from the lattice to the spin system .

B., The results obtained for the Mg:Ce alloys indicate the unsuitability of this particular alloy system for adiabatic demagnetization . The magnetic entropy being approximately of the same value as that of the conduction electrons , the total

entropy is not as sensitive function of the temperature as necessary .

It is interesting to note that the interaction leading to the magnetic ordering is probably of the same nature as that found in Cu:Co alloys . It seems to be different from that of Cu:Mn where the specific heat has a different behaviour . The resistivity behaviour of these two classes of alloys are also different . The Cu:Mn alloys have have a resistivity minimum and a maximum at low temperatures whereas the Cu:Co alloys have resistivity minimum only at these temperatures . It would be interesting to perfcrm resistivity measurements on our Mg:Ce alloys in order to see if their resistivity is similar to that of the Cu:Co system .

C., The specific heat as a suitable thermometric quantity is shown to be worth considering . It is reasonably easy to obtain pure substances and it is also easy to reproduce specific heat data for a substance of a given purity . These qualities are of primary importance in the selection of a suitable thermometer. It is also shown that this method is easily applicable for the establishment of the absolute temperature scale below $1^{o}K$. It would also be a useful thermometer between $4.2^{o}K$ and $10^{o}K$ i.e. in the region where no liquids are available for calibration purposes and most other thermometers are not yet sensitive enough . The lattice specific heat on the other hand of any solid will become quite sizeble and will have at least T^{3} dependence .

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