SPECIFIC HEATS AND ENTROPIES AT LOW TEMPERATURES. HEAT OF ADSORPTION ZERO

BODLEIAN LIBRARY OXFORD
DEPOSITED
THESIS

ABSTRACT

The heat capacity of a substance can be measured under adiabatic or non-adiabatic conditions. Modern experimental techniques allow measurements made under adiabatic conditions to yield values for the specific heat accurate to 0.1%. However, knowledge of the solid state at low temperatures is still in the prospecting stage and new information that is accurate only to 1% or 2% is valuable. The non-adiabatic method with its comparatively simple apparatus and ability to produce more rapid results is, therefore, a useful technique to employ. The measurements on solid hydrogen below 4°K., and irradiated polythene from 15°K. to room temperature, are good examples of the proper application of the method.

The specific heat of solid hydrogen has been measured as a function of the ortho-para concentration from 0.2°K. to 4°K. There are two species of hydrogen molecule: ortho-hydrogen and para-hydrogen. The ortho-hydrogen molecule in its ground state is nine-fold degenerate, being

three-fold degenerate with respect to both the molecular rotation and the nuclear spin. The specific heat anomaly due to the lifting of the ground rotational level of the ortho-hydrogen was found by Simon, Mendelssohn and Ruhemann (1929) below 10°K. Hill (1956) repeated the measurements with improved experimental techniques, but was unable to make measurements below 2°K. using standard calorimetric practices, due to the spontaneous heat of conversion of the ortho- into para-hydrogen. The total anomalous entropy per mole of ortho-hydrogen above 2°K. was only 0.8 E.U. of the expected 2.10 E.U. (R Log 3).

In consequence, the experiments reported here were undertaken to extend the temperature range of the measurements down to 0.2°K. This was accomplished by a novel design of calorimeter. The calorimeter was made with two compartments. The first contained liquid helium and had a large diameter pumping tube attached to it; the second contained a powdered paramagnetic salt, iron alum, and the hydrogen specimen, which was condensed between the grains of the salt. By rapid pumping on the liquid helium it was possible to reduce the temperature of the calorimeter to 1.3°K., afterwhich a demagnetization of the iron alum

reduced the calorimeter and the sample temperature to 0.2°K. A time-temperature curve was taken until the calorimeter was above 2°K., as the rate of warm-up was too rapid for conventional specific heat points to be made. As it could be shown that the heating due to the ortho-para conversion was sensibly temperature independent, it was possible to calculate the specific heat of the sample from the slope of the heating curve and a knowledge of the heating rate. The heating rate was found from conventional specific heat measurements made above 2°K.

The results showed that at ortho-concentrations greater than 60%, a modified λ-anomaly existed in the temperature range 1°K. to 2°K. The form, height, and the temperature of the maximum varied with concentration. For 73% ortho-hydrogen, the peak is at 1.60°K. and 5 calories.degree^{-1}.mole^{-1} high, while with a sample of 63% ortho-hydrogen, a small peak, 1 calorie.degree^{-1}.mole^{-1} high, appears with a maximum at 1.12°K.

At ortho-concentrations below 60%, there is no λ-anomaly. The specific heat becomes appreciable at about 0.2°K., rises steeply until a temperature of about 0.6°K. has been reached, afterwhich it rises slowly to a maximum between 1°K. and 2°K., before falling steadily towards the triple point.

Whether a λ-peak occurs or not, the total entropy of the anomaly is the same within experimental error. The arithmetical average of the entropy for the different runs is 2.14 E.U., which is in excellent agreement with 2.18 E.U. expected theoretically from a lifting of a three-fold degenerate state.

The existence of a λ-point is consistent with the changes in the nuclear resonance spectrum reported by Hatton and Rollin (1949) and Reif and Purcell (1953) for normal hydrogen, and Sugawara et al (1955) for other ortho-hydrogen concentrations. These experiments only indicate whether or not transitions occur among the substates. They would have obtained the same low temperature resonance pattern, indicating no transitions among states, if the molecules were frozen into arbitrary substates. It is only the existence of the specific heat anomaly of the correct entropy, that indicates that an ordered state is obtained at very low temperatures.

These experiments also show that there is no indication of the entropy of mixing of the ortho- and para-molecules. Further, the rate of change of ortho-concentration was found from the libration of heat due to the ortho-para

conversion. If $\underline{o}$ is the ortho-concentration expressed in percent and t is the time in hours, then $\frac{d\underline{o}}{dt} = 1.79 \times 10^{-4} \underline{o}^2$. The constant is in good agreement with Gremer and Polanyi's value of 1.9×10^{-4}.

The specific heat of irradiated Polythene was measured from 15°K. to room temperature with standard calorimetric methods. This sample was the most heavily irradiated out of a set, the remainder of which was measured by Smith (1959). The specific heat per gram was smaller over the whole temperature range than the other polythenes. A theoretical calculation of the specific heat of normal polythene was made, which seemed to indicate that the rapid rise in specific heat of the polythene above 180°K. was due to molecular vibration at natural CH_2 characteristic frequencies, and not to a disorder change in the crystallites of the polythene, as had been assumed by previous workers.

The specific heat of Potassium Bromide was measured from 4°K. to room temperature. A comparison with the measurements of Clusius, Goldmann and Perlick (1949) indicated that their values between 40°K. and 80°K. were probably too high. The change in the Debye θ at low temperatures could be explained qualitatively with reference to Blackman's (1933, 1937) calculations.

References.

BLACKMAN, M. Z. Physic. 86, 421, 1933.

BLACKMAN, M. Proc. Roy. Soc., 159, 416, 1937

CLUSIUS, K., COLLMAN, J., PERLICK, A., Zeits. fur Naturforschung A 4, 425, 1949.

GREMER, E., POLANYI, M., Zeits.f.Phys.Chem. B 21, 459, 1933.

HATTON, J., ROLLIN, B.V., Proc. Roy. Soc., A 199, 222, 1949.

HILL, R.W., (To be Published), 1956.

HSIP, E., PURCELL, E.M., Phys. Rev. 91, 631, 1953.

SIMON, F.E., MENDELSSOHN, K., MUHLMANN, M., Naturwissenschaften 18, 34, 1929.

SMITH, P.L., Thesis, Oxford, 1954.

SUGAWARA, T., MASUDA, Y., KANDA, T., KANDA, E., Science Reports of the Research Institutes, Tohoku University, A 7, 67, 1955.

SPECIFIC HEATS AND ENTROPIES

AT LOW TEMPERATURES

A Thesis Submitted

for the Degree of

Doctor of Philosophy

in the

University of Oxford

B.W.A. RICKETSON
New College
OXFORD
1956

C O N T E N T S

Page

PREFACE

CHAPTER 1. NON-ADIABATIC CALORIMETRY 1

The Thermometric Parameter (x) 4

The Measurement of Δx 10

The Heating Period 16

Conclusion - Error in C_p 18

CHAPTER 2. LOW TEMPERATURE APPARATUSES 20

Apparatus I 21

Apparatus II 23

Apparatus III 24

Comparison of the Apparatuses 28

CHAPTER 3. THE SPECIFIC HEAT OF SOLID HYDROGEN

Part I - Experimental.

1. Introduction 31

2. Heat of Ortho-Para Conversion 37

3. The Plan 38

4. Design of the Apparatus 39

5. An Experiment 42

6. The Temperature Independence of the Ortho-Para Conversion 51

Part II - Results. Page

1. The Method of Calculation and the Accuracy of the Experiment 56

2. The Anomalous Specific Heat of Solid Hydrogen with ortho-concentrations greater than 60% 60

3. The Anomalous Specific Heat of Solid Hydrogen with ortho-concentrations of less than 60% 63

4. Entropy of the Anomaly 65

5. Time-Rate of Change of Concentration . . . 66

Part III - Discussion.

1. Introduction 69

2. The Hydrogen Molecule 69

3. Two Experiments 71

4. Qualitative Explanation 71

5. Nuclear Resonance Measurements 73

6. Analogue in the behaviour of the Ni-Cu Alloys 74

7. Tomita's Considerations of the Problem . . 76

8. Non-Uniformity of Solid Hydrogen 77

CHAPTER 4. IRRADIATED POLYTHENE.

1. Introduction 81

2. Experimental 82

Page

3. Results 83

4. Discussion 83

5. Discussion on Normal Polythene 84

CHAPTER 5. POTASSIUM BROMIDE.

1. Introduction 87

2. Experimental and Results 87

3. Comparison with Clusius et al 89

4. Discussion 90

APPENDIX I.

Thermodynamic Functions of Irradiated Polythene

APPENDIX II.

Thermodynamic Functions of Potassium Bromide

APPENDIX III.

θ_D and γ for the Elements

REFERENCES.

ACKNOWLEDGEMENTS.

An Extract from "Science since 1500"

by H.T.Pledge, B.A.

(H.M.Stationery Office 1939).

"Distilleries forced another practical use of heat. They were booming. In the early 18th century, gin engulfed Britain in an overwhelming wave of drunkenness. We may, fancifully, see in these new sciences of Chemistry and of heat one reaction to this ! For not only is distillation one of the best methods of preparing pure substances, but distillers, Black found, were aware, as users of fuel, of a quantitative aspect of heat other than mere temperature.... By 1760 he (Black) was able to formulate a correct and applicable measure of quantity of heat, and thus, also, of specific heat.".

PREFACE

So that no reader will waste his time in reading chapters, whose matter is of no interest to him, there follows a short sketch of the general layout of this thesis.

New experimental information may be found for Hydrogen in Part II, Chapter 3; for Irradiated Polythene in Chapter 4; and, for Potassium Bromide in Chapter 5. Tables of the Thermodynamic functions of the latter two substances will be found in the Appendix, which also includes a list of Debye Θ for the elements.

Chapter 1 considers the possible experimental errors, when measurement of specific heats is made under non-adiabatic conditions. Chapter 2 describes three apparatuses. The first and second were used for the measurements reported in the following pages, but the third is included only for its own merits. No experiment had been successfully completed with it before the author left the Clarendon Laboratory.

In Chapter 3, while Part I deals with experimental techniques, some of the possible consequences of the results of the specific heat measurements of Solid Hydrogen will be found in Part III.

CHAPTER I

NON-ADIABATIC CALORIMETRY

The science of Low Temperature Physics is little over half a century old. From the beginning the measurement of specific heats below room temperatures has been a constant battle with unsuitable thermometers and poor vacuums. Only in the last thirty years have techniques been developed and the new properties of substances studied, to enable the heat capacity of a solid to be measured to an accuracy of a tenth of one per cent.

To achieve this precision an adiabatic method must be used. However, the disadvantage of the adiabatic method is the very poor return of information per man-hour worked. It is recognised that the extra decimal place is necessary in Chemistry to calculate the Thermodynamic relationships used in studying the behaviour of chemical reactions, but since the science of Low Temperature Physics is still in its infancy an overall picture of the solid state has still to be built up. The author has, therefore, adopted the non-adiabatic method, which yields quick results with small and simple machines and a minimum of manpower.

In this chapter we will discuss the measurement of heat capacity by non-adiabatic methods between the absolute temperatures of 0.1°K. and 300°K. First, we will define heat capacity and the units that

will be used, and then show how the measurements may be made most accurately at a known temperature.

Heat capacity is defined as the quantity of heat necessary to raise the temperature of a given body one unit on a temperature scale. It is the practice in calorimetric work to compare the heat capacity of the substance under investigation with the heat capacity of 1 gram of water at 15° centigrade. The amount of heat required to raise the temperature of one gram of water from 14.5°c. to 15.5°c. is known as the 15° calorie and is equivalent to 4.1855 abs. joules. We may then write for the heat capacity, H, measured in calories per degree centigrade:-

$$H = \frac{\Delta Q}{T_2 - T_1} \qquad 1.1.$$

where ΔQ is the quantity of heat in calories necessary to raise the temperature of the body from T_1 to T_2 degrees centigrade.

The heat capacity is still not uniquely defined, as it depends on the state of the body. When different substances are to be compared, we define the conditions under which the measurement is made. There are two important quantities: the specific heat at constant pressure, C_p, is the heat capacity of a mole of the substance under a constant pressure; the specific heat at constant volume, C_v, is the heat capacity of a mole of the substance at a constant volume. The first quantity is the one usually measured, and from a practical point of view is very important. The second quantity is very difficult

to measure except in the case of gases, but is of considerable theoretical value. It is, however, possible to deduce C_v from the measured C_p, since an important equation of thermodynamics gives:-

$$C_p - C_v = -T\left(\frac{\partial V}{\partial T}\right)_P^2 \left(\frac{\partial P}{\partial V}\right)_T \qquad 1.2$$

The heat capacity of a substance is measured in a calorimeter. This is usually a small metal box containing thermometers and heaters, into which the sample is placed, but, alternatively, may be the substance itself carrying its own measuring equipment.

A non-adiabatic heat capacity point is obtained as follows: the temperature, and the change of temperature with time of the calorimeter is first measured. This change of temperature with time is known as the fore-drift and should have a constant value. Heat is then applied for a measured time, which we will call the heating period. After this, the temperature and the rate of change of temperature are again noted. This change of temperature with time is called the after-drift, and does not always become constant immediately. It is then assumed, that the extrapolation of the linear temperature drifts to the middle of the heating period gives the two temperatures, between which the body has been heated by the heater, and that only.

To consider all the errors that are involved in this heat capacity measurement, let us take a calorimeter with a heat capacity, H_{cal}, that has been previously measured and place in it N moles of the substance, whose specific heat at constant pressure we wish to find. Let the thermometric parameter χ be related to the absolute

temperature scale, T, by x=f(T). Then the rise in x, Δx, due to the heat supplied in calories, Q, is related to the absolute temperature scale by:-

$$dx = f'(T)dT \qquad 1.3$$

We may now write for the specific heat of our substance:-

$$C_p = \frac{1}{M}\left(\frac{C\,\frac{dx}{dT}}{x} - H_{cal}\right) \text{ cal/degree abs./mole.} \qquad 1.4$$

We will now consider each variable on the right hand side of this equation, discussing the most suitable methods and materials for obtaining the greatest accuracy in the measurements of C_p at a known temperature T.

The Thermometric Parameter x

Any parameter that changes with temperature may be used as a thermometer. Parameters associated with heat capacity measurements are:-

1. Pressure of a gas in a constant volume at a low pressure.
2. Vapour pressure of a liquid.
3. Electrical resistance.
4. Magnetic susceptibility.
5. Thermo-electric force.

The first gives rise to the helium gas constant volume thermometer, and is a primary thermometer.

The vapour pressure thermometer, although a secondary type, is used in the work for calibrating all other thermometers. The helium vapour pressure tables that have been used are those recommended by an informal meeting between representatives of the cryogenic laboratories of Holland, U.S.A., and Great Britain in Amsterdam, in July, 1948. The hydrogen tables used are due to Woolley, Scott and Brickwedde (1948). The oxygen vapour pressure tables have been taken from C.T.Linder's compilation (1950).

Electrical resistance and magnetic susceptibility thermometers have both been used for the work in this thesis, and will be discussed in detail (Page 8).

Thermocouples are used extensively in adiabatic calorimetry to indicate temperature differences, but the author has had no use for them in his experiments, so they will not be discussed.

In heat capacity measurements a thermometer should have the following properties:-

1. It should vary rapidly, smoothly, and mathematically simply with temperature.
2. It should have a heat capacity very much smaller than the heat capacity being measured.
3. It should be stable over the period of the experiment, and from experiment to experiment.
4. It should generate little or no heat.
5. It should be easy to construct and simple to use.

We will now discuss the magnetic and resistance thermometers available in different temperature ranges and assess their usefulness in relation to the above requirements.

From 0.1°K. to 4.0°K. the author has used two thermometers successfully: a magnetic thermometer and a carbon resistance thermometer.

The MAGNETIC THERMOMETER is dependent on the measurement of the susceptibility of a paramagnetic salt. The susceptibility χ of a paramagnetic salt above the Curie point has a simple relation with the temperature, namely:

$$\chi = \frac{C}{T - \Theta} \qquad \text{Where C and } \Theta \text{ are constants} \qquad 1.5$$

It is not necessary to know or find the numerical value of the susceptibility, since, if the susceptibility is proportional to the readings on a mutual inductance bridge, or the throw of a ballistic galvonometer, δ :-

$$T - \Theta = \frac{A}{\delta - B} \qquad \text{Where A, B, and } \Theta \text{ are constants} \qquad 1.6$$

It is, therefore, possible to find A, B, and Θ by calibrating δ against the temperature in the helium vapour pressure region and extrapolating these values to the lower temperatures (see chapter 3, Part 1, Section 5).

Paramagnetic salts have usually very high specific heats, making them suitable for calorimetric measurements, except in a few special cases as in the specific heat work on solid hydrogen reported in

Chapter 3. It should be mentioned that the discovery by Cooke, Duffus and Wolf (1953) of the low specific heat and excellent magnetic properties of Cerium Magnesium Nitrate make it a suitable thermometer for calorimetric work below 1.0°K. on metals and other paramagnetic salts

A magnetic thermometer usually needs calibrating each time it is used, as it is highly dependent on the geometry of the circuit. Also, as many paramagnetic salts are unstable at room temperatures, their magnetic properties may change between successive runs.

The construction and employment of the associated measuring equipment, although more complicated than the bridge circuits used in measuring resistance, do not present any difficulties.

An extra and important attribute of this thermometer is its ability to cool itself and the calorimeter to a starting temperature below 1°K. by carrying out an adiabatic demagnetization.

The most sensitive thermometer available in the 0.1°K. to 4°K. region is the CARBON RESISTANCE, but it is impossible to predict its behaviour below 1°K. and it must, therefore, be calibrated against a magnetic thermometer - a difficult undertaking in a region of poor thermal contact. There are two carbon thermometers that the author has used: a normal carbon radio resistance, which will be reported on in the section dealing with the experiments on helium gas; and the resistance of a thin film of carbon between copper strips, which was used for the work on solid Hydrogen. The sensitivity of the former is greater, but this is not always advantageous. For example,

if the value of the resistance is chosen to be 300Ω to give a suitable sensitivity at 4°K, the value at .1°K. will be very much greater than can be measured on a 10,000Ω bridge. The thin film of carbon on the other hand only changes its resistance by 20 times between these two temperatures. With sensitivities greater than 100Ω/degree, it is never necessary to depend on the linearity of the galvonometer for interpolation between the smallest unit ($\frac{1}{10}\Omega$) of the bridge.

Carbon having a very poor thermal conductivity in this temperature range, the thermometer is liable to be self heating unless very small currents are used. However, it has been found that reproducible results may be obtained with comparatively large currents, as long as this current varies smoothly, as for example, under a constant e.m.f.

The day to day reproducibility of the radio resistance type is within half of one per cent., but the thin film type, being highly sensitive to heat and light, becomes quickly unusable unless kept below room temperature.

Two other materials have been used by other workers as resistance thermometers in this region, namely, the two alloys LEAD BRASS, and PHOSPHOR BRONZE. However, the obtaining of a suitable resistance temperature dependance by controlled mixing of the constituents seems to be largely luck, and thermometers made from these alloys are, therefore, not readily available.

The temperature range from 4°K. to 25°K. is one of the most

difficult ranges in which to find a good thermometer. The carbon thermometer is still sensitive in this range but it is difficult to specify its behaviour between the vapour pressure calibrations in the helium and hydrogen regions. It has been the author's good fortune to have had available a reel of CONSTANTAN wire whose resistance changed almost linearly with temperature from 8°K. to 20°K. This thermometer varies only 1 Ω/degree per 700 Ω, so to obtain the necessary sensitivity in a wheatstone bridge circuit, a high current must be passed through the thermometer. The heat developed in consequence makes this thermometer unusable when very small heat capacities are to be measured.

The PLATINUM RESISTANCE thermometer can be employed from 20°K. to 800°K. The high purity available today, coupled with the excellent mechanical and chemical properties, make platinum the most suitable metal for a resistance thermometer, whose behaviour may be accurately predicted. The relation of the resistance with temperature between 20°K. and 90°K. is a complicated function which has been tabulated by C.F.Linder (1950). The criterion that the platinum has a high purity and will therefore obey the above function, is that the ratio of the resistances at the boiling point of water and at the ice point is greater than 1. 3910.

Between 90°K. and room temperature the resistance may be expressed in terms of the temperature by:-

$$R = A + BT + CT^2 \qquad 1.9$$

where A, B, and C are constants.

differentiating, we have:-

$$\frac{dR}{dT} = B + 2CT \qquad 1.10.$$

The constants can be found by measuring $\frac{dR}{dT}$ in the oxygen vapour pressure region, and the resistance at the oxygen boiling point and at the ice point. The constants B and C can be checked by finding $\frac{dR}{dT}$ near the ice point.

We have seen how to find the relation between the thermometric parameter and the absolute temperature scale. These relations must be known very accurately as their differential, $\frac{dX}{dT}$, is a parameter in our equation for the specific heat. If $\frac{dX}{dT}$ is a constant, or nearly so, throughout a known temperature range, it is possible to measure it with a much greater accuracy than if it is a complicated function of the temperature. It is not always necessary to use the measured parameter as the thermometric parameter. For example, in the case of the carbon thermometer in the helium region, one may use a thermometric parameter $\rho = \frac{1000}{R}$. It is then found that $\frac{d\rho}{dT}$ is a manageable function of the temperature. (See Fig.3·5 Chapter III).

The Measurement of ΔX

ΔX is the change in the thermometric parameter due to the heat developed by the heater and by that only.

There are two circumstances that militate against measuring Δx exactly:-

1. It is never possible to isolate the calorimeter completely.
2. It is never possible to have instantaneous thermal equilibrium within the calorimeter.

Remembering that the greatest accuracy is obtained when the heat leak to or from the calorimeter is at a minimum and the equilibrium time is short compared with the heating period, we will now consider separately the two effects.

HEAT LEAK between the calorimeter and its surroundings is due to three causes:-

1. Heat conduction through connecting tubes and wires.
2. Conduction by the gas.
3. Radiation.

1. The first heat leak can be reduced by choosing a small cross sectional area for the wires and tubes, and making them as long as possible commensurate with spatial, electrical, and vacuum requirements, and by selecting metals with low conductivities. The author has used three alloys extensively: German silver for tubes, and manganin and constantan for the leads.

The ratio of the conductivities of these alloys between room temperature and 4°K. is 50:1, while the ratio of the specific heats between these temperatures is of the order of 10,000:1. From Fig.1.1.

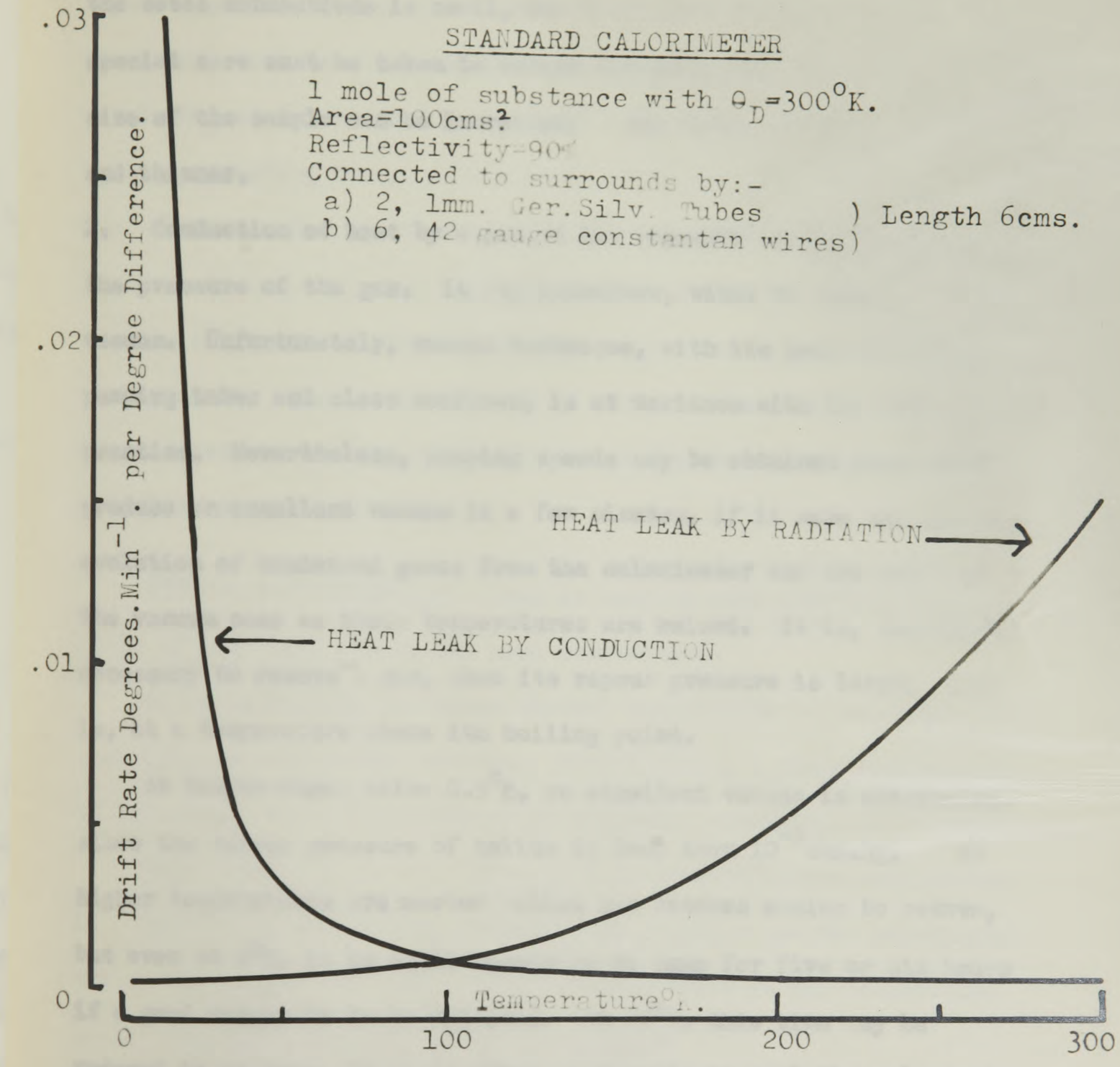


FIG. 1.1. THEORETICAL DRIFT RATE FOR STANDARD CALORIMETER.

it can be seen that above 100°K. the drift due to the conduction in the metal connections is small, but that at temperatures below 10°K. special care must be taken to reduce the heat leak. For example, the size of the sample can be increased; the wires and tubes made longer and thinner.

2. Conduction of heat by a gas at low pressure is proportional to the pressure of the gas. It is, therefore, vital to obtain a good vacuum. Unfortunately, vacuum technique, with its need for large pumping tubes and clean surfaces, is at variance with low temperature practice. Nevertheless, pumping speeds may be obtained that would produce an excellent vacuum in a few minutes, if it were not for the evolution of condensed gases from the calorimeter and the walls of the vacuum case as their temperatures are raised. It is, therefore, necessary to remove a gas, when its vapour pressure is large; that is, at a temperature above its boiling point.

At temperatures below 0.5°K. an excellent vacuum is obtainable, since the vapour pressure of helium is less than 10^{-5} cms.Hg. As higher temperatures are reached helium gas becomes easier to remove, but even at 4°K. it is still necessary to pump for five or six hours if a good vacuum is to be obtained. At 20°K. this time may be reduced to an hour, so it is often preferable to cool the calorimeter below 20°K. by means other than exchange gas. There are very few substances present, whose boiling point is in the temperature range, 20°K. to 200°K., so a good vacuum is always possible. Above the

latter temperature, condensed gases, whose boiling points are above room temperature (water for example), exert an appreciable vapour pressure, which is difficult to remove unless the whole pumping system can be raised to temperatures of 400°K. or more. This is impossible with the existing design of low temperature apparatuses.

3. Heat transfer due to radiation follows Stefan's law. Below 90°K. it is small compared with the other heat leaks, but above 200°K. it becomes an important factor (see Fig. 1.1). It is possible, however, to reduce the effect considerably by making the calorimeter with a large volume to surface ratio, and by giving this surface a high reflection coefficient.

THERMAL EQUILIBRIUM in a body is said to have occurred when all parts of that body are at the same temperature.

It is impossible to obtain thermal equilibrium in the calorimeter when using non-adiabatic methods. Nevertheless, a close approximation to this ideal state is necessary if accurate results are to be obtained.

There are three errors introduced by disequilibrium conditions:-

1. There is disequilibrium between the specimen and the calorimeter due to the heat leak. This causes a small shift in the temperature scale relative to the recording thermometer.

2. There is disequilibrium due to the heater during the heating period. Extrapolation of the fore- and after-drifts to the centre of the heating period only takes into account the change in heat leak, if the temperature of the outside of the calorimeter rises linearly through-

out the heating period. This implies equilibrium conditions throughout the calorimeter. If there is overheating or underheating of the body of the calorimeter, the heat leak is not the same as that allowed for in the extrapolation of the fore- and after-drifts. A correction term for disequilibrium conditions, that may be applied to Δx, as defined above, has been calculated by Parkinson and Quarrington (1954). They have carried out calculations for a calorimeter with the thermometer and heater on the outside and have used two simplifying assumptions: all the calorimeter is at the temperature indicated by the thermometer; the temperature of the inside of the specimen is at the same temperature as its surface. Two temperature dependent parameters are found that are related to the heat exchange between the specimen and the calorimeter, and, the calorimeter and its surrounds, and may be deduced from the temperature-time curve during and after the heating interval. These two parameters may then be inserted into a formula to give the correction term, which is only under the worst conditions greater than 1% of Δx.

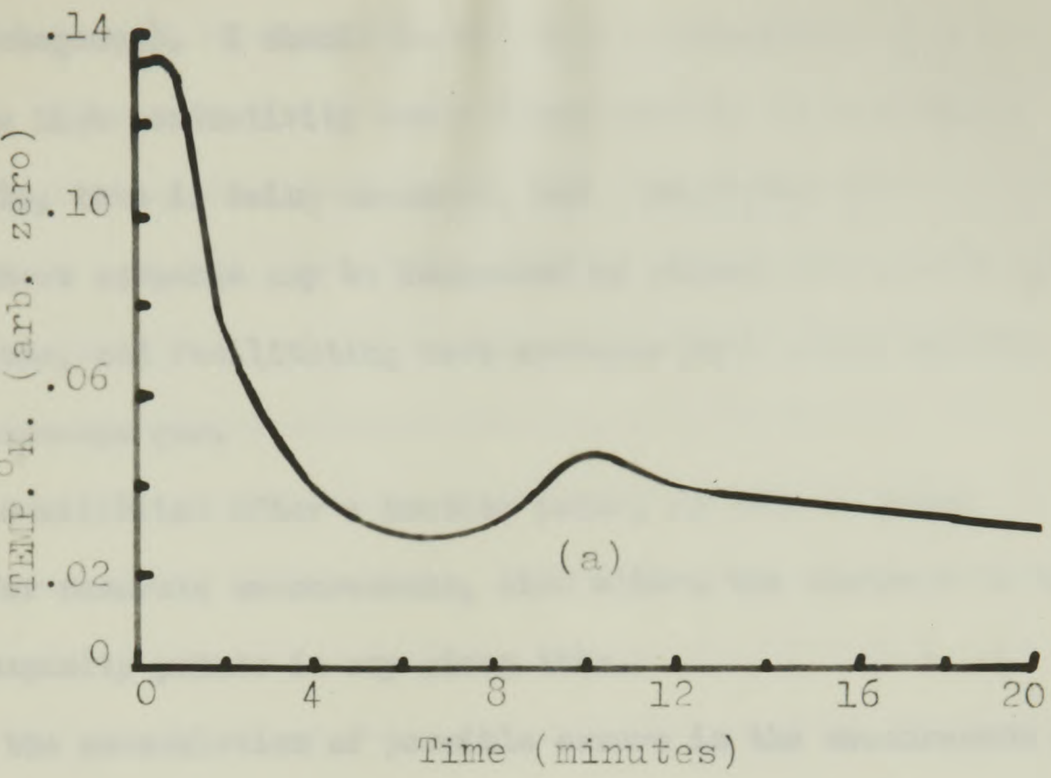
3. Once disequilibrium has been set up in the calorimeter during the heating period, the time (t) necessary for the drift to become linear is dependent on the conductivity (K), heat capacity (H), and the geometry (G) of the sample and calorimeter. This may be expressed in the form:-

$$t \sim f(G)\frac{H}{K} \qquad 1.11$$

If it is long, the extrapolation from the linear section of the drift to the centre of the heating period is also long, which increases the uncertainty in the value found for Δx. $\frac{B}{C}$ is temperature dependent. At low temperatures it is small and constant, but, as higher temperatures are reached, it increases rapidly.

As an illustration of the drifts found when measuring a sample of poor thermal conductivity, two drifts obtained during the measurement of a polythene sample at 20°K. and 250°K., are shown in Fig. 1.2, a and b. At 20°K. equilibrium is achieved rapidly, but at the higher temperature the drift is highly complex. It can be seen that there are two time constants associated with the sample and the calorimeter before equilibrium is established. The thermometer, registering these drifts, is suspended in the centre of the calorimeter and registers the temperature of the exchange gas near it, (see Fig. 4.1.). After the end of the heating period, the copper body of the calorimeter is very much hotter than the sample. Heat flows to the polythene until the thermometer only sees the cooler parts of the sample that are near it at the centre. The inner part of the sample then equilibrates with the outer, and a linear drift is at last obtained. The very large extrapolation of over ten minutes that is necessary in this case considerably reduces the accuracy of the heat capacity point.

From the thermal equilibrium point of view, a calorimeter should be designed so that the t in equation 1.11 is small. The calorimeter should have small dimensions. (N.B. the use of a large sample is not



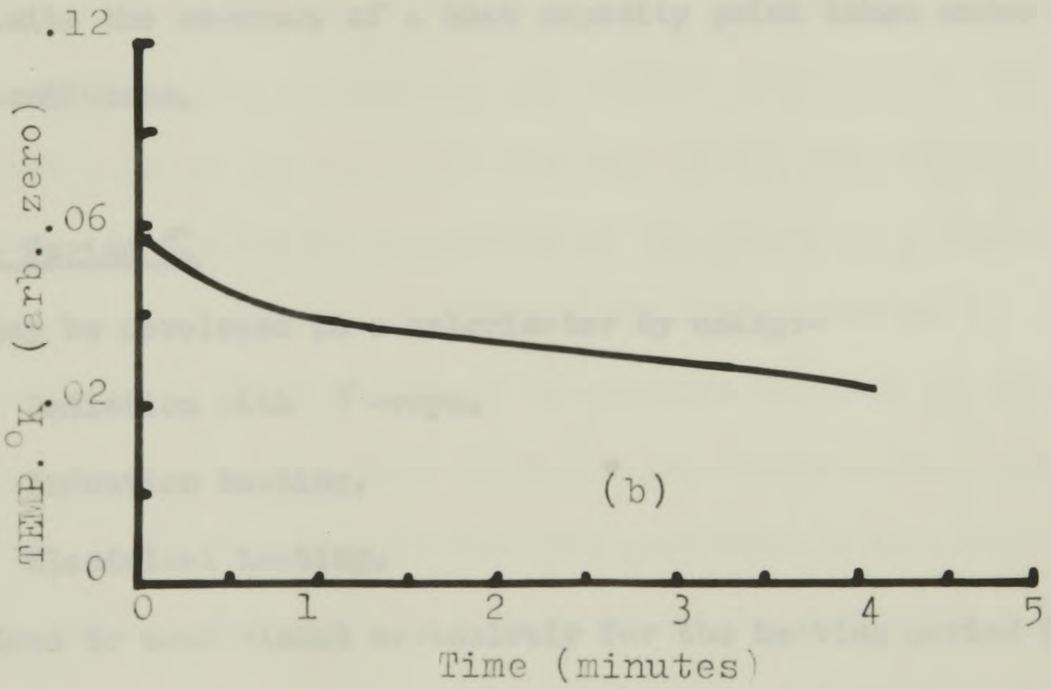


FIG. 1.2. TEMPERATURE DRIFTS AFTER HEATING PERIOD.

always advantageous). K should be as large as possible, by using a metal with a high conductivity and a large area of cross section. If the sample, that is being measured, has a very poor thermal conductivity, heat exchange may be increased by slicing the sample into small sections, and facilitating heat exchange by a small quantity of helium exchange gas.

Rapid equilibrium after a heating point, as well as being necessary for accurate measurements, also allows the observer to take more heat capacity points in any given time.

It is the accumulation of possible errors in the measurement of Δx that limits the accuracy of a heat capacity point taken under non-adiabatic conditions.

The Heating Period t_2.

Heat may be developed in a calorimeter by using:-

1. Radiation with γ-rays.
2. Induction heating.
3. Electrical heating.

The first is used almost exclusively for the heating period in work below 1°K. on paramagnetic salts. Its chief advantage is in the evenness with which heat is developed in the sample. In a temperature region of poor thermal conductivity this is essential. Induction heating has been used for the heating period, but only in special cases (Laby and Hercus 1927). However, it is an important factor when

demagnetisations of a paramagnetic salt are carried out in a metal calorimeter. This effect will be described in Chapter III. The author has used electrical heating for all the measurements reported in this thesis; we will, therefore, discuss this method in detail.

The heat developed by a resistance may be found by measuring any two of the variables, current, voltage, and resistance. As circumstances often require short heating periods, it is often best to find the resistance of the heater before the experiment, leaving only the current to be measured during the heating interval. But it is important in this case, that the resistance should not change, due to a rise in temperature. The use of wire, made from an alloy with a small temperature dependence, and careful attention to the thermal contact made by the wire with the body of the calorimeter, can reduce any uncertainty in the resistance of the heater to a minimum.

A more important error arises due to the heat generated in the leads to the heater. It is difficult to estimate how much of this heat is given to the calorimeter. At low temperatures a good approximation to the truth is that half the heat generated in the leads is conducted to the calorimeter. This is based on the assumption that all the heat is removed by conduction to the ends of the leads. At higher temperatures where radiation and poor vacuum are important factors, this approximation is probably an overestimate. It is, therefore, important that the heater should be designed with a large resistance in comparison with the leads, in order to reduce the percentage

value of this doubtful correction.

The time during which the current is flowing can be measured by a stop watch actuated by the current switch. The error introduced by the watch is proportional to the smallest interval of time that the watch is capable of indicating and inversely proportional to the heating period, so that it is possible to make the error negligible. But if experimental circumstances require a short heating period, it should be noted, as an example, that a $\frac{1}{5}$ th second stop watch, used for a heating period of 30 seconds, may be only accurate to 1.3%.

The Heat Capacity of the Empty Calorimeter, $H_{cal.}$

H_{cal} should be as small as possible. Its actual value is dependent on its size, which is dictated by the design required by each particular experiment. All the errors that have been discussed are also present in H_{cal}.

The Size of the Sample M.

The use of a very large sample does not necessarily increase the accuracy of C_p. (See section on thermal equilibrium).

Conclusion - Error in C_p.

We have now considered all the parameters used in the calculation of C_p, and the errors that are associated with them. The size of the error of C_p varies with the temperature. At low temperatures and at

high temperatures, the error is greater than in the range between, where C_p may be large in comparison with the heat leaks, and where the conditions for rapid equilibrium are still good.

We can now make a rough estimate of the probable error in C_p.

Parameter	Probable Error
$\frac{dx}{dT}$	about 1.0%
Δx	2% to 0.5%
$Q\ (=i^2Rt)$	Less than 1.0%
H	Total approx. 4.0% to 2.0%

For a series of heat capacity points the error in $\frac{\Delta x}{\lambda}$ and Q may be positive or negative, so that it should be possible to draw a curve through points with a 3% scatter, accurate to 1%. The error in $\frac{dx}{dT}$, however, will displace this line in one direction. If the heat capacity of the calorimeter is an appreciable fraction of the total, the error in this measurement must be added to the error in H.

It can be seen that only under the best conditions will the non-adiabatic method give information on the specific heat of a substance with an error of 1% or less.

NOTE. The calorimeters employed by the author will be described in the chapters relating to their use. The design of a calorimeter is always a compromise between conflicting requirments, but it will be seen that the calorimeters employed take into account the different effects described in this chapter.

CHAPTER 2

LOW TEMPERATURE APPARATUSES

The three machines, that the author has used, are all of very different construction. These differences are due more to the increased availability of liquified gases in the laboratory, than to the needs of a particular experiment. The first machine was built before free liquid helium was available, and therefore contains its own helium liquifier. When the second machine was erected, a few litres of liquid helium were being made in the laboratory, so the apparatus was designed accordingly. The third machine was constructed this year (1955), when large quantities of liquid helium became available from an outside source, (H.P.L.).

In general, a low temperature apparatus must be capable of carrying out three operations: first, it must cool the specimen; second; isolate it from the coolant; and third, have some method of bringing information on the state of the specimen to room temperature.

There are four points to consider when designing an apparatus:

1. The cost of construction and of running the machine in relation to the useful knowledge it will give. It must be economical in use of liquid hydrogen and helium. It should not be unnecessarily complicated: a part, which enables the saving of £1 worth of helium and costs £40 in materials and mechanics time, is not worthwhile.

2. Good mechanical strength. This conflicts with the first part, with which a compromise is always necessary.

3. Accessability. It should be possible to reach most parts of the apparatus easily and quickly for maintenance and repair.

4. Ease of Operation. Under this heading, we will also place "Gentlemanly Behaviour", or the ability of an apparatus to work within the laws of physics without a form of hoodoo being practised upon it.

The three apparatuses will be discussed separately, but only the last will be considered in detail as it is of unusual design, and has not been described elsewhere.

Apparatus I - A general purpose machine for measuring the specific heat of solids between 1.5°K. and room temperature.

The apparatus is shown in Fig.2.1. It has been described by Hill (1953) and will not be discussed in detail. Essentially, the apparatus consists of three concentric spaces. The dewar, into which liquid hydrogen or oxygen may be placed, surrounds a vacuum case containing the helium expansion liquifier, on the bottom of which is attached another vacuum case containing the calorimeter.

The operation of a Simon expansion liquifier is well known, so will not be discussed.

When measurements are made from 1.5°K. to room temperature, it is always necessary to keep the vacuum case surrounding the calorimeter within a few degrees of the temperature of the calorimeter to

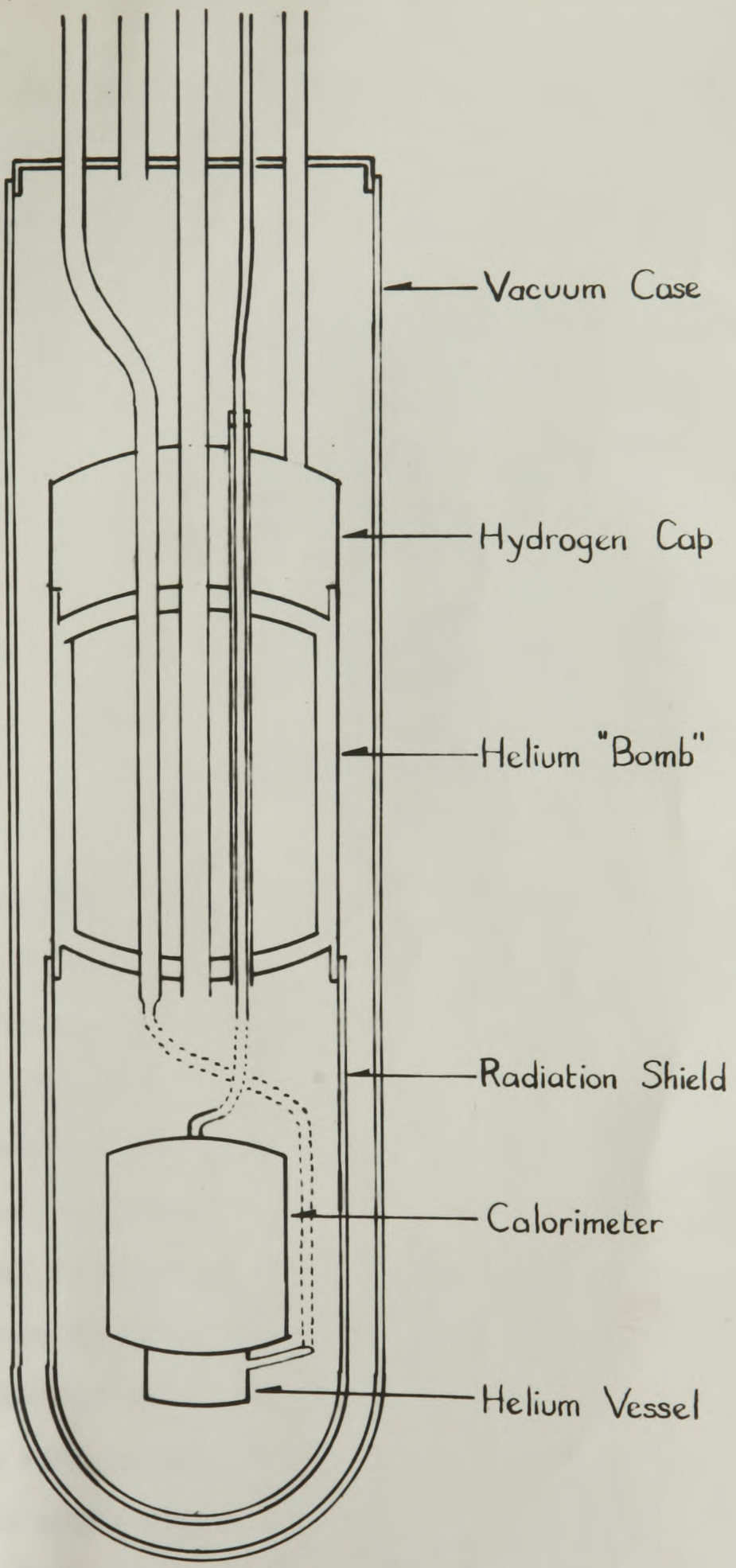


FIG. 2.1 GENERAL PURPOSE MACHINE.

reduce the heat leak to a minimum. (See Chapter 1, measurement Δx).

This is accomplished as follows:

Temperature Range of Measurement	Temperature of Surrounds
1.° - 8.°K.	4°K. Liquid helium boiling under atmospheric pressure.
8.° - 12.°K.	10°K. Hydrogen in cap pumped.
12.° - 16.°K.	14°K. Hydrogen triple point.
16.° - 30.°K.	20°K. Hydrogen boiling under atmospheric pressure.
30.° - 90.°K.	Electrical heating of surrounds to balance heat leak from 20°K. Liquid hydrogen in dewar
90.° - 300°K.	Electrical heating of surrounds to balance heat leak from 90°K. Liquid oxygen in dewar.

The electrical heating of the surrounds was accomplished by an automatic electronic device, which was capable of holding the shield at any desired temperature to within 0.2°K. (Smith 1954). The total heat capacity of the shield and the expansion bomb above 150°K. is very large. In consequence, the time required to establish a steady temperature with small quantities of heat, such as are needed to balance the heat leak, is about one hour. The author, therefore, constructed an inner shield which fitted into the inner vacuum space around the calorimeter (See Fig.2.2.). Having a small heat capacity in comparison to the bomb, it could be moved quickly from one temperature to another, and attain thermal equilibrium in a relatively short time. The bomb was also heated, the temperature being kept roughly

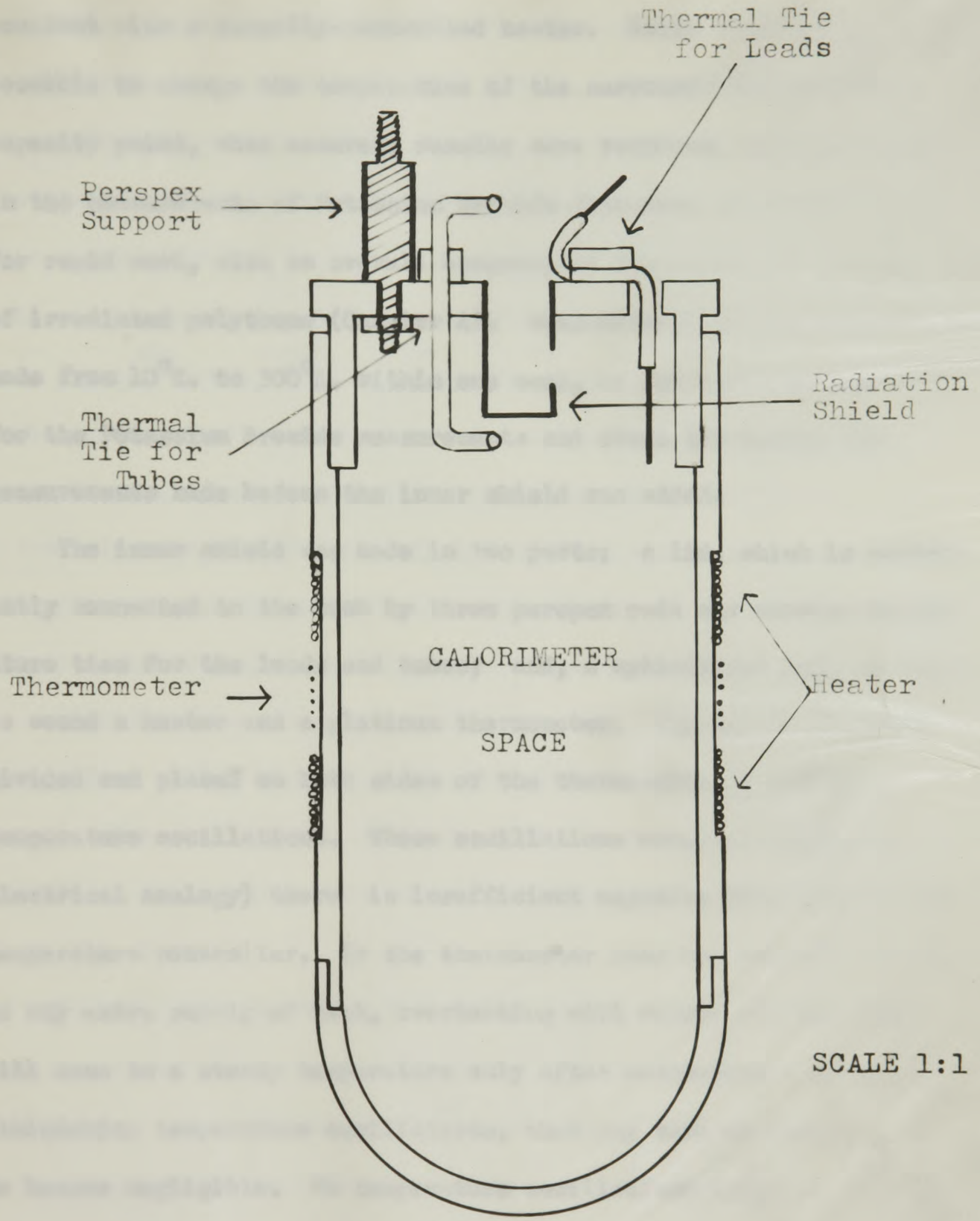


FIG. 2.2 CROSS-SECTIONAL VIEW OF SHIELD

constant with a manually-controlled heater. Using this shield, it was possible to change the temperature of the surrounds for each heat capacity point, when accurate results were required, as for example, in the measurements of Potassium Bromide discussed in Chapter 5, or, for rapid work, with an overall accuracy of 3%, as in the measurements of irradiated polythene (Chapter 4). Measurements of the latter were made from 10°K. to 300°K. within one week, as compared with one month for the Potassium Bromide measurements and about two months for measurements made before the inner shield was added.

The inner shield was made in two parts; a lid, which is permanently connected to the bomb by three perspex rods and carries temperature ties for the leads and tubes; and, a cylindrical body on which is wound a heater and a platinum thermometer. The heater has been divided and placed on both sides of the thermometer to minimise temperature oscillations. These oscillations occur if (using an electrical analogy) there is insufficient negative feed back to the temperature controller. If the thermometer does not respond quickly to any extra supply of heat, overheating will occur, and the shield will come to a steady temperature only after completing a series of diminishing temperature oscillations, that may take an hour or more to become negligible. No temperature oscillations occurred with the above shield, a steady temperature being obtained in about 10 minutes.

Apparatus 11 - A machine used for measuring the specific heat of solid Hydrogen from 0.1°K. to 4°K.

This apparatus is illustrated in Fig.2.3. It is a modification of the apparatus described by Hill (1953). The restriction of the temperature range below 20°K. the use of a common vacuum space, and the absence of the helium expansion liquifier have all contributed to a simple design. To carry out adiabatic demagnetizations a long tail was necessary, as the calorimeter had to be placed in the 5 cms. pole gap of the λ magnet. In this space the dewar, the magnetic thermometer coils, the vacuum case and the shield had to be mounted leaving a 2.5 cms. diameter tube in which to hang the calorimeter. As a 1mm. clearance between the shield and the calorimeter was considered sufficient, an inspection cap on the bottom of the shield was incorporated to ensure that the calorimeter was not touching.

Liquid helium was syphoned into the 100cc. can by the application, with a rubber bladder, of an overpressure in the transfer vessel. When the can was full, the transfer vessel and its supports, as well as the syphon, were removed to allow the magnet to be brought up to the cryostat.

The two extra german silver tubes of the syphon leading from room temperature are responsible for a considerable heat leak to the helium can. An evaporation rate of 18 c.c. an hour is reduced to 12 c.c. an hour by removing the syphon and inserting in its place a radiation shield.

Apparatus III - A Machine for Measuring the Specific Heat of Helium Gas at constant volume and at high pressure between 1.5°K. and 12°K.

This machine was designed by the author, and was built during

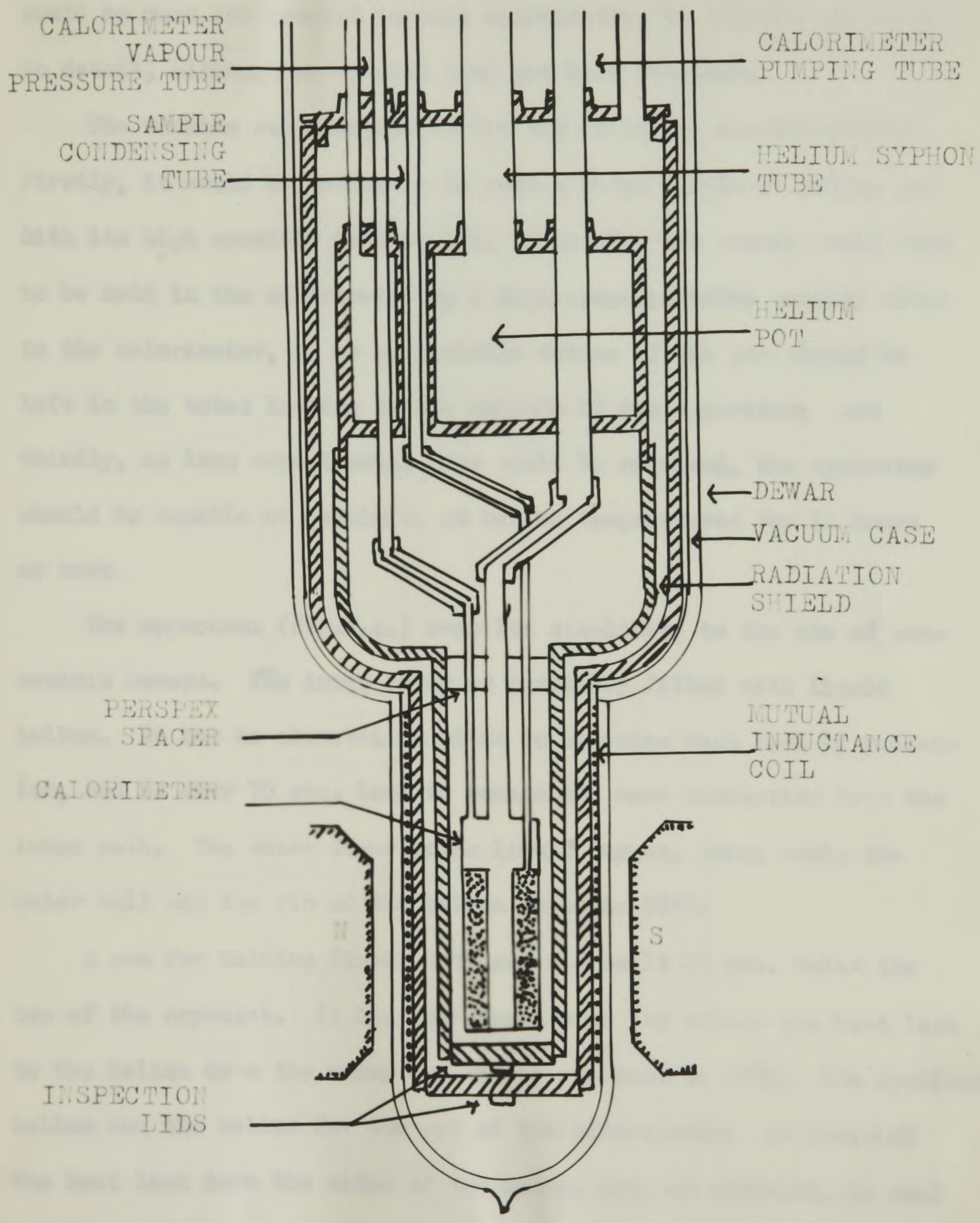


FIG. 2.3 HYDROGEN APPARATUS (DIAGRAMATIC).

the middle of 1955. Since the cryostat has many novel features and could be used for general purpose calorimetry, it will be described in detail, although no results have yet been obtained.

The machine was designed to fit the following specifications. Firstly, it would be necessary to cool a large sample of helium gas with its high specific heat to 4°K. Secondly, the sample would have to be held in the calorimeter by a high pressure valve working close to the calorimeter, as no appreciable volume of the gas should be left in the tubes leading to the outside of the apparatus; and thirdly, as long experimental runs would be required, the apparatus should be capable of remaining at helium temperatures for 12 hours or more.

The apparatus (Fig.2.4.) owes its simplicity to the use of concentric dewars. The inner dewar is partially filled with liquid helium. It has no observation slits to minimise heat leak by radiation, and is over 70 cms. long to reduce the heat conduction down the inner wall. The outer dewar holds liquid oxygen, which cools the outer wall and the rim of the helium dewar to 90°K.

A can for holding liquid hydrogen was built 20 cms. below the top of the cryostat. It has four functions: to reduce the heat leak to the helium down the valve and tubes; to cool to 20°K. the specimen helium and the helium for the pot of the calorimeter; to diminish the heat leak down the sides of the dewar, and, in addition, to cool the whole apparatus from oxygen to hydrogen temperatures.

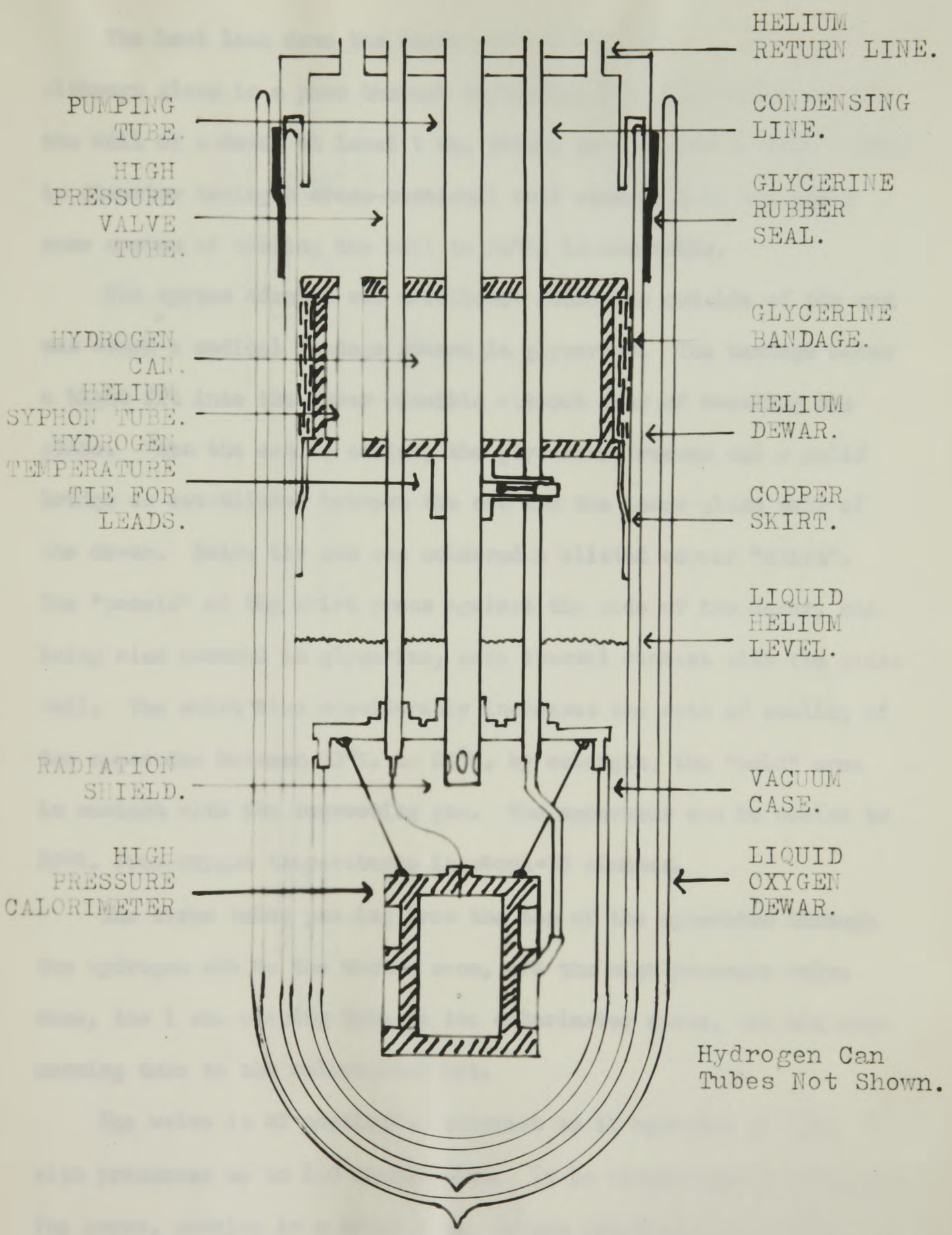


FIG. 2.4 HELIUM APPARATUS (DIAGRAMATIC).

The heat leak down the inner wall of the dewar is considerable. Although glass is a poor thermal conductor, it is necessary to make the wall of a dewar at least 1 mm. thick, so that for a dewar 7 cms. in diameter having a cross-sectional wall area of 2.2. sq. cms., some system of cooling the wall to 20°K. is desirable.

The system adopted was as follows: round the outside of the can was wound a medical bandage soaked in glycerine. The bandage makes a tight fit into the dewar possible without fear of breaking the glass. When the can is cooled, the glycerine freezes and a solid bridge is established between the can and the inner glass wall of the dewar. Below the can was soldered a slitted copper "skirt". The "panels" of the skirt press against the side of the dewar, and being also covered in glycerine, make thermal contact with the glass wall. The skirt also considerably increases the rate of cooling of the apparatus between 90°K. to 20°K. by enlarging the "cold" area in contact with the convecting gas. The apparatus can be cooled to 20°K. from oxygen temperatures in about 90 minutes.

The three tubes passing from the top of the apparatus through the hydrogen can to the vacuum case, are the high pressure valve case, the 1 cm. pumping tube to the calorimeter space, and the condensing tube to the calorimeter pot.

The valve is of particular interest as it operates at 4°K. with pressures up to 120 atmospheres. It is illustrated in Fig.2.5. The screw, working in a brass case, raises and lowers a closely fitting steel cylinder that is prevented from turning by a locking

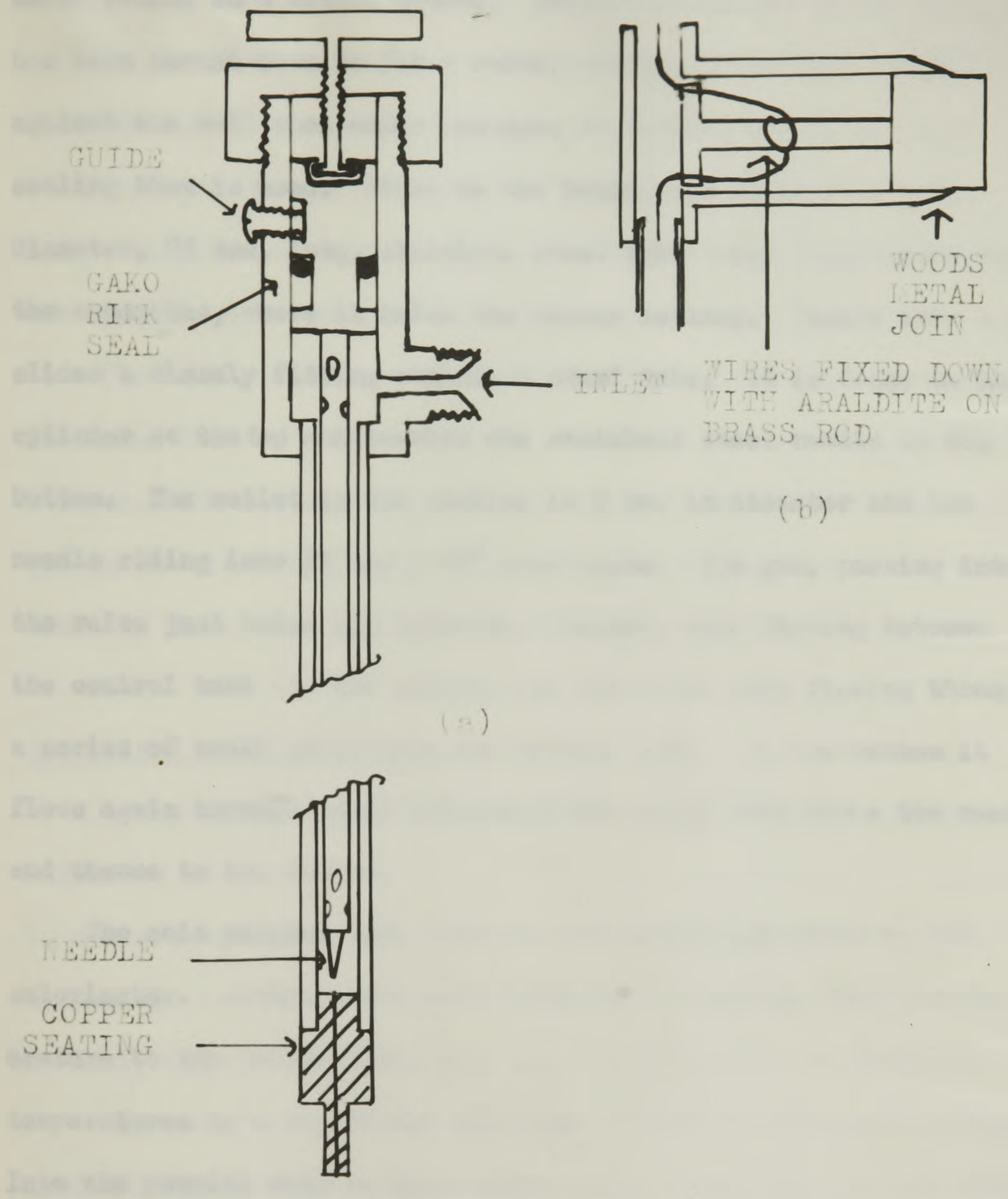


FIG. 2.5 (a) HIGH PRESSURE VALVE
(b) LOW TEMPERATURE TIE FOR LEADS
(Diagramatic).

screw riding in a milled groove. Half a centimetre of the cylinder has been turned down to fit a rubber O-ring. This ring presses against the wall when under pressure or vacuum, and is the only sealing that is used. Fixed to the brass case is an 0.52 cms. diameter, 75 cms. long, stainless steel tube which passes down into the apparatus, where it holds the copper seating. Inside this case slides a closely fitting stainless steel tube. It is fixed to the cylinder at the top and carries the stainless steel needle at the bottom. The outlet in the seating is $\frac{1}{2}$ mm. in diameter and the needle riding into it has a 20° apex angle. The gas, passing into the valve just below the cylinder, divides, some flowing between the central tube and the casing, but the major part flowing through a series of small holes into the central tube. At the bottom it flows again through small holes into the outer tube above the needle and thence to the outlet.

The main pumping tube contains the electrical leads to the calorimeter. Although the same constantan wires run from room temperature to the helium bath, they are thermally tied to hydrogen temperatures by a simple but effective method, illustrated in Fig.2.9. Into the pumping tube is connected a copper T-piece. A 1 mm. thick copper disc on the end of a 2 cm. long rod is attached to a short cylinder, which fits into the end of the single arm of a T-piece. A wire is passed through a hole in the disc, looped twice round the rod, and passed back through another hole in the disc. When all the wires have been thus treated, the whole is dipped in Araldite and

baked. The wires are then pulled through the machine from the top and the bottom simultaneously until the cylinder may be fitted and soldered for a vacuum tight join.

The condensing line, made of 2 mm. german silver tube, has no heat exchanger in the ordinary sense, but is very efficient due to the long length sitting in the helium gas above the liquid.

The machine has worked well and efficiently. The apparatus may be cooled from 20°K. to 4°K. with about 200 c.c. of liquid helium. A further 200 c.c. is used in condensing the sample and the cooling helium for the calorimeter pot. The machine may then be run for about 12 hours on about 600 c.c. of liquid helium.

Comparison of the Apparatuses.

Although the apparatuses that have been described are very different in pattern and size, some useful comparisons can be made. In conformity with the previous sectional headings and to eliminate verbage in the following paragraphs, we will designate the apparatuses as I, II, and III.

The structural SIMPLICITY of II and III, compared with I, is obvious. The liquifier in I and its associated high pressure system could be dangerous, and is therefore undesirable. The three tubes that are necessary also increase the heat leak to the system, with a consequent loss in running time. The advantage of I is that it can operate at helium temperatures without being dependent on an outside source for its coolant.

Another comparison is afforded by the different TIMES OF COOLING to helium temperatures from 90°K. If long hours of extra work and waiting precede every series of measurements, the operator will be tired and in consequence make an indifferent experiment. For apparatuses I, II, and III, we have 3 hours, 1 hour, and 2 hours respectively.

The RUNNING TIME at helium temperatures of I is about 6 hours, at the end of which time, it is necessary to bring the bomb back to 20°K. if another liquefaction is to be undertaken. Machines II and III have maximum running times with one helium transfer of 6 and 15 hours respectivaly, but both apparatuses may be kept indefinitely at 4°K. if more outside helium is available.

The EVAPORATION RATES per hour of the helium are:

I - 13 c.c.; II - 12 c.c.; III - 50 c.c.

Let us now define the EFFICIENCY of the machine as the number of litres of hydrogen needed per hour of useful running time. This includes the hydrogen needed for cooling from 90°K. and in the case of II and III, the hydrogen necessary in the separate helium liquifier calculated on the basis that 4 litres of hydrogen are needed to make 1 litre of helium.

The efficiency of these machines is then I - 1.3, II - 1.0, and III - 0.7. This may not seem a natural corollary to the figures given for the evaporation rate, but it should be noted that I is at hydrogen temperatures for two hours (while liquid helium is being

made) before experiments can begin. Apparatus III has its high efficiency due to the very small amount (40 c.c./hour) of liquid hydrogen necessary during running, advantage being taken of the enthalpy of the evaporating helium. The ability of this apparatus to run for 12 hours also reduces the value.

CHAPTER 3

THE SPECIFIC HEAT OF SOLID HYDROGEN

Part I - Experimental

1. Introduction

An absolute entropy of a substance in the gaseous state may be found by three methods, which can be designated as the calorimetric, spectroscopic, and the ideal gas reaction methods. We will discuss each method separately.

The calorimetric entropy is obtained by measuring the specific heat of the substance from the lowest temperature "attainable" to a chosen temperature in the gaseous state, account being taken of the latent heats of melting and vapourization (or sublimation) and any expansion or compression of the gas. Two important corrections must be made to an entropy derived in this manner. First the specific heat below the lowest attainable temperature must be guessed. For example, the lattice specific heat of many substances obeys a Debye T^3 law at temperatures below 4°K., so it is sufficient to make an extrapolation of the specific heat curve to the absolute zero to find the entropy due to lattice vibrations. Second, a correction must be made during any compression or expansion of the gas for non-ideality.

The spectroscopic entropy is calculated statistically from known parameters, that are applicable to a particular gas. The contribution

to the entropy by the translational motion may be found with the Sackur-Tetrode equation. Spectroscopic data, however, give the parameters necessary to find the vibrational and rotational contributions. An important correction must be made to account for the non-ideality of the gas since the Sackur-Tetrode equation is only applicable to a perfect gas. The correction is simple to make if the second virial coefficient of the equation of state is known, but theoretical considerations only give a rough approximation of the non-ideality present. This entropy calculation assumes a completely ordered state as the reference point from which a value may be derived.

The entropy derived from the ideal gas reaction is an extension of the calorimetric entropy. Consider the simplest gas reaction of three components: $A \rightarrow A_2 + A_3$. If the calorimetric entropy of any two of the components is known, the third may be calculated as soon as the heat of the reaction has been found. There are comparatively few gas reactions that are amenable to measurement, but with these it is possible to obtain an entropy for a substance without actually undertaking specific heat measurements.

It is an experimental fact that the entropies derived from the calorimetric, spectroscopic and ideal gas reactions methods are often the same for a given substance, within experimental error.

If the exceptions are excluded, it is possible to identify the state of complete order with the state at the absolute zero. But

before a law can be formulated, the exceptions to the rule must be explained.

Firstly, the discrepancy between the two entropies may be due to our ignorance of the behaviour of the substance. The correction for non-ideality of the gas may not be accurately known. Again, in large molecules, the assumption as to the behaviour of the molecule may be incorrect, free or hindered rotation occurring within the molecule. The lowest temperature at which calorimetric measurements have been made, may not be low enough and an undetected state of complete disorder may still exist. Nevertheless, the existence of disorder may be suspected, and ordering can be assumed to occur if the temperature was reduced. This is particularly true of the entropy from the degeneracy of the nuclear spins which would only be observed between temperatures of the order of 10^{-3} to 10^{-6}°K. If, when the measurement is made, no entropy is found, a metastable state is established.

Secondly, a degree of freedom in the specimen may become "frozen in". If the ordering expected at any particular temperature does not occur, or occurs slowly, we may infer the existence of some sort of potential barrier, which resists the change. In many cases, the rate of change is so slow, that metastability may be considered permanent.

Remembering that the discrepancies due to the second cause were natural rather than human, Simon (1937) defined the third law of

Thermodynamics as follows:

"The contribution of the entropy due to each factor within the system, which is in internal equilibrium, becomes zero at the absolute zero."

When the entropy of hydrogen was first found by the three different methods, the spectroscopic and calorimetric entropies agreed, but the gas reaction entropy disagreed. In 1927, Hind analysed the band spectrum of hydrogen and showed the existence of two types of hydrogen. The species differ in the alignment of their nuclear spins. Para-hydrogen has the spins opposed, and therefore (Pauli principle), the molecular rotation may only exist in even states (K=0,2,---). Ortho-hydrogen has the nuclear spins parallel and exists in the odd rotational states (K=1,3,---). The ground state of the ortho-molecule is nine-fold degenerate, a three-fold degeneracy of the molecular rotation and a three-fold degeneracy of the nuclear spin.

When a hydrogen atom from a hydrogen molecule combines with the atom of another element to form a molecule, it loses its identity with respect to the nuclear spin of the remaining atom. It can therefore be seen that the gas reaction entropy was correct as it measured the entropy change due to the degeneracy of the ortho-molecules.

A new statistical calculation using the extra spectroscopic information, brought agreement between the spectroscopic and ideal gas reaction entropies. The calorimetric entropy was now wrong. However, the statistical calculation of the specific heat did not agree with

the measured values at low temperatures. However, it had been assumed that para and ortho-hydrogen molecules were in equilibrium at all temperatures, i.e., a mixture of 75% ortho-hydrogen and 25% para-hydrogen at room temperature and a mixture containing only 0.3% ortho-hydrogen at 20°K. It was Dennison (1927) who suggested that in the time taken for a specific heat measurement, the change in the direction of true equilibrium between the ortho and para molecules was negligible. Eucken and Hillier (1939) and Clusius and Hillier (1929) made specific heat measurements with samples of different ortho-concentrations, and showed that the statistical and experimental values were in remarkable agreement when Dennison's suggestion was taken into account.

However, a discrepancy still existed between the calorimetric and spectroscopic entropies for samples containing ortho-hydrogen. Measurements down to 10°K. had shown that the specific heat of the solid was the same within the experimental error for both para-hydrogen and normal hydrogen. The third law was still in its infancy at that date and was still in need of experimental evidence to establish its validity. The question to be answered was whether the full entropy due to the degeneracy of the ground state of the ortho molecule would be found at a lower temperature, and thereby bring better agreement between the calorimetric and spectroscopic entropies and add another substance to the number that obeyed the Third Law of Thermodynamics with no doubt.

It was Simon, Mendelsohn and Ruhemann (1930,1931) who first discovered the anomalous behaviour of the specific heat of solid hydrogen

between 3° and 10°K., and demonstrated that its magnitude varied with the ortho-concentration of the sample. However, their results could not be very accurate owing to the use of a gas thermometer in the calorimeter and to the estimation of the ortho-concentration from their method of preparation.

In 1950, Hill repeated the measurements with greatly improved techniques. His conclusions may be summarised as follows:-

1. Pure parahydrogen has a specific heat which can be represented by a Debye θ that changes smoothly from 90° at 13°K., to a constant 114° below 4°K.

2. The shape of the anomaly is not of the Schottky type, showing that the molecules are interacting with each other, a fact which can also be deduced from the height of the anomaly at any given temperature not being proportional to the ortho-concentration.

3. The entropy of the anomaly found down to about 2°K., was only 0.7 E.U. per mole of ortho-hydrogen, out of the expected total of 2.18 E.U. ($R \log 3$).

4. There is no effect that can be attributed to the entropy of mixing ortho- and para-molecules.

5. It was impossible using conventional calorimetric methods to reach a lower starting temperature than 2°K. due to the spontaneous heat of conversion of ortho- into para-molecules (See below).

In 1952 the author started working with Hill. The following sections of this chapter describe the experiments on hydrogen carried out under his supervision.

The experiments were designed to answer the following questions:

1. Is the full entropy of the anomaly to be found at lower temperatures, or is there a part that remains "frozen in"?

2. In what manner is the entropy removed as lower temperatures are reached?

2. The Heat of the Ortho-Para Conversion.

Since the main difficulties of this experiment arose from the spontaneous conversion of ortho into para-molecules, we will first consider the magnitude of the heat involved by this change.

The energy of the lowest ortho-hydrogen rotational state is 337 cals.mole^{-1} (Giauque 1930). For normal hydrogen, the conversion rate is almost 1% an hour. The rate of liberation of heat is therefore 0.056 cals.mole^{-1} min^{-1}. At 4°K. this heat will cause the sample to warm up at a rate of about 0.1 degrees min^{-1}. This quantity of heat and the consequent drift rate are very large compared to normal low temperature calorimetric standards.

The experimental difficulties caused by the conversion heat are as follows. First, the lowest starting temperatures that can be reached by pumping liquid helium in thermal contact with the specimen are affected. Second, the hydrogen may become hotter than the thermometers, especially at very low temperatures where thermal contacts become poor. Third, the time in which measurements can be made is severely restricted. Fourth, the sample is never exactly defined, the concentration changing continuously with time. Fifth, exchange

gas cannot be used to cool the specimen, as in the time necessary to remove the exchange gas, the specimen will have warmed up to a high temperature.

3. The Plan.

From a consideration of the expected entropy of the anomaly and the value of the specific heat at 3°K., a guess can be made that the maximum of the anomaly would be somewhere between 0.8°K. and 2.0°K. with the low temperatures tail going to very much lower temperatures. It would therefore be necessary to use an adiabatic demagnetization technique to reach a temperature of about 0.2°K.

The general plan of the experiment was then as follows. Since it was impossible to use helium exchange gas for cooling a calorimeter below 10°K., liquid helium would have to be forced into it to reduce its temperature to 4°K. The calorimeter would therefore be designed with two compartments, that were in very good thermal contact with each other. In one compartment liquid helium would be forced in and condensed. By means of a large diameter pumping tube and special pumps it should be possible to reduce the temperature of the calorimeter to about 1.2°K., by pumping this condensed helium. The second compartment would contain a finely-ground paramagnetic salt and the hydrogen specimen, which would have previously been condensed between the grains of the salt. Demagnetization of the salt from 1.3°K. would reduce the temperature of the calorimeter and specimen to about 0.1°K. The susceptibility of the salt could then be used as a thermometer

and the rate of rise of temperature measured. If it could be shown that the rate of liberation of heat from the hydrogen was temperature independent, heat capacity measurements at higher temperatures could be used to establish the heating rate at all temperatures. Then the rate of rise of temperature at lower temperatures could be converted into heat capacity, and the long time necessary for normal heat capacity measurements would not occur. The rate of liberation of heat would also give the rate of change of concentration, which would enable the exact concentration at any moment to be found from a concentration measurement, made after the experimental run.

4. The Design of the Apparatus.

The measurements on the specific heat of hydrogen were carried out in apparatus II, described in Chaper 2 where a drawing of the cryostat appears.

The CALORIMETER (fig.3.1 and 2) is in the shape of a cylinder and consists of two copper compartments - the sample space and the condensing pot. The latter is the full diameter of the calorimeter at the top, but has an extension in the form of a thin hollow cylinder that passes down the full length of the calorimeter. From this cylinder six thick copper vanes are radially attached to provide good thermal contact between the sample space and the pot space. Two tubes lead from the pot: a 3mm. pumping tube with a 1mm. constriction to reduce the heat leak caused by the helium λ -phenomena, and a 1mm. line for measuring the vapour pressure of the liquid helium in the pot. This

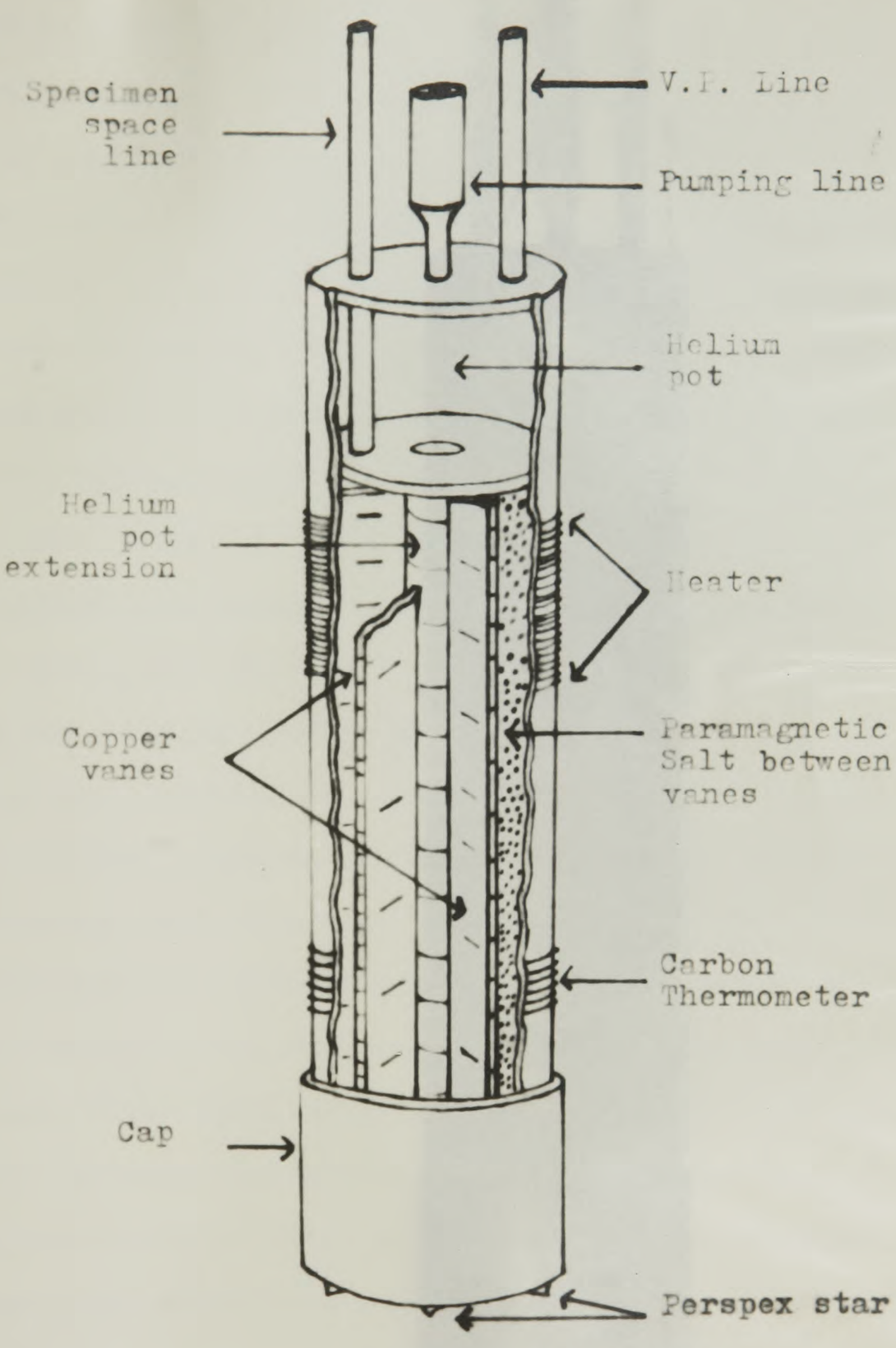


FIG. 3.21. THE HYDROGEN CALORIMETER



FIG. 3.2. HYDROGEN CALORIMETER.
$1\frac{3}{4}$ times natural size

second line is essential, since it is necessary to pump the helium continuously if steady temperatures are to be maintained while calibrating the thermometers.

In the sample space, between the vanes, a finely-ground paramagnetic salt is compressed. Iron alum was chosen as the salt, as it has a good "cooling power" due to the Fe^{+} having a spin of $\frac{3}{2}$, and its susceptibility is known to obey a Curie-Weiss law down to $0.1^{\circ}K$. It is readily available in large quantities, and has a comparatively good chemical stability at room temperature. The magnitude of its volumetric heat capacity is also suitable. Its specific heat only rises appreciably below $0.4^{\circ}K$.

Since the pressures involved in compressing the salt are high, the walls of the calorimeter are made 1mm. thick, so that no distortion can occur. By using a suitably shaped punch and a light hammer, a 75% packing fraction can be obtained.

The bottom of the calorimeter is closed with a ground copper cap, lubricated with glycerine, which freezes at low temperatures and forms a vacuum seal. This method was chosen because the salt would decompose if warmed to soldering temperatures. Also a solder ring would have become superconducting at helium temperatures, which would affect the calibration of the magnetic thermometer. A 1mm. tube leads from the top of the specimen space through the condensing space to the sample supply line. This line is connected directly to the hydrogen vacuum case and does not touch the helium can of the cryostat. This makes it possible to syphon liquid helium into the can without losing the specimen

from the calorimeter by condensation on any part of the tube cooler than the calorimeter.

On the outside of the calorimeter are wound a manganin heater and a carbon thermometer. This thermometer is made by winding two enamelled copper wires in parallel round the circumference and, after fixing, scraping the outer surface to bare the copper. The surface is then covered in a colloidal graphite (Aquadag), which bridges the bared strips of copper, forming a carbon resistance with a very small ohmage.

Since the calorimeter hangs 20 cms. below the helium can, the tubes are centralized and fixed in the narrow neck of the helium radiation shield by a perspex spacer. This helps when hanging the calorimeter freely in the radiation shield. Nevertheless, the time consumed in "lining up" after any inspection or alteration of the apparatus, was one of the worst aspects of this machine, two or more hours being necessary to complete the task.

Another part of the apparatus peculiar to this experiment is the SAMPLE HANDLING AND MEASURING EQUIPMENT (Fig.3.3). However, the detailed use of this will be reported in the next section.

The MAGNETIC THERMOMETER is shown in Fig.3.4. The ballistic circuit is a normal one except for the sensitiser in the secondary circuit. This was found necessary, as the ballistic throw of the galvonometer was not exactly proportional to the current flowing in the primary. This was possibly due to the ferromagnetic impurities in the copper of the calorimeter and the Wood's metal, where the three

1. Storage flask
2. Charcoal trap
3. Rotary pump
4. To hydrogen cylinder
5. To compressed air
6. Rubber balloon in compressed air bottle
7. Measuring cylinders in water bath
8. Backing bottle
9. Oil monometer
10. Mercury monometer
11. Pot line
12. Calorimeter line
13. Calorimeter

X - Tap

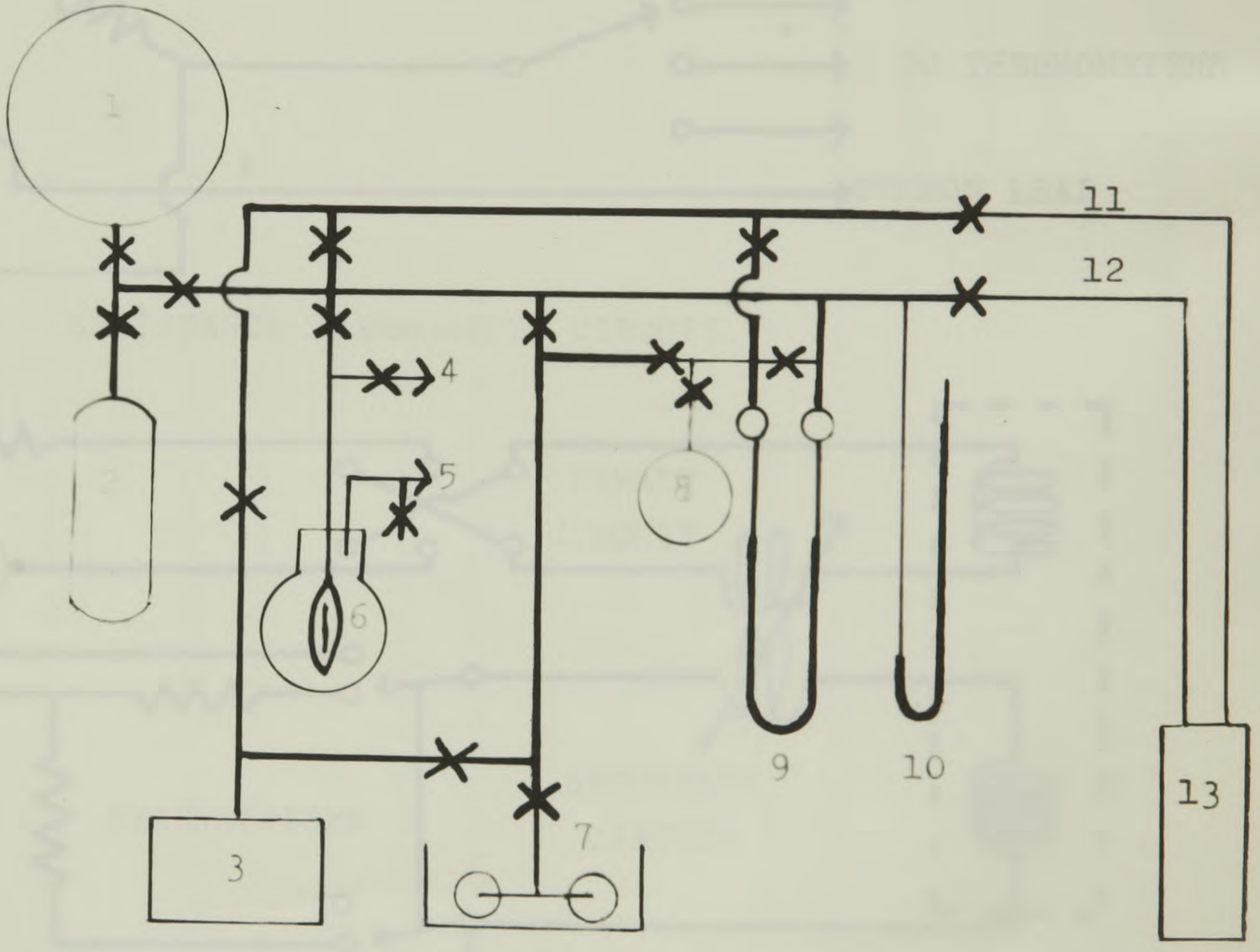
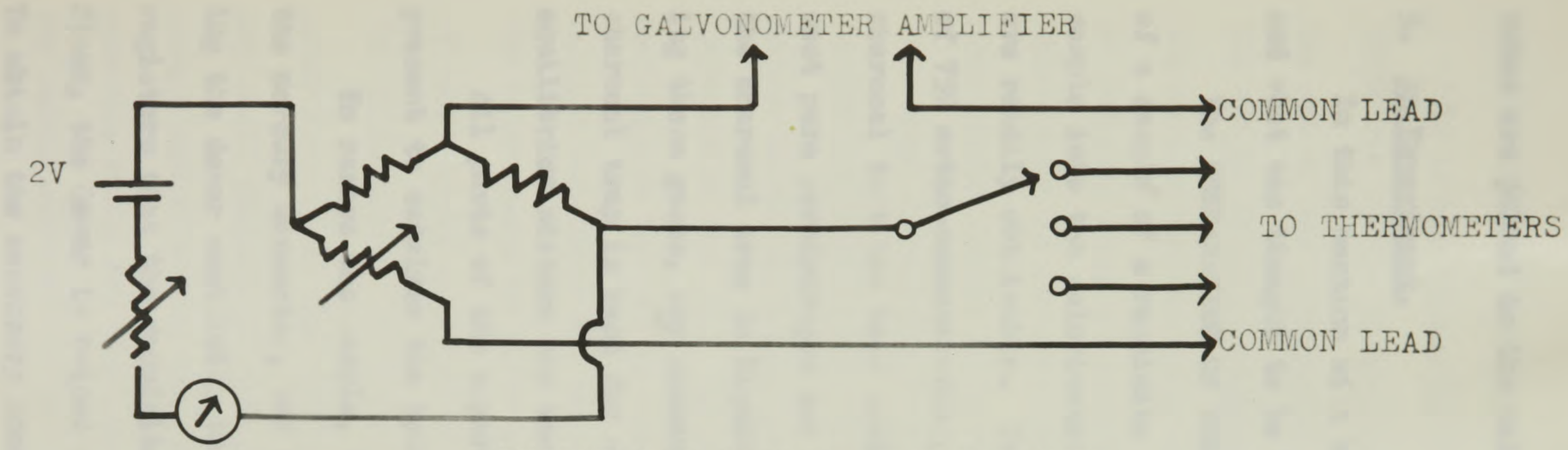
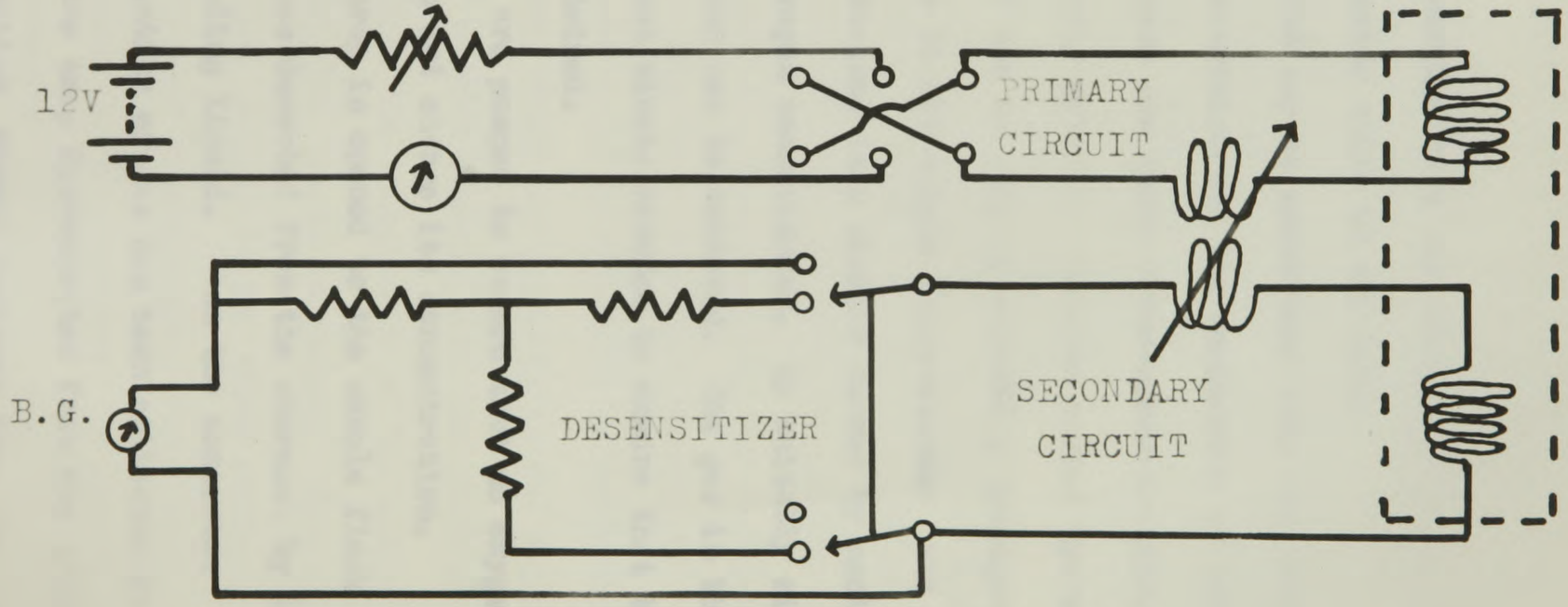


FIG 3.3. SCHEMATIC DIAGRAM OF SAMPLE HANDLING AND MEASURING EQUIPMENT.



RESISTANCE THERMOMETER CIRCUIT.



MAGNETIC THERMOMETER CIRCUIT.

FIG. 3.4.

tubes are joined to the calorimeter top.

5. An Experiment.

In this section will be described what was done, why it was done, and what was thought to be happening while it was done.

The PREPARATION OF THE SAMPLE may be subdivided into the making of a sample of a requisite concentration and the condensing of this sample into the calorimeter. There are three ortho-concentrations that are readily obtainable. The supply cylinder contains normal hydrogen of 75% ortho-concentration; 57% can be made by absorbing hydrogen on charcoal that has been cooled to liquid oxygen temperatures: and almost pure parahydrogen can be obtained in a similar manner by cooling the charcoal trap to liquid hydrogen temperatures. By suitably mixing these gases, any concentration can be achieved. The gas in the charcoal trap is kept for at least ninety minutes to ensure that the equilibrium mixture has been attained.

All parts of the apparatus are pumped to ensure that no oxygen is present to catalyse the hydrogen and change its concentration.

To remove the sample, the trap is opened to the sample flask and the mercury manometer, and the gas desorbed from the charcoal by lowering the dewar containing the cooling liquid. When the manometer registers that the requisite quantity of gas has been collected in the flask, the dewar is raised and the trap disconnected from the system. To obtain the necessary concentration, normal hydrogen from the supply cylinder is admitted, until there is 76 cms.Hg pressure in the sample

flask, which is then shut off from the rest of the apparatus.

It is now necessary to transfer the sample to the calorimeter. About six litres of hydrogen from the cylinder are condensed into the pot of the calorimeter. After all tubes have again been pumped, the sample flask is connected to the sample space. By pumping on the hydrogen in the pot, the calorimeter is cooled causing the sample to condense into the sample space. The size of the sample in the calorimeter is directly proportional to the difference of the pressures in the sample flask before, and after, condensing.

When the requisite sample has been obtained, the sample flask is disconnected and the CALORIMETER IS COOLED to a few tenths of a degree above the triple point (13.96°K.) of hydrogen by pumping the hydrogen in the pot. By supplying heat electrically, the remaining hydrogen in the pot is removed. This is a very slow process if carried out below the triple point as it is difficult to vapourize the last traces of solid hydrogen, which are probably in the form of small loose crystals in poor thermal contact with the walls of the calorimeter. To further reduce the temperature of the calorimeter from above the triple point, the sample is pumped. This avoids any small amounts of hydrogen being trapped in the tube, which, although not affecting the specific heat measurements, would cause a spurious value for the concentration to be measured. By pumping on the calorimeter it can be shown whether the line is partially blocked, since solid hydrogen formed below the triple point reduces the pumping speed. The effect is indicated by the final temperature of the

calorimeter being high. The loss of sample, about 10%, is immaterial as it is not necessary to have a full calorimeter, (see Part II, Section 1.).

Liquid helium is now transferred into the can of the cryostat, the calorimeter remaining at 10°K. To cool the calorimeter even from this temperature is quite difficult, since it still has a very large heat capacity, but the following technique has been found successful. About $\frac{1}{3}$ of a litre of helium gas is condensed in the 3mm. pot line, which it probably fills. Then, with an over-pressure of about 15 cms. Hg., small oscillations of pressure of the order of 1 cm.Hg. are made to force the liquid down into the pot, where it evaporates cooling the calorimeter. This oscillative process is continued until the temperature of the calorimeter is lowered to 4°K. About 4 c.c. of liquid helium are then condensed into the pot.

The THERMOMETERS ARE NOW CALIBRATED against the helium vapour pressure. Since the hydrogen sample is evolving heat, the helium must be pumped continuously if a constant temperature is to be realised. As the rate of pumping is very critical, a fine control valve in parallel with the main pumping valve, is adjusted to hold the temperature constant, as indicated by the very sensitive carbon thermometer. The manometers are connected to the calorimeter by the 1 mm. pot line, so that no differential gas flow pressure is included in the manometer readings. The resistance of the carbon thermometer and the throw of the ballistic galvonometer are now taken.

The resistance thermometer is in close thermal contact with the helium bath through the thick copper body of the calorimeter, but the salt is surrounded by the hydrogen and must be warmer than the liquid helium. It is possible to check that the temperature difference is at least less than 3/1000°K. by calibrating the magnetic thermometer against the carbon thermometer under different thermal conditions. A calibration made while the calorimeter is warming up under the ortho-para conversion without helium in the pot, shows no shift in relation to a calibration taken at a constant temperature with liquid helium in the pot.

Both thermometers are calibrated down to 1.6°K. below which the thermomolecular pressure and the small differential of the oil manometer readings make the results uncertain. Specimen calibrations are shown in Fig.3.5. and Fig.3.6.

It will be noticed that the plot of the reciprocal of the temperature against the throw of the ballistic galvonometer is a straight line. This is fortuitous as the susceptibility of the salt is known to have a negative Weiss constant. χ . But the salt is not in the form of a sphere, so that its susceptibility should only obey a Curie-Weiss law, after an appropriate magnetisation correction has been applied. The linearity of the calibration is due to the fact that the first effect annuls the second.

The thermometric parameter used in plotting the resistance of the carbon thermometer against the temperature is $\rho = \frac{1000}{R}$. This parameter is more convenient since the sensitivity in these units is

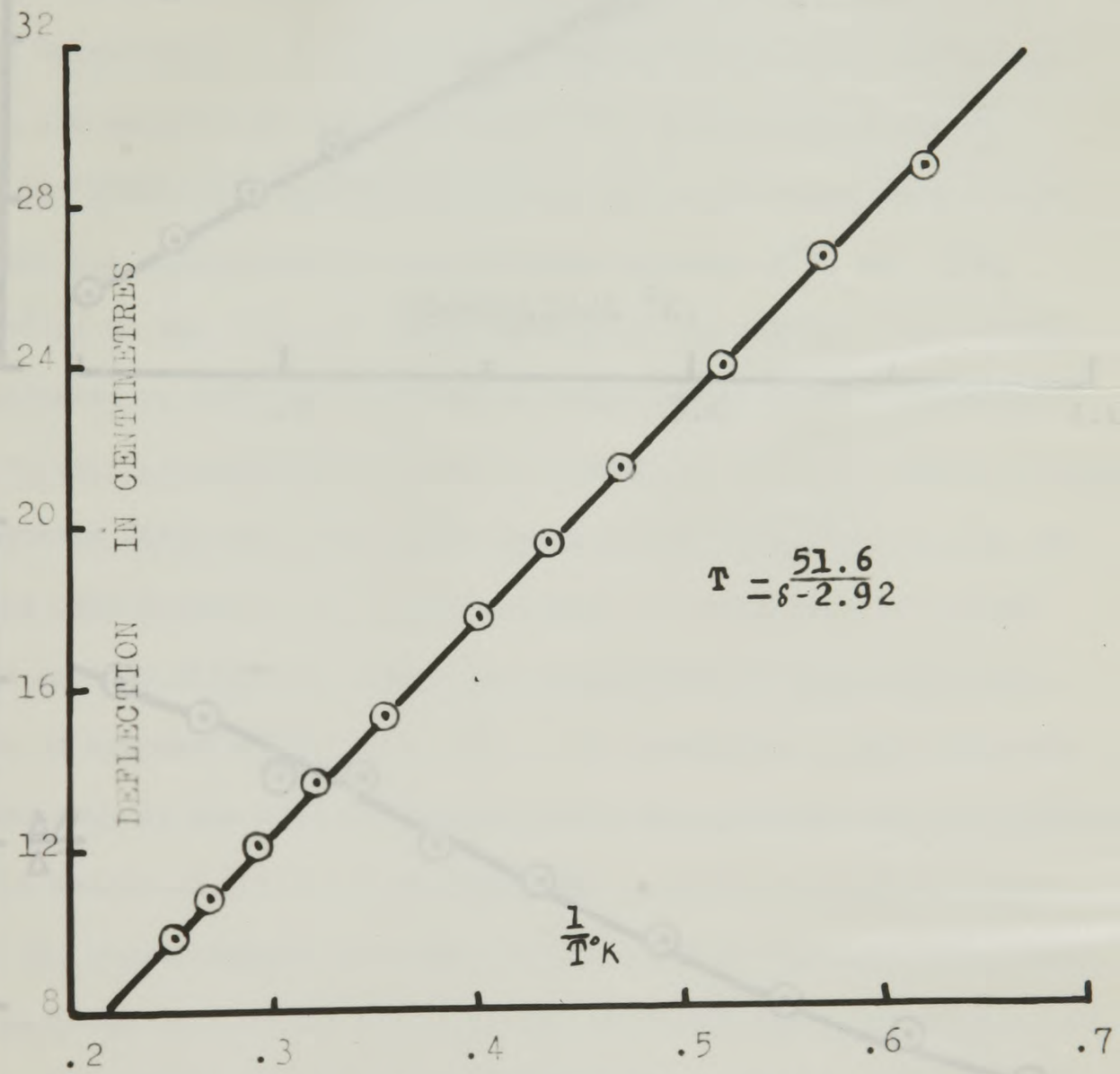
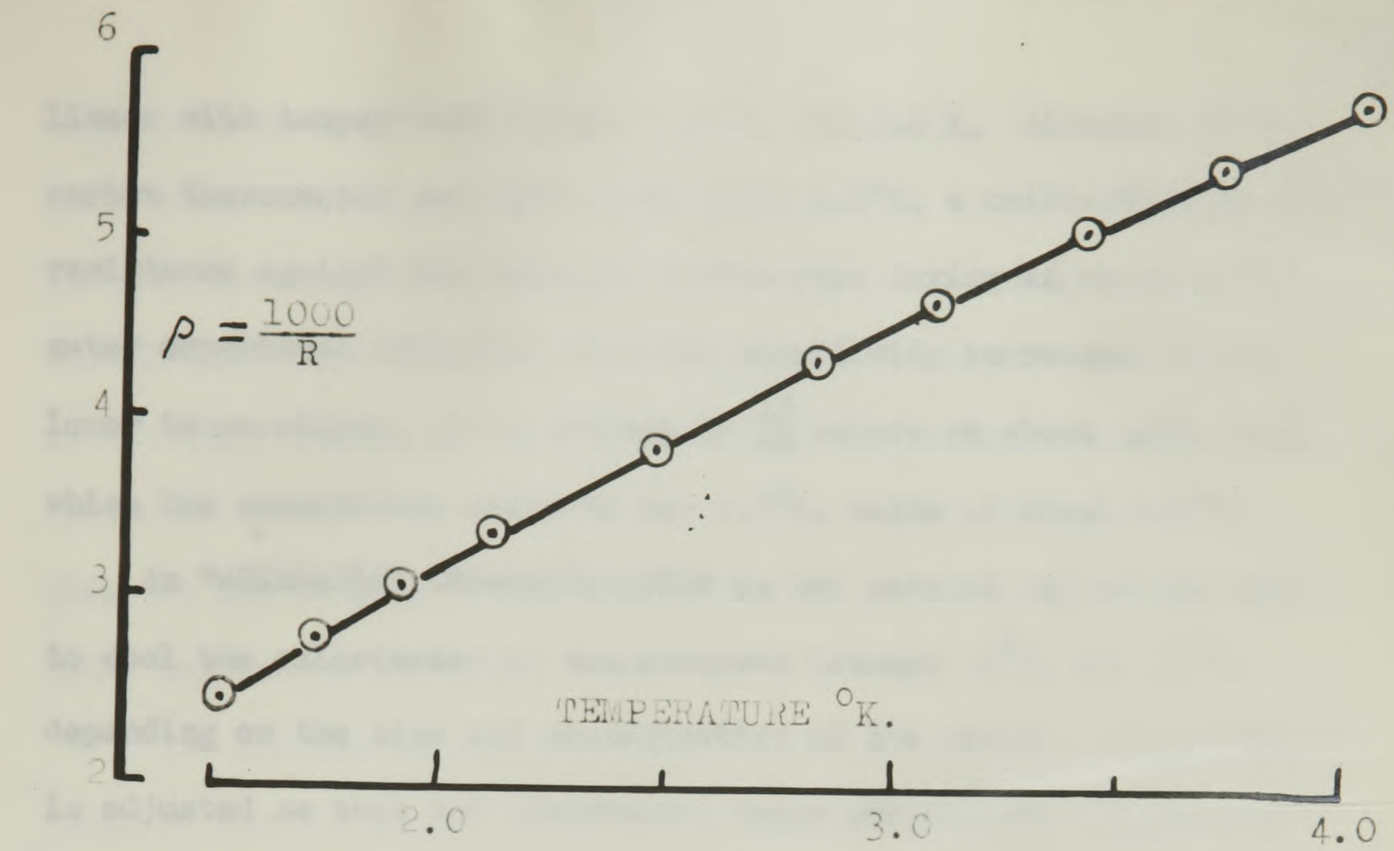


FIG. 3.5 CALIBRATION OF THE MAGNETIC THERMOMETER.



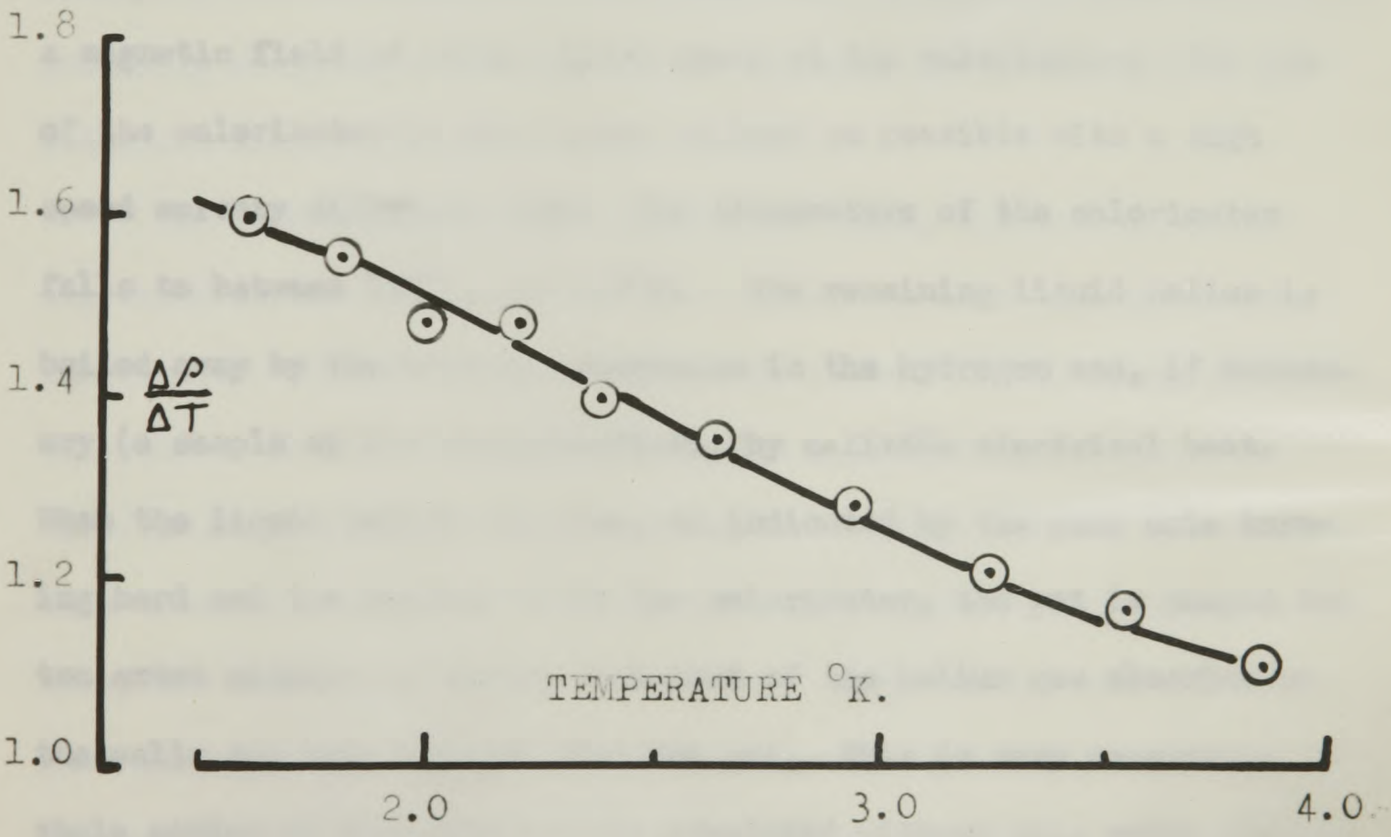


FIG. 3.6 SPECIMEN CALIBRATION OF THE CARBON THERMOMETER

linear with temperature between 1.6°K. and 3.0°K. Although the carbon thermometer was never used below 1.6°K. a calibration of its resistance against the magnetic thermometer during an empty calorimeter experiment indicated that its sensitivity increases towards lower temperatures, and a maximum in $\frac{d\rho}{dT}$ occurs at about .4°K. below which the sensitivity falls to its 2.0°K. value at about 0.1°K.

An "ADIABATIC" DEMAGNETIZATION is now carried out on the salt to cool the calorimeter to temperatures between .2°K. and .4°K. depending on the size and concentration of the sample. The magnet is adjusted so that the calorimeter hangs perpendicularly between its poles. An energising current of about 150 amps is used to produce a magnetic field of about 11,000 gauss at the calorimeter. The pot of the calorimeter is now pumped as hard as possible with a high speed mercury diffusion pump. The temperature of the calorimeter falls to between 1.1°K. and 1.3°K. The remaining liquid helium is boiled away by the heat of conversion in the hydrogen and, if necessary (a sample of low concentration), by a little electrical heat. When the liquid helium has gone, as indicated by the pump note turning hard and the warming up of the calorimeter, the pot is pumped for two extra minutes to ensure that most of the helium gas absorbed on the walls has been removed from the pot. This is very necessary. A whole series of experiments were completed without this extra pumping, and all the results showed too small a specific heat below 1.0°K. The reason for this is obscure, since any remaining gas in the pot should be gettered on demagnetization, so that during the warm up heat

would have to be given to vapourise this condensed gas, and too large a specific heat would be calculated. It is very unlikely that the gas condenses during the warming up when too low a result to the specific heat might be expected. A short calculation shows that in either case, the small volume of gas that might conceivably be present could not account for the effect. It can only be assumed that the residual gas in some manner acts as exchange gas between the calorimeter and the helium can.

The current through the magnet is then reduced to its minimum value of about 5 amps, before the magnet is lowered to remove the remaining residual field of 800 gauss. The magnet is not pulled horizontally away, as this drags the calorimeter on to the side of the radiation shield producing a heat leak.

The temperature of the calorimeter falls, but not as far as one would expect from the cooling power of the Iron Alum salt. The inefficiency is due to the irreversible effects of the demagnetisation. The removal of the field induces in the copper of the calorimeter an e.m.f., which gives rise to a current that generates heat of the order of a tenth of a calorie. A slower demagnetisation would generate less heat, but the longer the demagnetisation time, the greater the heat generated by the ortho-para conversion in the hydrogen. Also the current controller used with the magnet works in steps, which cause a very high rate of change of field with time between each unit of the regulator. The overall efficiency is about 50%.

This loss of efficiency, which was much greater than allowed for when designing the experiment, did not affect the completeness of the results for two reasons. First, it was found possible to work with small samples and still achieve equilibrium between the salt mixed with the hydrogen, and the salt in vacuum above it. Second, the results are such that the higher the specific heat of the sample, the quicker this specific heat falls to zero on approaching a lower temperature. These two facts are partly responsible for the success of the technique, and are due to luck, a goddess that is not always with the experimental physicist.

The calorimeter does not reach EQUILIBRIUM AFTER DEMAGNETIZATION for about 60 seconds. This can be observed by the falling temperature of the body of the calorimeter, indicated by the carbon thermometer, for the first 10 seconds after demagnetization, and the low value and the rapid rise of temperature, as recorded by the magnetic thermometer during the first 60 seconds. These figures are not an indication of the thermal equilibrium present during the experimental run, since on demagnetization, the salt falls to a very much lower temperature (0.05°K.) than the hydrogen, and has a very large specific heat, so that a considerable transfer of heat from the hydrogen to the salt must first be accomplished before a form of equilibrium becomes apparent.

The DRIFT is now measured with the magnetic thermometer. Readings of the ballistic galvonometer are made as quickly as possible,

the time of the current reversal and the deflection being noted by a second observer. For a few weeks this assistant was not available, but it was found possible to take accurately-timed readings in the following manner. The microphone of a tape-recorder was mounted close to the reversing switch and could receive anything said in a loud voice in any part of the room. The tape recorded the click of the reversing switch and the voice of the observer reading the galvonometer, the primary current and a time check from a watch. The observer did not need to write anything down. After the experiment, the tape was played back and the time of the ballistic throw was noted against a watch; other relevant data were transcribed into the observations book. The commercial recorder used reproduced the time intervals to within 0.2%.

If the first HEAT CAPACITY POINT is to be taken between 1.0°K. and 1.6°K. the magnetic thermometer is used, as the carbon is not calibrated in this region. Above 1.6°K. the carbon thermometer is the better due to its very much higher sensitivity. The drifts between the individual points are made by noting the time at which the galvonometer spot passes through its zero, for different settings of the bridge. This was found to be more accurate than the continual balancing of the bridge at given intervals of time, because at low temperatures, where the carbon thermometer has a very high sensitivity, the bridge has to be balanced so rapidly, that there is a lack of manual precision, and at higher temperatures of lower sensitivity, the tenth ohm intervals are too large, giving rise to a

loss of exactness.

The time, during which measurements are made from the lowest temperature to 4.0°K, varies from 25 to 40 minutes. Depending on the concentration, four to six heat capacity points are taken above 1°K. The measurements may be repeated (for a slightly lower concentration) by recondensing more helium and carrying out the same operations that have been described. When measurements are finished, exchange gas is introduced into the vacuum space, and the temperature of the helium can and the calorimeter are returned to 20°K.

To measure the ORTHO-PARA CONCENTRATION of the sample, a litre of para-hydrogen, that has been made in the charcoal trap cooled to hydrogen temperatures, is desorbed into the rubber balloon, and, from there, condensed into the pot of the calorimeter. The vacuum space is evacuated and the parahydrogen in the pot gently pumped to reduce the temperature of the calorimeter to about 19°K. which ensures that there is no liquid hydrogen in the tubes at a different temperature from the specimen. The pot and the specimen space of the calorimeter are now connected across the oil manometer. The differential pressure observed is the difference of the vapour pressures of the specimen hydrogen and the 99.7% para-hydrogen for the temperature indicated by the pressure of the sample hydrogen read on the mercury manometer. Three readings at two-minute intervals ensure that true equilibrium has been obtained and that there are no leaks into the system.

The SIZE OF THE SAMPLE is measured next. Any residual pressure in the cylinders is first measured on the oil manometer, which it is now possible to back by a mercury diffusion pump. The specimen space and the cylinders are connected after exchange gas has been admitted to the vacuum space. The specimen vapourizes and flows into the cylinders, whose pressure is again measured on the oil manometer, when the transfer has been completed. The temperature of the cylinder bath is read to complete the information needed for measuring the size of the sample.

When the final result required is the entropy of the hydrogen at a known concentration, a single slip in any of these measurements reduces the value of the experimental run to zero. In fact, only 10 perfect runs are necessary for the results discussed in Part II, but more than forty experiments were actually made, which for different reasons were complete failures as far as results were concerned, but they were nevertheless invaluable in developing the design and the technique of the experiment.

6. The Temperature Independence of the Ortho-para Conversion.

It was stated in Section 2 that unless the rate of the ortho-para conversion in solid hydrogen could be established, the value of the calculated entropy of the anomaly would have little meaning. In this section, it will be shown how this point is resolved.

It is possible to find the rate of conversion by four methods. It will be assumed in the four paragraphs below that there is no

heat leak to the calorimeter in which the measurement is made.

1. In the temperature range from 1.5°K. to 4.0°K. where the heat capacity is known from traditional measurements, the slope of the fore and after-drifts $(\frac{dT}{dt})$ is a measure of the rate of evolution of heat due to the ortho-para conversion in the sample (q). If H is the heat capacity of the sample and calorimeter combined:

$$q = H \frac{dT}{dt} \qquad 3.3$$

2. If the heat of conversion is transferred to liquid helium boiling under constant pressure, the heat of conversion is a function of the latent heat (L) of the helium and the volume (V) vapourised in a given time (t):

$$q = L \frac{dv}{dt} \qquad 3.4$$

3. If extra heat is added to the hydrogen as it warms up, the rate of heat evolution by the sample can be calculated. Let the heat of conversion be a function of the temperature, q(T). If the sample warms itself from T_1 and T_2 in time t, then:

$$\int_{T_1}^{T_2} H dT = q(T)t \qquad 3.5$$

Repeating the experiment with added extra heat q' per unit time, so that the sample warms from T_1 to T_2 in t', we have:

$$\int_{T_1}^{T_2} H dT = (q(T)+q')t' \qquad 3.6$$

Solving equations 3.5 and 3.6 for q(T), we have:

$$q(T) = \frac{q't'}{t-t'} \qquad 3.7$$

All the terms on the right hand side can be measured directly.

4. The change of concentration (Δx) can be measured before and after a period (t') during which the hydrogen may be kept in the solid state. Then:

$$q = \frac{337M}{t'\Delta x} \qquad 3.8$$

where M is the size of the sample in moles, and 337 is the number of calories evolved in converting one mole of ortho-hydrogen into para-hydrogen.

The first method has been used between 1.0°K. and 4.0°K. A plot of q against T is shown in Fig.3.9 (C). The slope of the line is attributed to heat leak and not to a change with temperature in the rate of evolution of heat by the hydrogen. Apart from the slope being of the correct order of magnitude when compared with the heat leak temperature dependence found in experiments on the empty calorimeter, it is possible to compare the heats evolved per mole of hydrogen for different concentrations at a temperature where there is no heat leak. If the values of the heat evolved falls into a recognizable form, it may be assumed that our attribution is correct. A complication arises in our calculation, since the temperature at which there is no heat flow into the calorimeter changes rapidly with the standard of the vacuum attained during the experiment. The

specimen space tube is the cause of the effect, for it is directly connected to the hydrogen cooled vacuum case. The better the vacuum, the higher the temperature from which heat is conducted to the calorimeter. It is possible to find a relation between the rate of change of heat leak with temperature and the temperature of zero heat leak from measurements on the empty calorimeter. A graph of this effect is shown in Fig.3.7. The temperature that must be used when calculating the heat of conversion can be read from this graph, once the rate of change of heat leak with temperature has been found for a particular specimen. In Fig.3.8 is the results of plotting the square of the concentration against the heat of conversion. The very small scatter of the points about the drawn line, shows that the slope in Fig.3.9 (C) may be attributed to the heat leak. It is then found from all the experiments with different concentrations, that the rate of the ortho-para conversion is independent of temperature to within 3% between the temperatures considered.

The second method was useful in checking that no sudden changes occurred in the conversion rate for high ortho-concentrations between 1.3°K. and 2.0°K. Due to the masking effect of the helium λ-phenomena heat leak, only rapid changes of 5% or more could be observed. No such changes were found.

The third method was used from 0.3°K. to 1.5°K. Down to 0.7°K. q(T) is a constant to within 5%. Below this temperature the results are not so satisfactory, but the apparent change of q(T) can be ex-

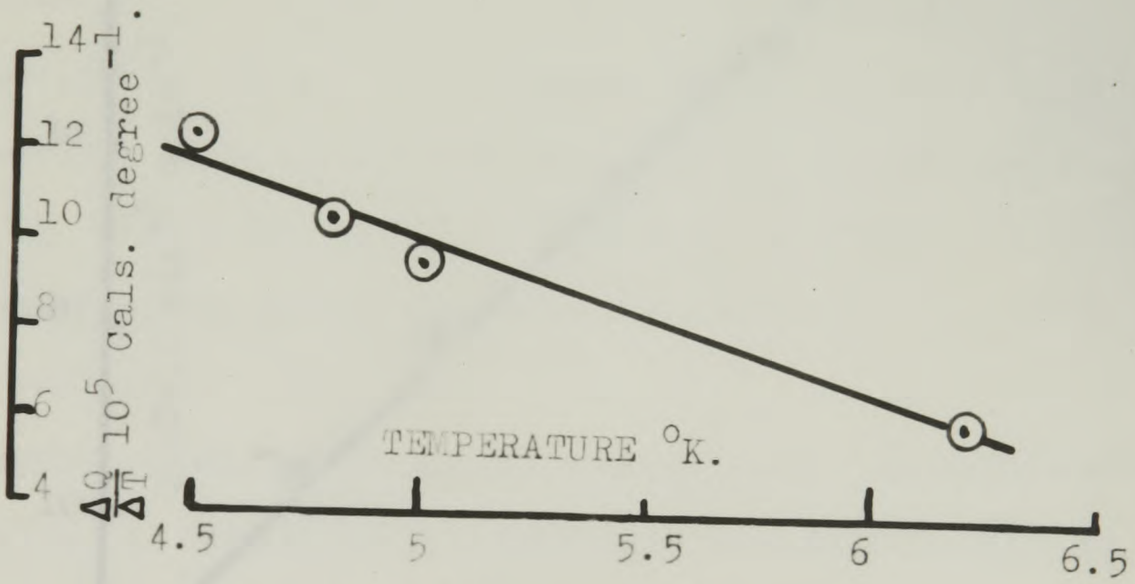


FIG. 3.7 SEE TEXT.

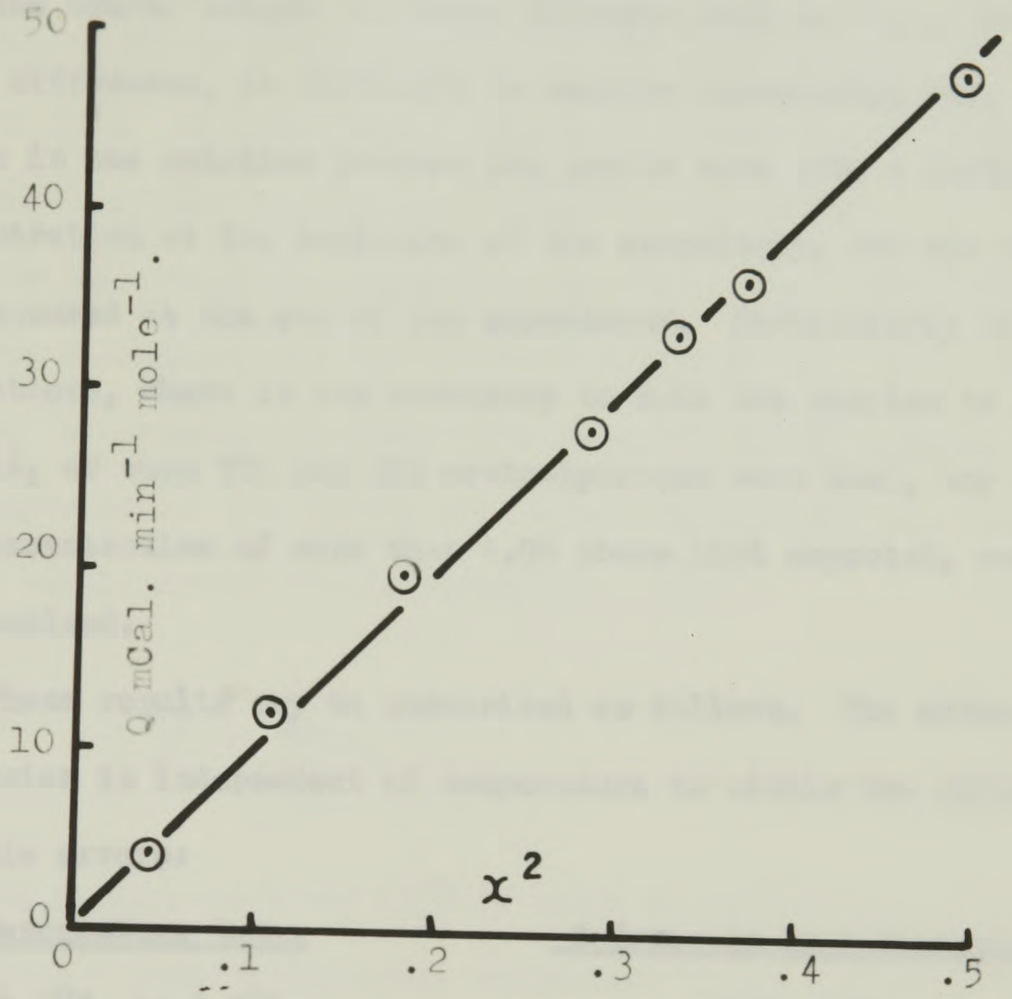


FIG. 3.8. THE RELATION BETWEEN THE HEAT GENERATED AND THE ORTHO-CONCENTRATION FOR SOLID HYDROGEN.

plained by considering the dis-equilibrium between the magnetic thermometer and the body of the calorimeter, where the extra heat is applied. We can, nevertheless, state that from 0.3°K. to 0.7°K. q(T) is a constant to within 15%.

The fourth method was never directly used as Δx, being a small difference, is difficult to measure accurately; but, a check exists in the relation between the sample made with a particular concentration at the beginning of the experiment, and the concentration measured at the end of the experiment. Particularly at high concentrations, where it was necessary to make the samples to better than 1%, or when 75% and 57% ortho-hydrogen were used, any change in the concentration of more than 1.0% above that expected, would have been noticed.

These results may be summarized as follows. The ortho-para conversion is independent of temperature to within the following possible errors:

Temperature Range	% Error in Heat Evolution
0.3°K. to 0.7°K.	15% - 5%
0.7°K. to 1.5°K.	5% - 3%
1.5°K. to 4.0°K.	3%

Part II - Results

1. The Method of Calculation and the Accuracy of the Experiment.

The method of deriving the low temperature specific heat will be discussed in detail. The errors involved will be considered and an estimate of the final accuracy of the specific heat and entropy will be made. An experimental run with a specimen of 69.0% ortho-concentration will be used to illustrate the method.

The heat capacity points and the drift rates associated with them are calculated for the temperature region 2° - 4°K. Fig.3.9 (a) and (b) show H, the total heat capacity and $\frac{dT}{dt}$ plotted against the temperature. The smooth line drawn through the heat capacity points should be correct to within 2%. Now:

$$\frac{\Delta T}{\Delta t} = \frac{\frac{\Delta \rho}{\Delta t}}{\frac{d\rho}{dT}} \qquad 3.9$$

The percentage error in $\frac{\Delta \rho}{\Delta t}$ is about 3%, since the drifts are taken over a temperature range equivalent to a $\Delta\rho$ of about 0.2, which can be measured to an accuracy of .003 . The $\frac{d\rho}{dT}$ of the carbon calibration is known to 1%.

The heat received by the calorimeter and sample per minute Q, is given by:

$$Q = \frac{\Delta T}{\Delta t} H \qquad 3.10$$

The calculated values of Q plotted against the temperature

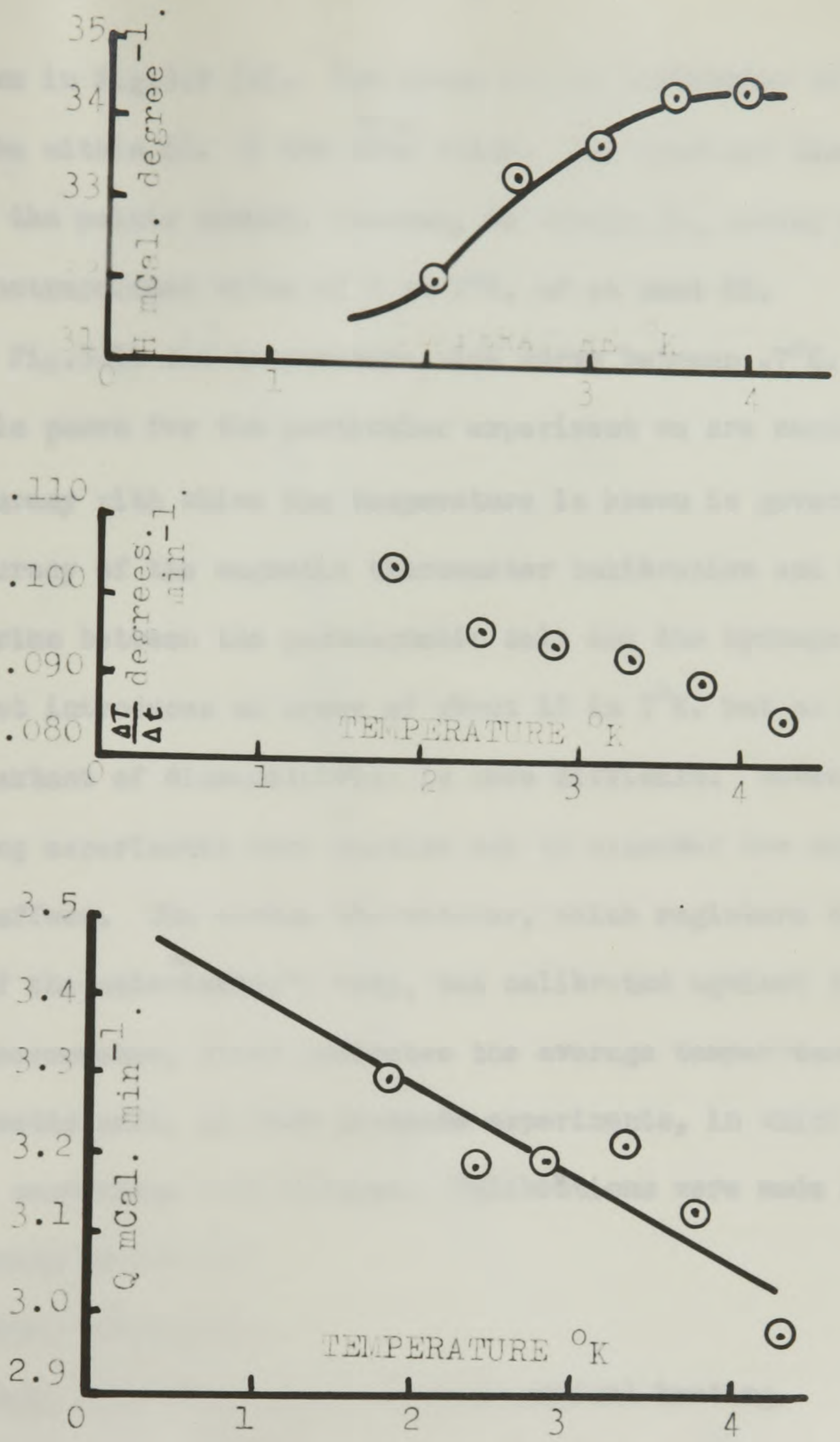


FIG. 3.9. SEE TEXT.

are shown in Fig.3.9 (c). The error in any particular value of Q will be within 6%. of the true value. The straight line drawn through the points should, however, be within 2%, making an error in the extrapolated value of Q at 1°K. of at most 6%.

In Fig.3.10 the temperature time curve between .7°K. and 1.9°K. is shown for the particular experiment we are considering. The accuracy with which the temperature is known is governed by the accuracy of the magnetic thermometer calibration and the disequilibrium between the paramagnetic salt and the hydrogen sample. The first introduces an error of about 1% in T°K. but an estimate of the extent of disequilibrium is more difficult. However, the following experiments were carried out to discover the magnitude of the effect. The carbon thermometer, which registers the temperature of the calorimeter's body, was calibrated against the magnetic thermometer, which indicates the average temperature of the paramagnetic salt, in four separate experiments, in which the thermal conditions were changed. Calibrations were made during the warming period for:

1. Empty Calorimeter.
2. Empty Calorimeter with extra electrical heating.
3. Calorimeter with a sample of 56% ortho-hydrogen.
4. Calorimeter as 3. with extra electrical heating.

If it is assumed that the carbon and magnetic thermometers are in equilibrium in experiment 1., it can be deduced from the disequilibrium conditions of 2. and 4. that in experiment 3. the

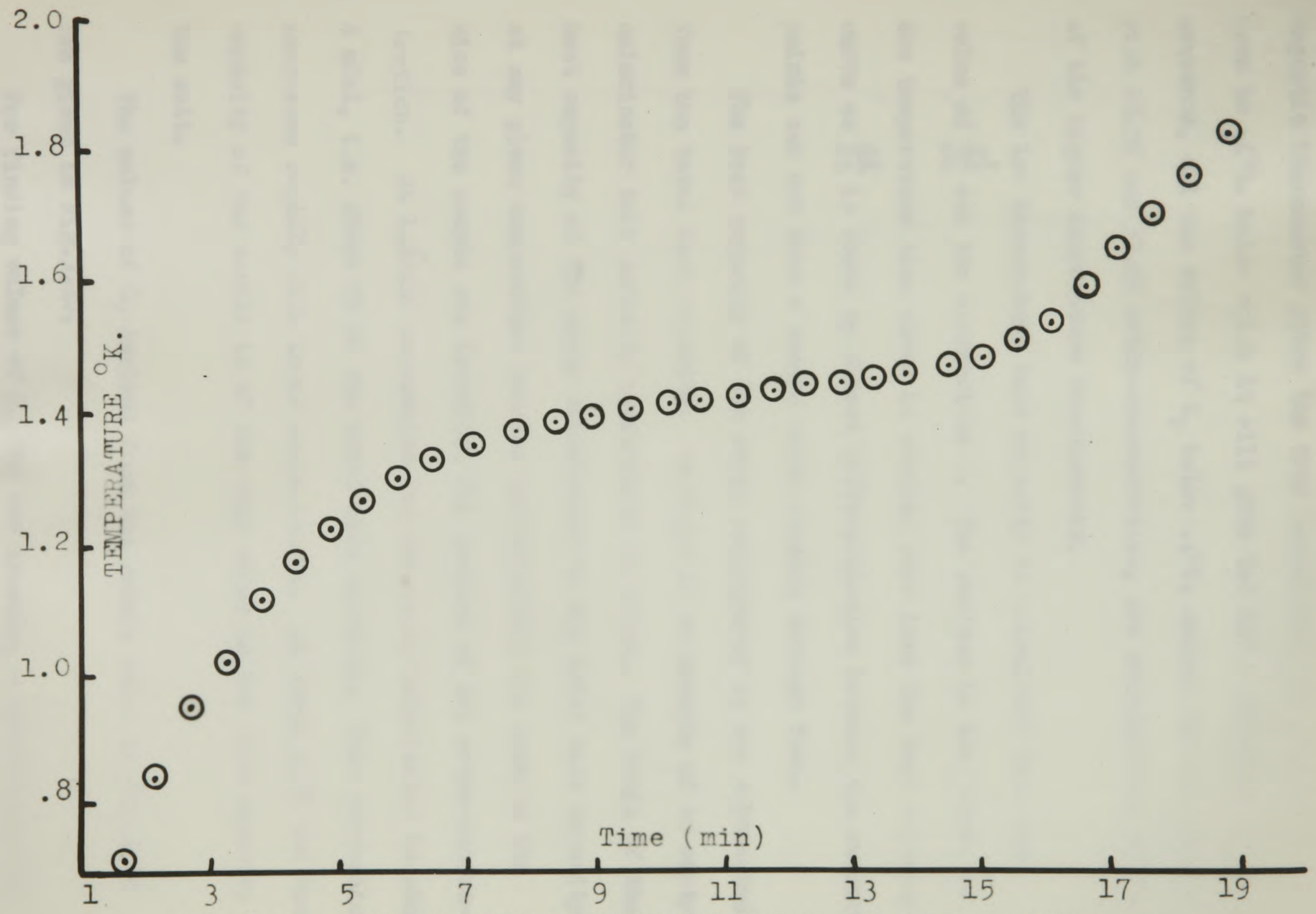


FIG. 3·10 TEMPERATURE-TIME GRAPH FOR A 69% ORTHO-SAMPLE.

magnetic thermometer gives the true temperature to within .005°K. down to .4°K. below which it will give too low a reading. In consequence, all the values of C_p below .4°K. except for the samples with 20.5% and 33.0% ortho-concentration, are extrapolated values of the higher temperature measurements.

The low temperature heat capacity is calculated from the value of $\frac{dT}{dt}$ and the appropriate Q. The scatter in the points in the temperature time curve is carried over into the heat capacity curve as $\frac{dT}{dt}$ is found by direct differentiation between the measured points and not from a smooth curve passing through them.

The heat capacity of the empty calorimeter is now subtracted from the total heat capacity. In Fig.3.11 an example of an empty calorimeter heat capacity measurement is shown. The ratio of the heat capacity of the empty calorimeter to the total heat capacity at any given temperature remains approximately the same as the size of the sample was increased for samples of low ortho-concentration. At 1.0°K the correction for the empty calorimeter is about 2 mCal, i.e. about 6% of the total heat capacity. This correction increases rapidly with lower temperatures. At about .4°K the heat capacity of the sample is of the same order as the heat capacity of the salt.

The values of C_p derived from the points shown in Fig.3.10 are given in Fig.3.12.

For finding values of C_p for the anomaly, a correction term for the lattice specific heat must be subtracted from C_p (total),

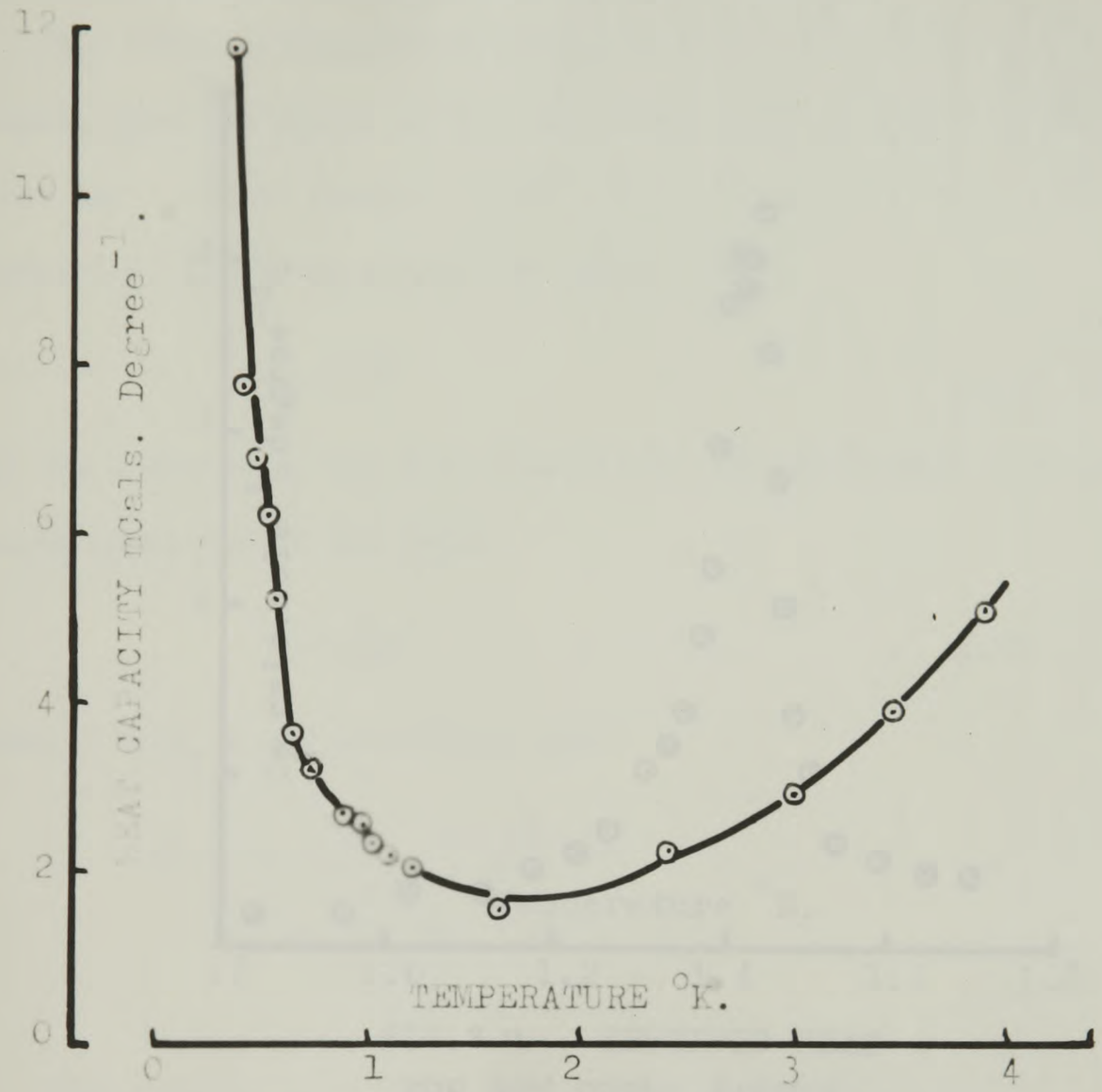


FIG. 3.11. EXAMPLE OF THE HEAT CAPACITY OF THE EMPTY CALORIMETER.

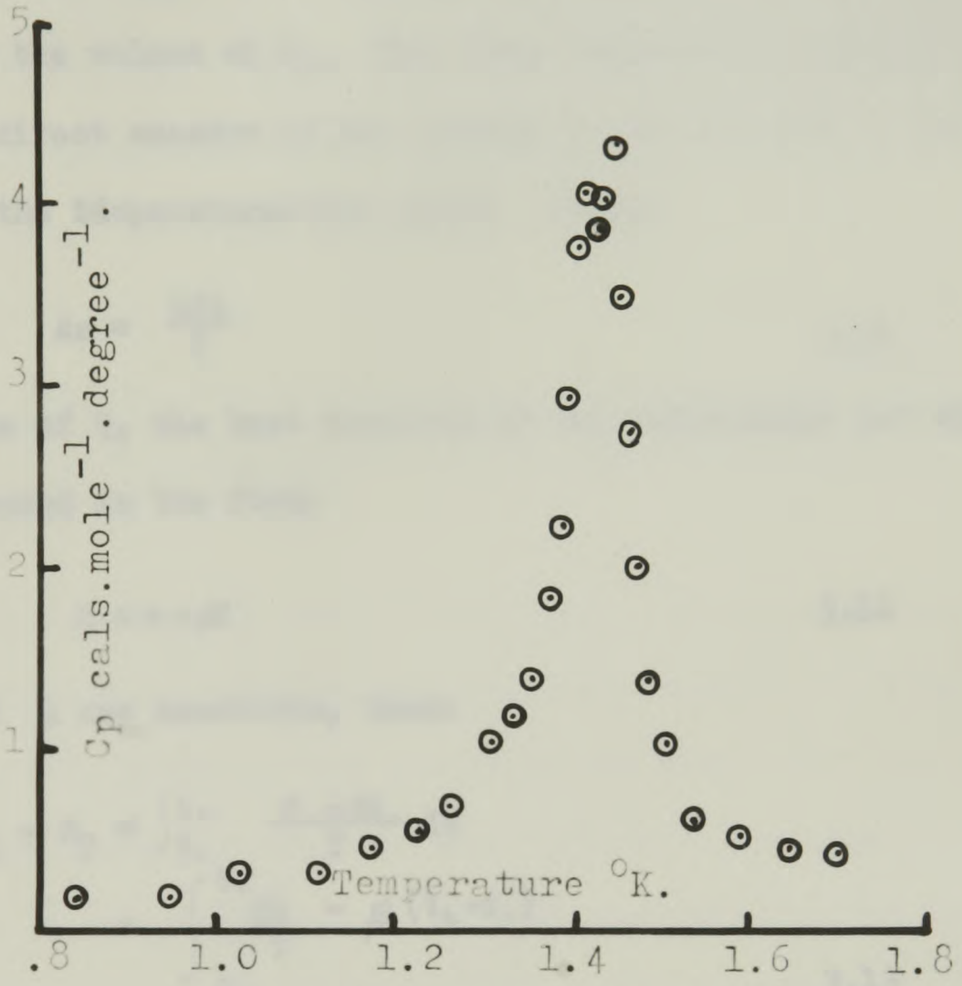


FIG. 3.12. SPECIFIC HEAT
FOR 69% ORTHO SAMPLE.

at temperatures above 2°K. It has been assumed that the lattice specific heat is the same as the specific heat of para-hydrogen. The values used have been taken from Hill (thesis).

The total entropy of the anomaly may be found, in the usual manner, from the values of C_p. The lower temperature data, however, allow for a direct measure of the entropy to be made from a reciprocal of the temperature-time graph. Since:

$$\Delta s = \frac{Q dt}{T} \qquad 3.11$$

and the value of Q, the heat received by the calorimeter per minute, can be expressed in the form:

$$Q = \alpha - \beta T \qquad 3.12$$

where α and β are constants, then:

$$S_1 - S_2 = \int_{t_1}^{t_2} \frac{\alpha - \beta t}{T} dt$$
$$= \int_{t_1}^{t_2} \frac{dt}{T} - \beta (t_2 - t_1) \qquad 3.13$$

The entropy below 2°K. which is about two-thirds of the total entropy of the anomaly will be accurate to within 8% using the errors for Q and T derived above. The entropy above 4°K. is calculated from specific heat measurements of Hill (thesis). The value of the entropy above 2°K. should not be in error by more than 3%. The total entropy of the anomaly should therefore be accurate to within 7%.

2. The Anomalous Specific Heat of Solid Hydrogen with Ortho-concentrations greater than 60%.

The results of the measurement of samples with high ortho-concentration will be considered together, since this group is peculiar, in that there is a form of λ-anomaly that appears between 0.9°K. and 1.3°K. The detailed graphical representation of the results is difficult due to the enormous variation of specific heat in the total anomaly. Therefore, four selected specific heat measurements are shown in the temperature region near the λ-peak in Fig.3.13, and the form of the curve outside the temperature range 0.9°K. - 1.3°K. will only be described and not graphically represented.

For ortho-concentrations of 70% or more, the specific heat becomes appreciable at about 0.3°K. and rises smoothly to a maximum at the top of the anomaly. The specific heat then falls to a constant value of about 0.5 calories.mole^{-1}.degree^{-1}. at about 1.8°K. Above 2.5°K. it falls slowly, and becomes negligible at the hydrogen triple point. The form of the curve above 3°K. is the same as the low ortho-concentration anomalous specific heats, which are shown in Fig.3.15.

As the ortho-concentration is reduced, the specific heat below 1°K. rises more quickly and from a lower temperature, until the λ-anomaly seems to sit on a specific heat plateau. This is shown best in the samples with 62.7% (Fig.3.13) and 60.9% (Fig.3.15) ortho-concentrations.

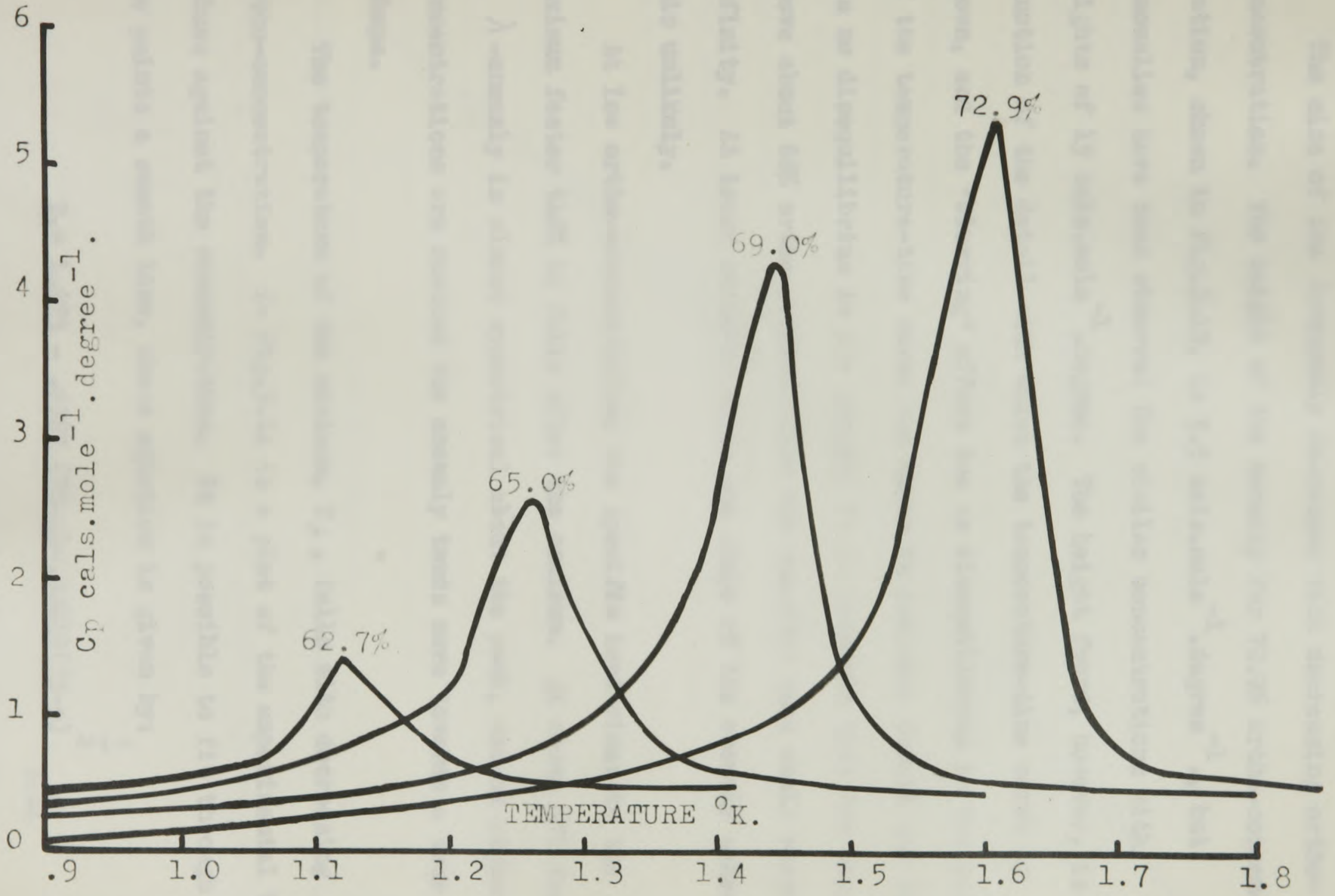


FIG. 3.13 SPECIFIC HEAT OF HYDROGEN OF HIGH ORTHO-CONCENTRATIONS.

The size of the λ-anomaly decreases with decreasing ortho-concentration. The height of the anomaly for 72.9% ortho-concentration, shown in Fig.3.13, is 5.5 cals.mole^{-1}.degree^{-1}., but -anomalies have been observed for similar concentrations with heights of 15 cals.mole^{-1}.degree. The height found, however, is a function of the detail with which the temperature-time curve is known, and the "blurring" effect due to disequilibrium in the sample. If the temperature-time curve was known in infinite detail and there was no disequilibrium in the sample, it is possible that for samples above about 68% ortho-concentration the specific heat would reach infinity. At lower concentrations the shape of the anomaly makes this unlikely.

At low ortho-concentrations the specific heat rises to the maximum faster than it falls after the maximum. At about 67% the λ-anomaly is almost symmetrical about the peak, and as higher concentrations are reached the anomaly tends more towards a true λ-shape.

The temperature of the maximum, T_λ, falls with decreasing ortho-concentration. In Fig.3.14 is a plot of the experimental T_λ values against the concentration. It is possible to fit through the points a smooth line, whose equation is given by:

$$T_\lambda = 1.675 - .0367\,(75-\underline{o}) - .00019(75-\underline{o})^{\frac{3}{2}} \qquad 3.14$$

where $\underline{o}$ is the ortho-concentration expressed as a percentage.

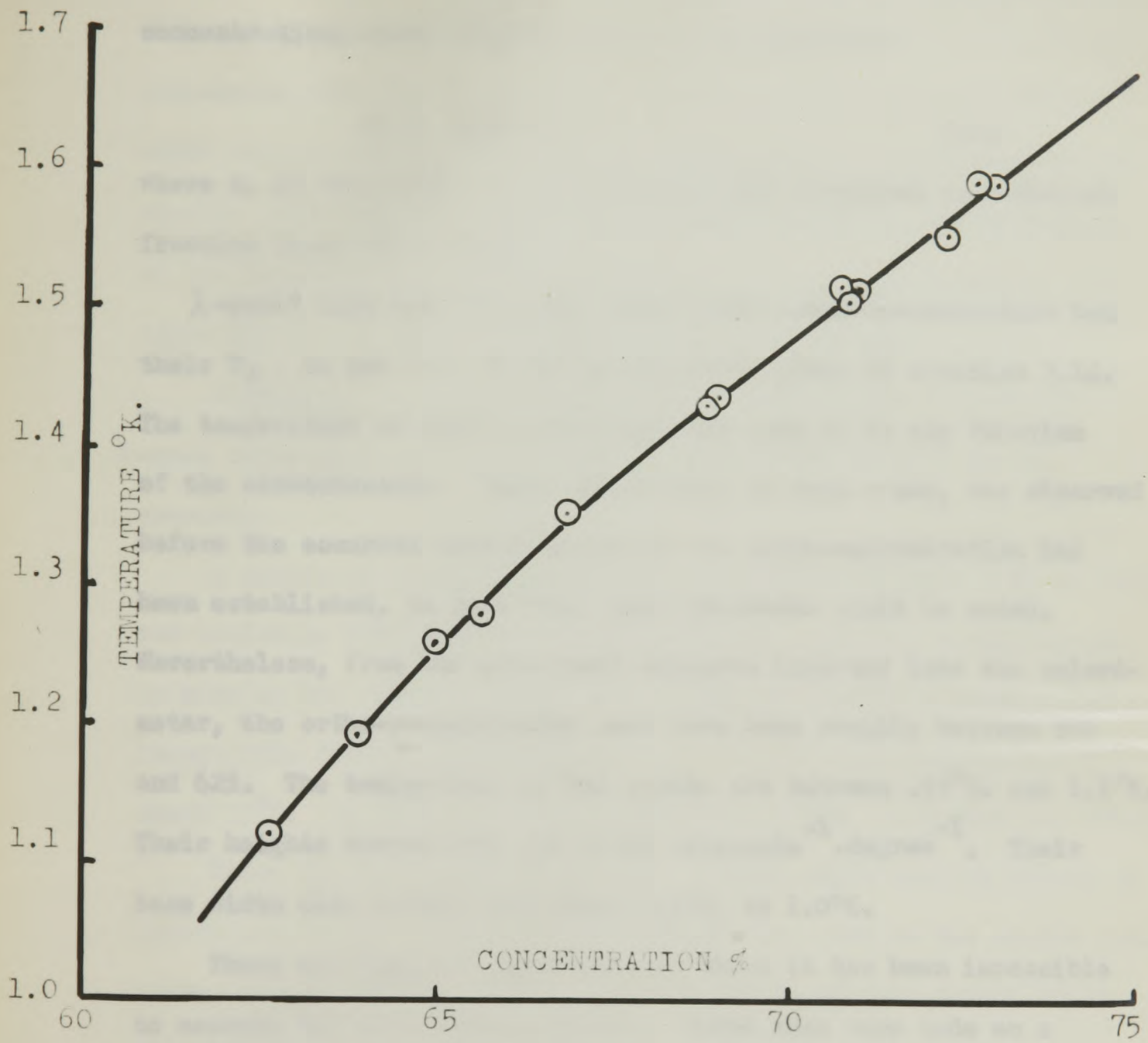


FIG.3.14 THE TEMPERATURE OF THE MAXIMUM OF THE λ-PEAK WITH ORTHO-CONCENTRATION.

For ready reference, the temperature of the λ-maximum for concentrations above 65%, is given by the equation:

$$T_\lambda = 3.02x^2. \qquad 3.15$$

where x, in this case, is the concentration expressed as a decimal fraction (i.e. 75% = .75).

λ-peaks have been observed below 62.7% ortho-concentration but their T_λ do not fall on the smooth curve given by equation 3.14. The temperature of their maxima does not seem to be any function of the concentration. Their appearance, in many cases, was observed before the accurate determination of the ortho-concentration had been established, so that only their existence could be noted. Nevertheless, from the ortho-para mixtures inserted into the calorimeter, the ortho-concentration must have been roughly between 59% and 62%. The temperature of the maxima are between .95°K. and 1.1°K. Their heights varied from .05 to 0.5 cals.mole^{-1}.degree^{-1}. Their base width also varied from about 0.4°K. to 1.0°K.

There has been one experiment in which it has been impossible to account for the observed results. Three runs were made on a decaying hydrogen sample, when it had ortho-concentrations of 71.4% 69.8% and 68.9%. In the first run a normal sized λ-peak with a maximum at 1.62°K. (instead of the expected 1.53°K.) was found. The second run showed a very small peak at 1.53°K. (instead of the expected 1.46°K.). The third run showed no λ-anomaly. It is reported by Reif and Purcell (1953) in their nuclear magnetic resonance

experiments on solid hydrogen (see discussion), that they occasionally and unaccountably were unable to obtain an effect, that can be associated with the λ-anomaly. It was thought that as a very rapid rate of cooling was used, it could result in a highly strained sample. The resulting change in the forces between the molecules of the lattice might possibly account for the disappearance of the above effect and the λ-anomaly in this experiment.

Therefore, experiments were carried out to test whether the λ-peak temperature was a function of the thermal history of the specimen.

A sample of normal hydrogen was solidified in under five seconds and cooled to 4°K. in about ninety seconds. This was accomplished by pumping the sample and the pot of the calorimeter together, and immediately forcing liquid helium into the pot at a temperature of about 11°K. No effect on the temperature of the λ-maximum was found.

Since the disappearance of the λ-peak might also be caused by impurities in the specimen, 2% of oxygen was added to the sample when it was in the gaseous state. Although little of this oxygen would dissolve in the liquid hydrogen, it is strongly paramagnetic and might effect the position of T_λ . No change, however, was found from the expected position of the λ-peak.

3. The Anomalous Specific Heat of Solid Hydrogen for Ortho-Concentrations of less than 60%.

The results of the specific heat measurements on samples with

low ortho-concentration are represented in the three figures 3.15, 16,17.

Fig.3.15 shows in detail the specific heat below 2°K. Fig.3.16 gives the results up to 4°K. and compares these results with Hill's measurements (thesis) made between 3.0°K. and 7.0°K. Both these figures include the measurements made on 60.9% ortho-hydrogen, which was the lowest concentration in which a λ-anomaly was found. The general shape of the curve is, however, of the low concentration type. Fig.3.17 is a plot of the specific heat against concentration for different temperatures. In this case, three measurements made in the λ-region are shown for comparison.

For the 60.9% ortho-sample, the specific heat rises sharply to a maximum at 0.65°K. from which temperature (if the λ-anomaly is ignored) it falls continuously. For the 53.4% sample, the specific heat rises quickly to .8°K. passes through a small minimum and only above 2°K. does it fall continuously to the triple point temperature. The minimum at 1.5°K. is difficult to explain as it does not fit into the general pattern of the other concentrations. It will be shown in the next section that the total entropy of the anomaly is smaller than expected, so that some unexplained experimental effect may be the cause. The 42.7%. 33.0% and 20% ortho-concentrations have specific heats of the same general shape. The heat capacity rises smoothly to flat maxima at 1.8°K., 1.4°K. and 1.2°K. respectively. It can be seen from Fig.3.15 that the 20% ortho-sample has too small

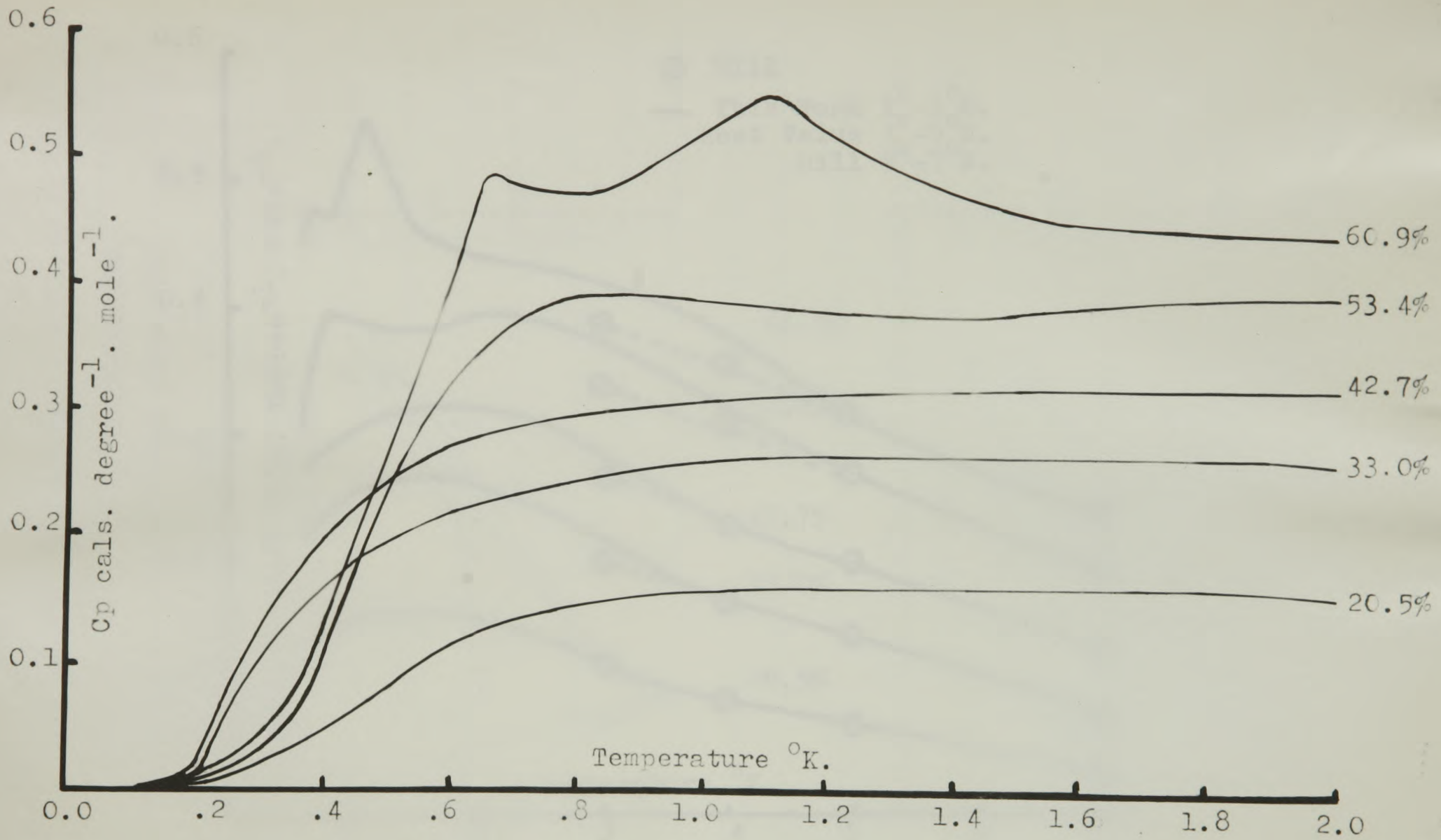


FIG. 3.15 SPECIFIC HEAT OF HYDROGEN BELOW 2.0°K.
FOR ORTHO-CONCENTRATIONS UNDER 61%.

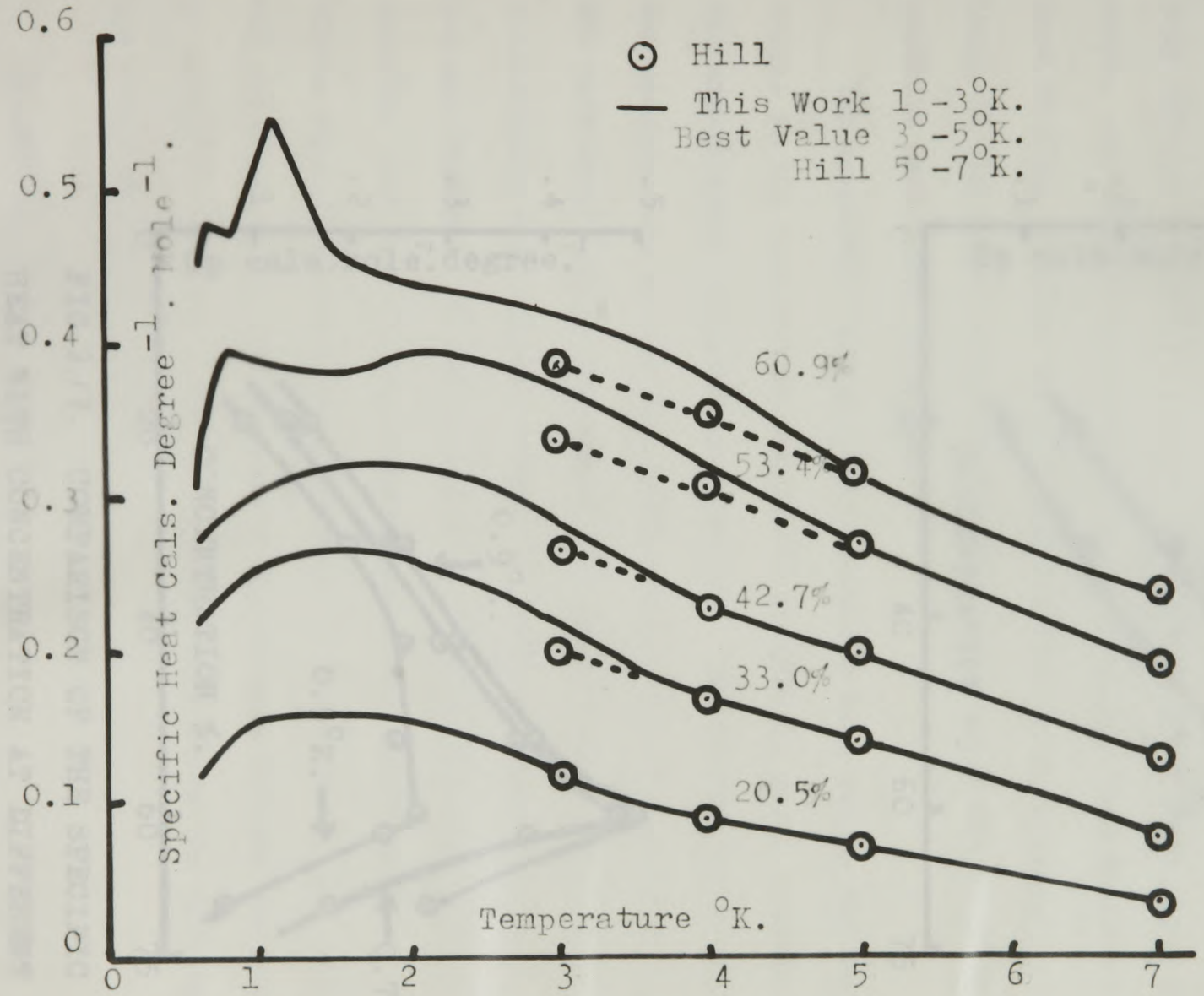


FIG. 3.16 ANOMALOUS SPECIFIC HEAT OF HYDROGEN OF LOW ORTHO-CONCENTRATIONS.

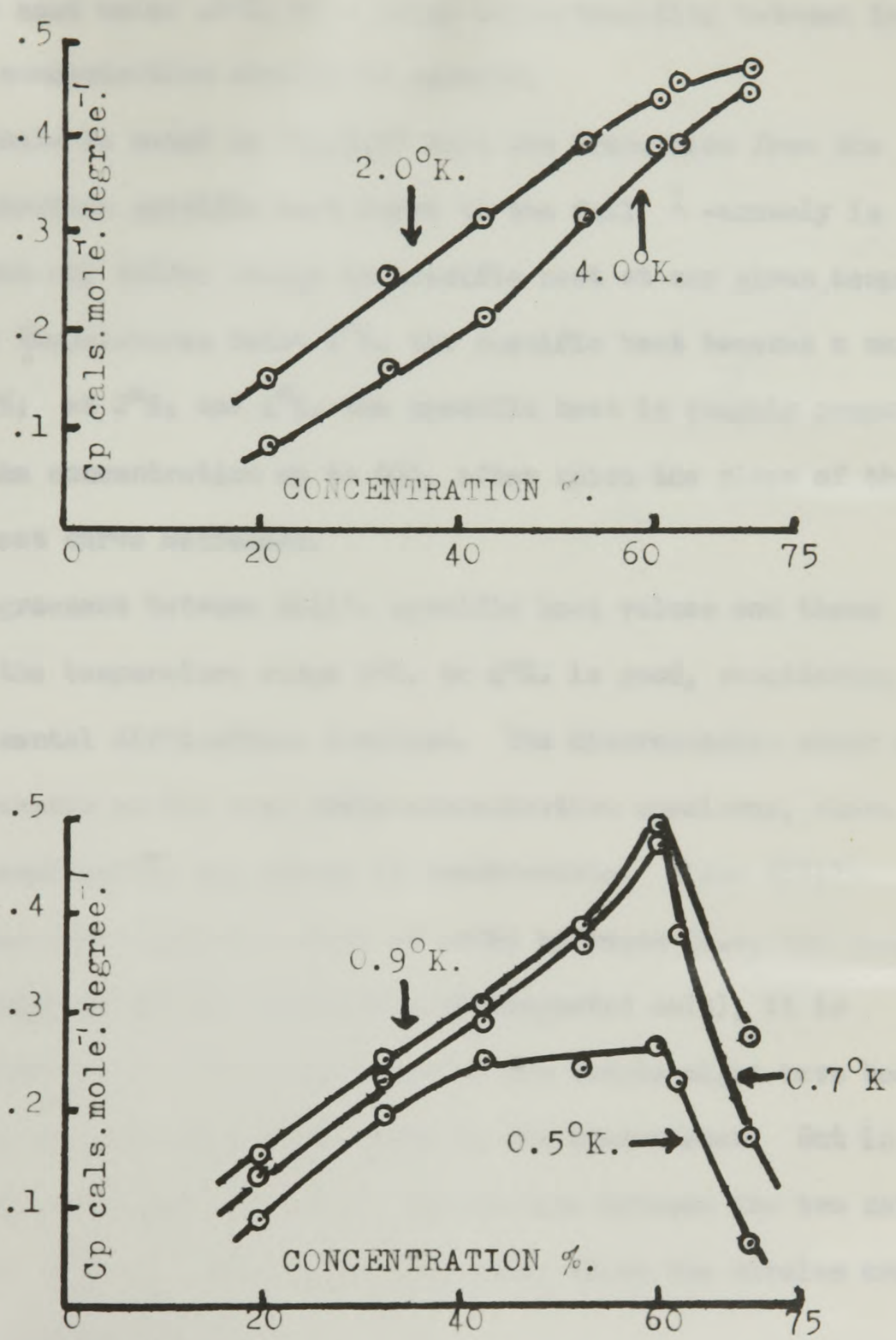


FIG.3.17. COMPARISON OF THE SPECIFIC HEAT WITH CONCENTRATION AT DIFFERENT TEMPERATURES.

a specific heat below .6°K. if a rough proportionality between the low ortho-concentration samples is assumed.

It should be noted in Fig.3.17 that the transition from the low concentration specific heat curve to the full λ-anomaly is made without any sudden change in specific heat at any given temperature. At temperatures below 1°K. the specific heat becomes a maximum at 60%; at 2°K. and 4°K. the specific heat is roughly proportional to the concentration up to 60%, after which the slope of the specific heat curve decreases.

The agreement between Hill's specific heat values and these values in the temperature range 3°K. to 4°K. is good, considering the experimental difficulties involved. The discrepancies occur in the measurements on the high ortho-concentration specimens, where the heat developed by the sample is considerable. Since Hill's measurements were made on a block of solid hydrogen (i.e. the sample was not broken up by the grains of a paramagnetic salt), it is possible that the average temperature of the sample might have been higher than the temperature indicated by his thermometer. But in all cases it is possible to draw a smooth line between the two sets of results. This has been done in Fig.3.16, where the circles are the values obtained by Hill.

4. <u>The Entropy of the Anomaly.</u>

In Fig.3.18 the values of the total entropy of the anomaly per mole of sample are plotted against the ortho-concentration. Fig.3.19

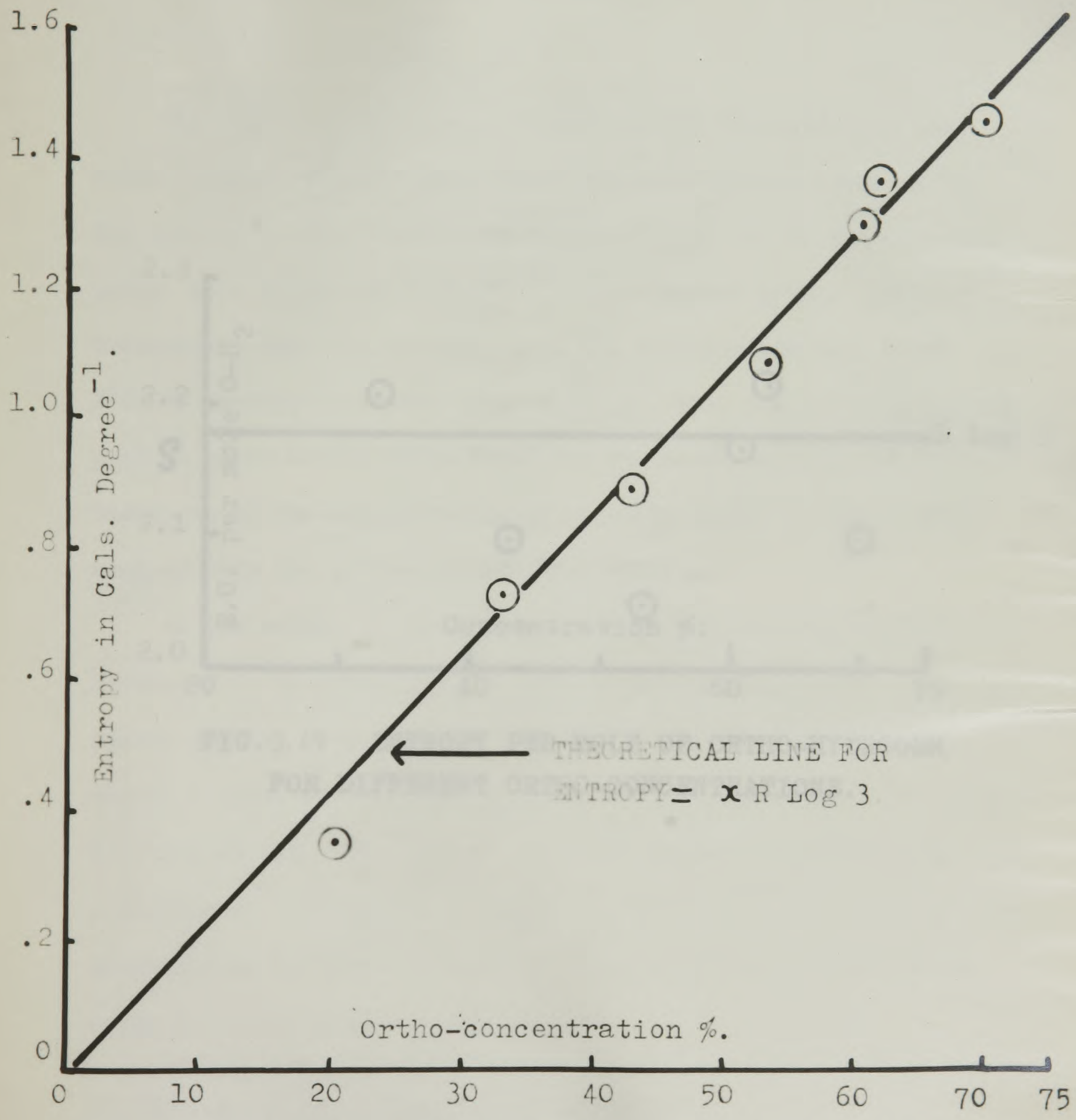


FIG. 3.18 TOTAL ENTROPY OF THE ANOMALY IN HYDROGEN FOR SAMPLES OF DIFFERENT ORTHO-CONCENTRATION.

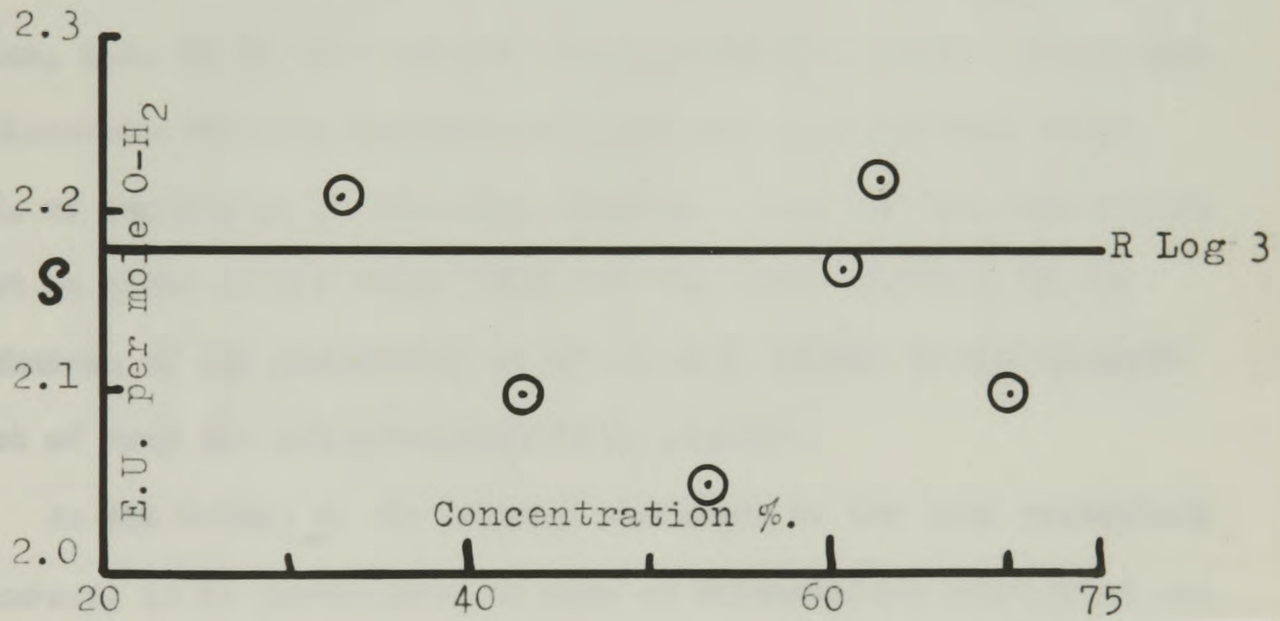


FIG. 3.19 ENTROPY PER MOLE OF ORTHO-HYDROGEN FOR DIFFERENT ORTHO-CONCENTRATIONS.

shows the entropy per mole of ortho-hydrogen. The straight line in both figures is the value of the expected entropy, namely:

$$S = xR \text{ Log } 3. \qquad 3.15$$

The value for the 53.4% sample is small compared with the other results, but it falls within the experimental error of 7%. The entropy of the 20.5% ortho-sample is only 80% of the expected value, i.e. it is well outside the experimental error. There were indications that the specific heat did not approach zero below $1^{\circ}K.$ as rapidly as in the other samples. But, not too much weight must be given to the value found for the total entropy, as the technique of the experiment is not ideally suited to the measurement of very low ortho-concentration samples.

As the values of the entropy are known to the same percentage accuracy, it is permissible to take an arithmetical average of the points plotted in Fig. 3.19, (except for the 20.5% sample) and obtain a value of 2.14 E.U. per mole of ortho-hydrogen. This should be compared with the value of 2.18 E.U. expected theoretically from a lifting of a three-fold degenerate state. The values are in very satisfactory agreement with each other, so that there can be no doubt as to the origin of the anomaly.

5. <u>The Time-Rate of Change of Concentration.</u>

In Fig.3.8 is a graph of the heat developed per minute for a mole of hydrogen in the solid state for samples of different concentrations. The method of calculating the experimental values of

the heat developed is described in Part I, Section 6, of this chapter. By using Giauque's value of 337 calories for the heat of conversion of one mole of ortho-hydrogen into one mole of para-hydrogen, we may derive a value for the rate of change of concentration.

If ϱ is the ortho-concentration expressed in percent., and the time t is in hours, we have:

$$\frac{d\varrho}{dt} = 1.79 \times 10^{-4} \varrho^2 \qquad 3.16$$

The value of the constant should be correct to within 3%.

The form of the equation is the same as that found by Cremer and Polanyi (1933). Their constant, which should not be in error by more than 5%, is 1.9×10^{-4}., which is in good agreement with the present value.

The only other measurement of the rate of conversion in the solid phase is reported by Sugawara, et al (1955). Their measurements give a change of 2% per hour for normal hydrogen, compared with 1.0% per hour derived from this work. Their value is so high in comparison to this work and Cremer and Polanyi's, that it is very probably wrong.

For ready reckoning purposes, the time in hours for the concentration to change 1% (e.g. from ϱ% to ϱ-1%) is given by:

$$\frac{5600}{\varrho^2} \qquad 3.17$$

Direct measurements of the concentration were also made on a

decaying sample of normal hydrogen in the liquid state. This was done to check that no rapid change of concentration occurred during the time the sample was in the liquid state, after condensation, and during the measurement of the concentration after the experimental run. It was possible that the Iron Alum salt would cause a rapid change in the concentration by catalysing the ortho-para conversion. The constant in equation 3.17 was calculated to be 1.59×10^{-4}. This value can be compared with Cremer and Polanyi's value for the liquid state of 1.2×10^{-4}. Therefore, the catalytic action of the paramagnetic salt only increases the rate of change of concentration by 30%.

Part III - Discussion

1. Introduction.

The most interesting result of these experiments is the appearance of a λ-anomaly in samples of high concentration. There is no doubt that the λ-peak is due to the same cause as the rest of the anomaly, as is shown by the total entropy per mole of ortho-hydrogen remaining constant, whether a peak occurs or not.

By comparison with other λ-anomalies found in experimental specific heat measurements, we can associate this anomaly with a co-operative effect. But even the anomalous specific heat above the temperature of the λ-anomaly does not roughly approximate to a Schottky function for independent particles, so a form of co-operation must exist also in this temperature range. It must then be explained why an anomaly with the same underlying mechanism should show itself in two separate forms of co-operative behaviour.

In the next sections, we will attempt to show that the observed effects may be described qualitatively with a simple model derived from classical theory. Afterwards, we will examine attempts to account for the change of temperature of the λ-anomaly with concentration, and consider the reasons why they do not give a very accurate quantitative description of the observed phenomena.

2. The Hydrogen Molecule.

The hydrogen molecule is described in classical theory as having two positive nuclei, around which circle two negative electrons.

It follows that the molecule is electrically neutral and can not exert a classical electro-static force on another molecule. Also, it has no dipole moment, The forces that are present are the force associated with the quadrupole moment, the attractive Van der Waals forces, which are due to the interaction of the electrons of a molecule with the electrons of neighbouring molecules, and the positive exchange forces due to the finite volume of the molecules.

These interaction forces split the three substates of the ground rotational state of the ortho-hydrogen molecule. However, it has been shown by Carlson (1950) that the splitting to be expected from the Van der Waals force and the repulsive exchange force are of nearly the same magnitude and of the opposite sign, so that it is only the quadrupole-quadrupole interaction that needs to be considered in the first instance.

The extent of the splitting will depend on the nearest neighbours of any particular molecule. In the twelve nearest sites there may be either paramolecules, which being in their ground state should not change with temperature their effect on the considered molecule, or ortho-molecules, whose contribution to the electrostatic field will change as their rotational energy falls into the lower substates.

It is possible, however, to describe the observed specific heat curves by considering only the interaction that changes with the temperature. The solid may be considered as consisting of

ortho-molecules, which have been diluted with comparatively inert paramolecules.

3. Two experiments indicating that the ortho-ortho interaction is sufficient for an explanation.

Measurements by Hill (1953) on the specific heat of solid Hydrogen near its triple point, showed that the anomalous heat capacity is proportional to the square of the concentration; that is, the anomalous heat capacity per mole of ortho-hydrogen is proportional to the first power of the concentration. This indicates that any ortho-para interaction must be very small in the temperature range considered. But as the paramolecule is already in its ground state, there is no reason to suppose the interaction would be any greater at lower temperatures.

Another indication that the interaction is small is given by the proton resonance work on normal solid Hydrogen which is discussed in section 5. In this work Reif and Purcell (1953) were able to describe the observed line shapes in normal Hydrogen by considering only the interactions between the ortho-molecules.

These two experiments justify the view that any interaction other than the ortho-ortho quadrupole interaction may be ignored in the first instant at any rate for the highest concentrations.

4. Qualitative Explanation.

That a co-operative process could occur can be seen by considering the effect on a particular molecule, say A, of its

neighbouring ortho-molecules as the hydrogen sample is cooled. At temperatures just below the triple point the substates of the neighbours will be nearly all equally occupied so that the field at A will not be greatly affected by transitions occuring among its neighbours. As the temperature is reduced the lower substates will be preferentially occupied and the field at A will be modified in consequence. If this change in field increases the energy of the higher substates of molecule A, the whole system must proceed towards the lowest energy state in a co-operative manner.

The effect of replacing ortho neighbours with inert para-molecules will be to reduce the electrostatic field at A. We would, therefore, expect the temperature of the anomaly to fall with decreasing concentration since:

$$\varepsilon \sim KT \qquad 3.13$$

The λ-effect at high concentrations is an indication of "strong" coupling between the ortho-molecules. To explain the disappearance of the effect, it is necessary to invoke a critical field, below which the "strong" coupling is reduced to a "weak" coupling. The resultant energy of the ortho-molecules and its differential with temperature, the specific heat, would then be expected to fall also.

At concentrations below 60%, the co-operative nature of the anomaly would still occur, but it would be expected that the maximum of the anomaly would fall with decreasing concentration.

This effect, however, has not been observed. Not until the small para-ortho interaction becomes the predominating influence, would one be likely to obtain a pure Schottky anomaly from the lifting of the degeneracy of the ortho-molecule. If the criterion is used that 90% of the ortho-molecules have no nearest neighbours, the concentration would have to be less than about 0.9%.

5. Nuclear Resonance Measurements.

Additional information on the state of solid hydrogen is obtainable from nuclear resonance experiments. Work in this field has been done by Hatton and Rollin (1949), Reif and Purcell (1953), and Sugawara et al (1955).

The resonance pattern in solid hydrogen consists of a double line when transitions between substates do not occur, and a single broad line when transitions occur in a time comparable with the periodic time of the resonance frequency.

In normal hydrogen, a single line is found at high temperatures. As the temperature is reduced the line broadens, indicating a decreasing transition probability, until at 1.5°K., the pattern suddenly splits into a double line.

The transition probability depends on the thermal energy of the lattice and the Bolzmann factors for the various transitions. A sudden change in the lattice energy is unlikely, so it is possible to attribute the change in the pattern to a change in the energy levels. It is therefore seen that the mechanism for des-

cribing the observed specific heat curves, by considering a change of energy levels, is consistent with the resonance work.

A comparison between the temperature of the sudden change in the resonance pattern (Sugawara et al) and the λ-point with concentration is shown in Fig.3.20b. The agreement can be considered satisfactory as the measurements characterise different aspects of the state of the solid. There was no rapid change in line shape in the resonance experiments below a concentration of 62%. It would be expected, however, that a slow change to two lines would occur, if a low enough temperature were reached, but in these experiments the lowest temperature recorded was only 1.17°K.

It should be noted that the resonance and specific heat experiments are complementary. The former experiments only state whether or not transitions occur. The same low temperature pattern would be obtained if the molecules were frozen into arbitrary substates. It is only the existence of the specific heat anomaly of the correct entropy, that indicates that an ordered state is obtained at very low temperatures.

6. <u>An Analogue in the behaviour of the Ni-Cu Alloys</u>.

The behaviour of the Hydrogen λ-anomaly with concentration is not completely unknown in specific heat work. It is interesting to consider the specific heat of the Ni-Cu Alloy system near its Curie temperature, and to note the similarities, which it bears to the present case.

Since the Ni-Cu alloy system may form a solid solution, any concentration is obtainable, the atoms being positioned at random in the face-centred cubic lattice. Our analogue is as follows. The Nickel, which gives rise to an order-disorder transition, can be associated with the hydrogen ortho-molecules, and the copper can be considered as the inert diluent like the hydrogen para-molecules.

Grew (1934) found that the temperature of the anomalous specific heat at the Curie point fell with increasing concentrations of Copper. His results may be tabulated as follows.

Ni %	Temperature of Max. of Anomaly (°K.)
100	620°K.
94	600°K.
87	530°K.
78	420°K.

The shape of the anomaly was such that the greater the Nickel concentration, the higher the peak, and the steeper the anomaly on the high temperature side, as in the hydrogen case. Also, if ΔT is the change in the temperature of the maximum of the anomaly for a 1% change in the concentration, then for a nickel concentration of 75%

$$\frac{\Delta T}{T} = .027$$

where T is expressed in °K. The same value is obtained from the measurements on the Hydrogen λ-anomaly at the same concentration.

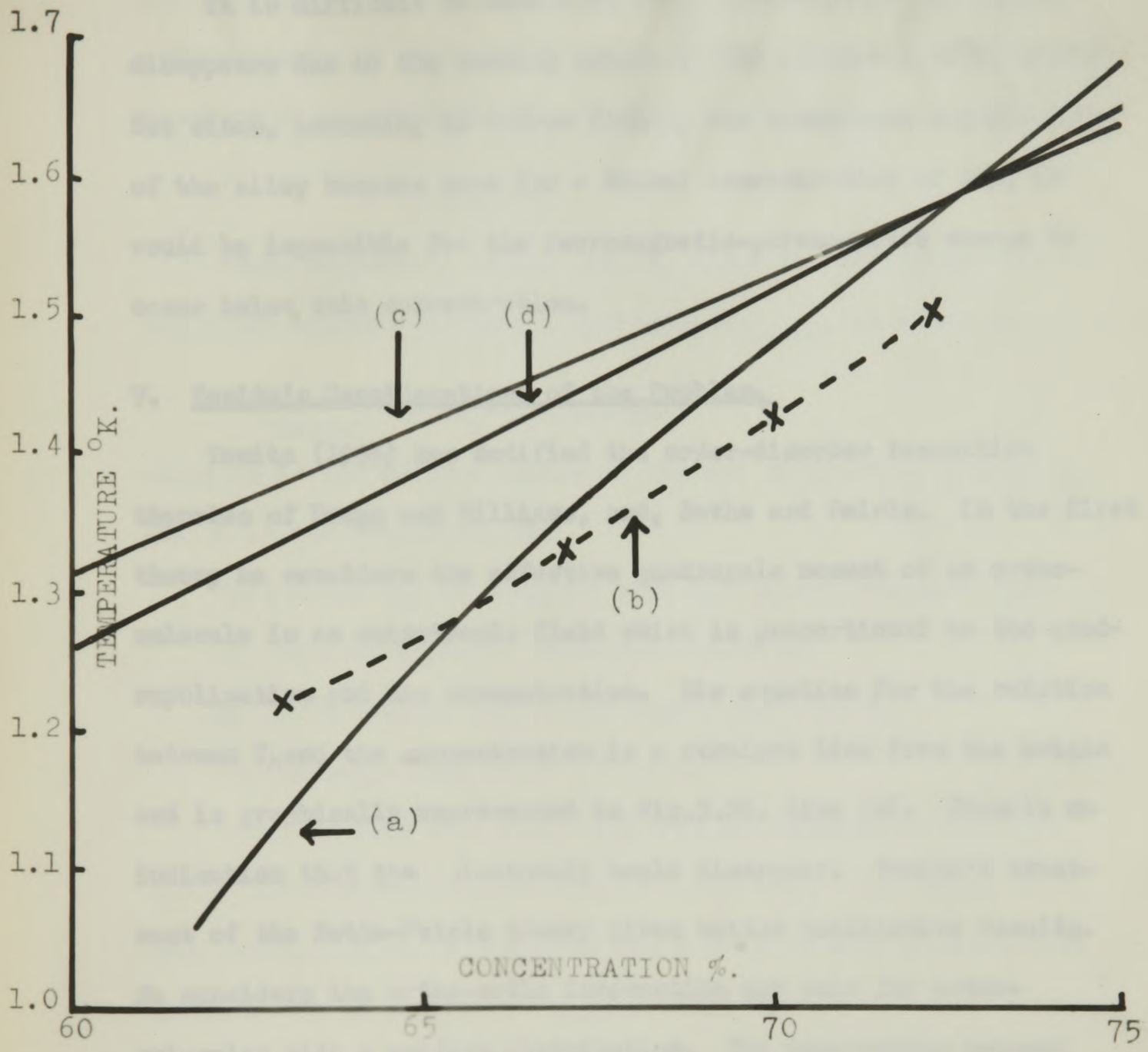


Fig. 3.20 THE RELATIONS BETWEEN T_λ AND THE ORTHO-CONCENTRATION FROM: a) THIS WORK. b) NUCLEAR MAGNETIC RESONANCE. c) BRAGG-WILLIAMS' THEORY. d) TOMITA'S MODIFICATION OF BETHE-PEIRLS' TREATMENT OF ALLOYS.

It is difficult to decide at what concentration the anomaly disappears due to the masking effect of the lattice specific heats. But since, according to Sadron (1932), the saturation magnetization of the alloy becomes zero for a Nickel concentration of 40%, it would be impossible for the ferromagnetic-paramagnetic change to occur below this concentration.

7. Tomita's Considerations of the Problem.

Tomita (1955) has modified the order-disorder transition theories of Bragg and Williams, and, Bethe and Peirls. In the first theory he considers the effective quadrupole moment of an ortho-molecule in an anisotropic field which is proportional to the quadrupolization and the concentration. His equation for the relation between T_λ and the concentration is a straight line from the origin and is graphically represented in Fig.3.20. line (c). There is no indication that the λ-anomaly would disappear. Tomita's treatment of the Bethe-Peirls theory gives better qualitative results. He considers the ortho-ortho interaction per pair for ortho-molecules with a uniform distribution. The interaction between the molecules of the pair depends on the rotational state of each molecule, as in the Ising model of ferro-magnetism. His resulting equation is:

$$T_\lambda = \frac{V}{\frac{1}{2}K \ln (Z^2 + 6Z - 6) - \ln(Z-2)} \qquad 3.18.$$

where V is to be compared with the excitation energy per molecule

pair. G is a weighting factor, and Z is taken to be the average number of nearest ortho neighbours. By fitting this equation to the experimental results, it is found that:

$$V = 0.447^{\circ}K.$$

"This suggests", writes Tomita, "that the excitation energy per ortho-molecule in normal hydrogen, V_{normal}, is given by:

$$V_{normal} = V Z_o x = 4.023^{\circ}K. \text{ "}$$

where Z_o is the maximum number of nearest neighbours, namely 12, and x is the concentration.

This value may be compared with the values obtained from:

a) Nuclear magnetic resonance - $4.10^{\circ}K$.

b) Spin-lattice relaxation time - 3.0°-$4.0^{\circ}K$.

c) Specific heat above $4^{\circ}K$. - $5.6^{\circ}K$.

Equation 3.18 also indicates that the anomaly should disappear at an ortho-concentration of about 16%. The change of T_λ with concentration is linear in the region 60%-75% ortho-concentration. It is plotted in Fig.3.20 line (d).

8. Non-Uniformity of Solid Hydrogen.

The qualitative explanation that we have given and the quantitive attempts made by Tomita are both based on the assumption that each ortho-molecule can be considered to have an average number of ortho-neighbours.

This assumption of uniformity in the lattice is only true in

the macroscopic sense. This may be shown by considering the fraction ($f(\chi)$) of the ortho-molecules that have a given number of nearest ortho-neighbours (χ). Using the Binomial distribution law, we have:

$$f(\chi) = c^{\chi}(1-c)^{12-\chi}\frac{12!}{\chi!(12-\chi)!} \qquad 3.19$$

where the last factor on the right hand side allows for the number of ways in which the para- and ortho-molecules may be placed in the twelve neighbouring sites.

The values of $f(\chi)$ for χ=10,11 & 12 are plotted against the ortho-concentration in Fig.3.21, as well as their sum, $f(\chi)_{10,11,12}$. It can be seen immediately that a third of the molecules have 10 or more nearest neighbours at a concentration of 75%, at which the average number of neighbours is nine. Therefore, it may be concluded that solid hydrogen is not of a microscopically uniform structure.

We will now consider whether this change in nearest neighbours would help to explain the experimental results. To do this, we must convert the specific heat measurements into a more convenient form. It is first assumed that the λ-anomaly is due to certain identifiable molecules, namely ortho-molecules with a large number of nearest ortho-neighbours, and to these only. The fraction of these molecules is given by the ratio of the entropy of the λ-anomaly to the entropy of the total anomaly, e.g.

$$f(\chi)_{EXP} = \frac{S_{\lambda}}{S_{TOT}} \qquad 3.20.$$

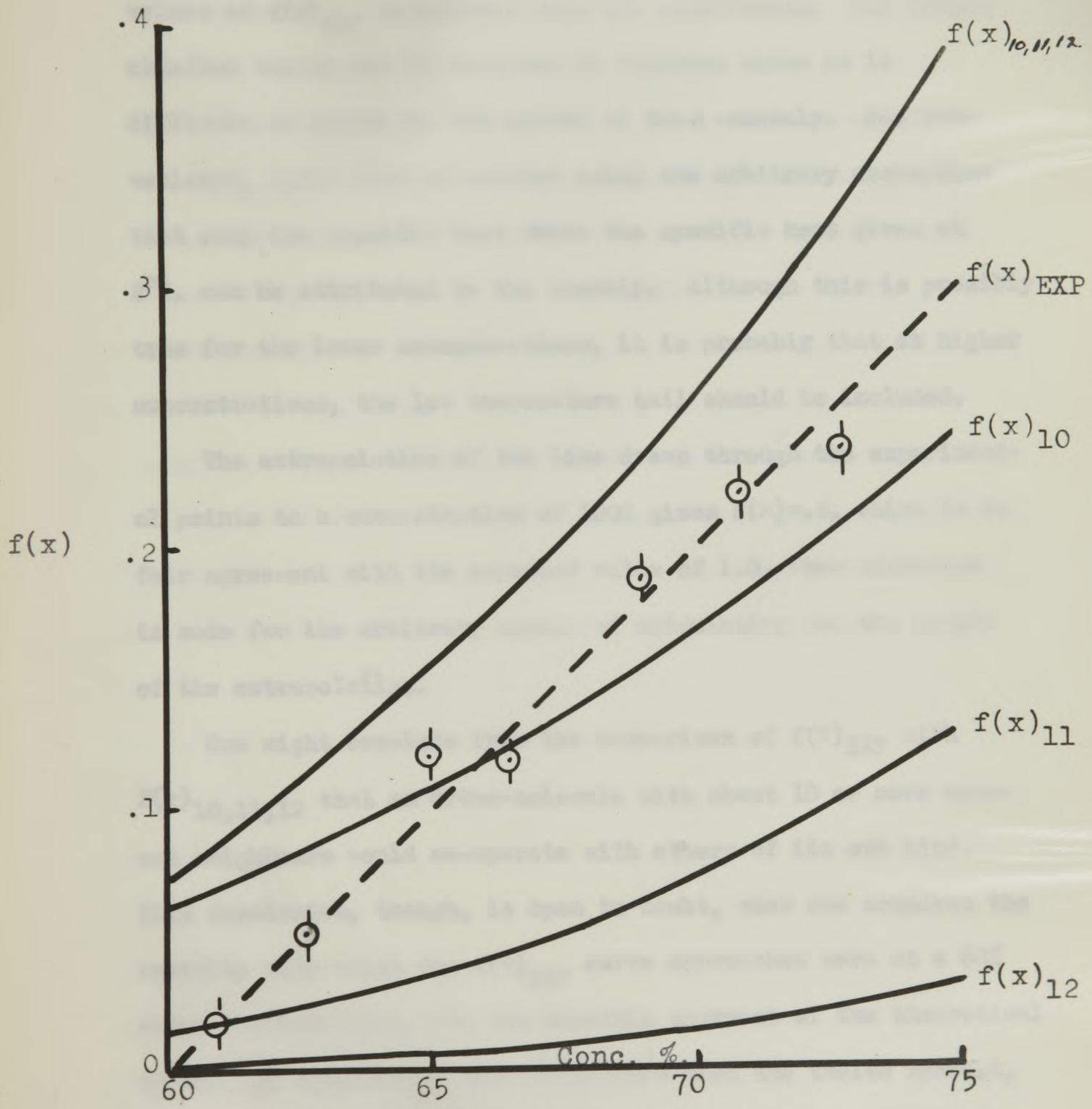


FIG. 3.21 SEE TEXT.

In Fig.3.21, a straight line has been drawn through the values of $f(\alpha)_{EXP}$ calculated from six experiments. The values obtained should not be accepted as rigorous since it is difficult to decide on the extent of the λ-anomaly. For convenience, S_λ has been calculated using the arbitrary assumption that only the specific heat above the specific heat given at $2^{\circ}K.$ can be attributed to the anomaly. Although this is possibly true for the lower concentrations, it is probable that at higher concentrations, the low temperature tail should be included.

The extrapolation of the line drawn through the experimental points to a concentration of 100% gives $f(\alpha)=.8$, which is in fair agreement with the expected value of 1.0, when allowance is made for the arbitrary method of calculating and the length of the extrapolation.

One might conclude from the comparison of $f(\alpha)_{EXP}$ with $F(\alpha)_{10,11,12}$ that an ortho-molecule with about 10 or more nearest neighbours would co-operate with others of its own kind. This conclusion, though, is open to doubt, when one compares the rapidity with which the $f(\alpha)_{EXP}$ curve approaches zero at $\approx$ 60% ortho-concentration with the asymptic approach of the theoretical curve. By considering more neighbours than the twelve nearest, it is possible to derive a theoretical curve with a comparatively rapid approach to zero at 60%. For example, if 100 neighbours are selected, it is found that the onset of "co-operation" would occur when 74 or more molecules were ortho-molecules. However,

this calculation leads to a much quicker rise in the theoretical curve than in the experimental curve.

The conception of non-uniformity may, however, explain the λ-peaks observed between the ortho-concentrations of 60% and 62%. In this range it is possible that only small finite volumes in the solid have a concentration of ortho-molecules, which would allow for the critical energy of the highly co-operative interaction to be reached inside, but not outside, them. It is possible that the method of preparation of the sample and its previous history would have a greater effect on the size and orientation of these zones than the measured (average) concentration. This could give rise to the anomalous behaviour observed in this concentration region.

CHAPTER 4

IRRADIATED POLYTHENE

1. Introduction

The measurement of the specific heat of a sample of polythene, that had been irradiated with slow neutrons in the atomic pile at A.E.R.E. Harwell, was undertaken to finish a series of experiments that was started by Smith in 1953. The earlier results are fully reported by Smith (thesis).

Normal polythene consists of long chain molecules, whose basic unit is CH_2. It is, therefore, the simplest elastomer that may be produced from the olefines ($C_n H_{2n}$). These chains may be either interwoven with, or lie parallel to, each other. In the first case, the polythene is considered amorphous and in the second, crystalline with an orthorhombic structure. Amorphous and crystalline regions may exist in the same specimen. A single chain may have one part in an amorphous region and the other in a crystalline region. The length of the chains depends on the method of preparation and may have a molecular weight anywhere between 2×10^3 and 200×10^3. The molecular weight of the samples used in this series of measurements was about 30,000, i.e. chain lengths of about 2,000 carbon atoms.

When polythene is irradiated, the slow neutrons knock off neighbouring hydrogen atoms, which unite to make molecules and

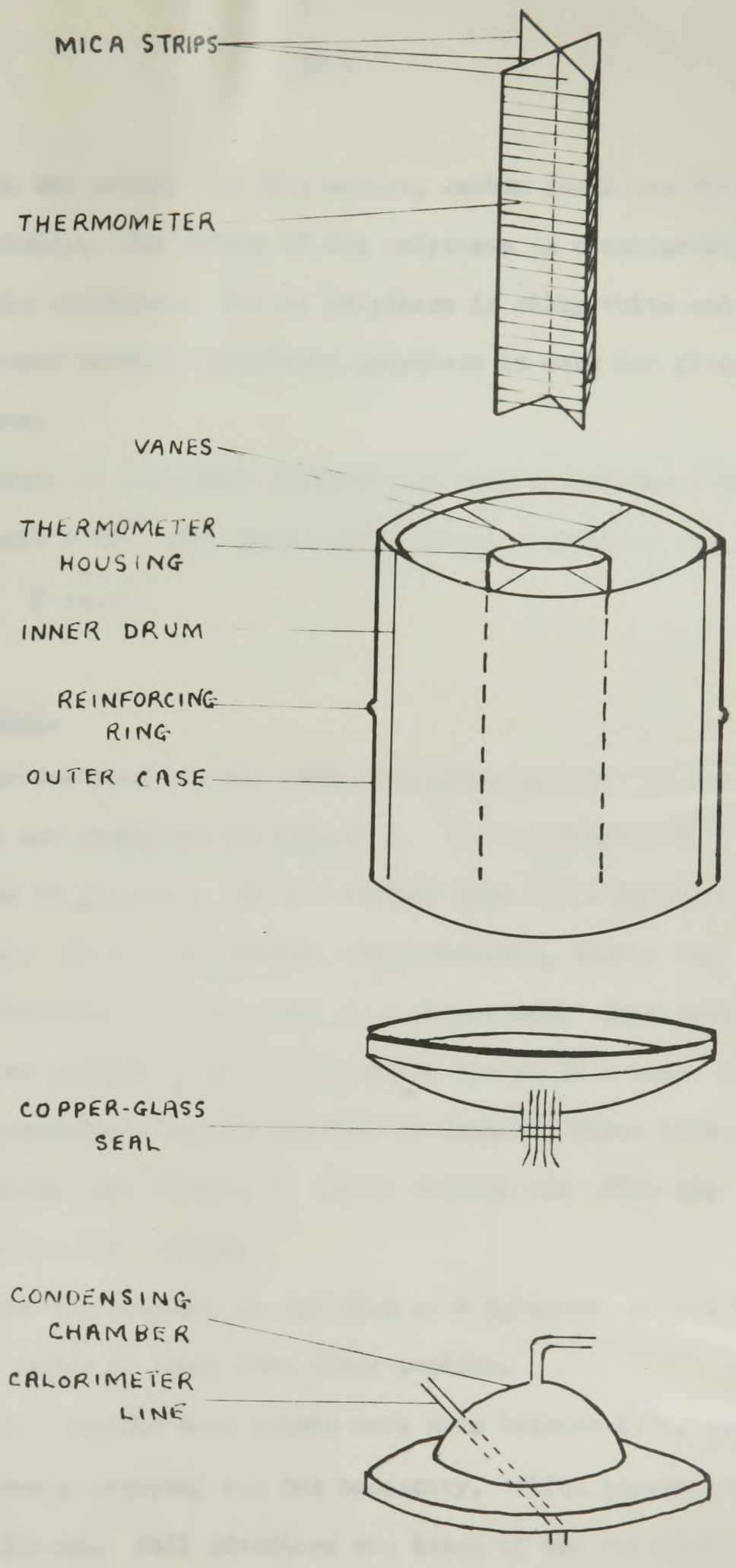


FIG. 4.1 CALORIMETER.

evaporate from the solid. In this manner, carbon links are formed between the chains. The nature of the polythene is considerably changed by this treatment. Normal polythene is milky white and flexible, whereas heavily irradiated polythene is dark and glass-like in texture.

The specimen of polythene measured had been irradiated with 80 units (1 unit = 10^{17} slow neutrons/cm^2. with associated fast neutrons and γ-rays).

2. Experimental.

The apparatus used was the general purpose machine with shield; both of these are described in Chapter 2. The calorimeter employed is illustrated in Fig.4.1., and has already been fully described by Smith (thesis). It has one unusual characteristic, namely the platinum thermometer, that is wound on a mica-cross. This method of construction permits a high ohmage to be housed in a small volume, while the thermometer's reproducibility is assured, since annealing and purity checks (see Chapter 1) can be carried out after the platinum wire has been coiled.

The sample was received in the form of a cylinder and was broken up into small chips of about 2mm. cross section.

Sixty-four specific heat points were made between 15°K. and 300°K. As extreme accuracy was not necessary, drifts greater than normal were allowed. Full advantage was taken of the rapidity with

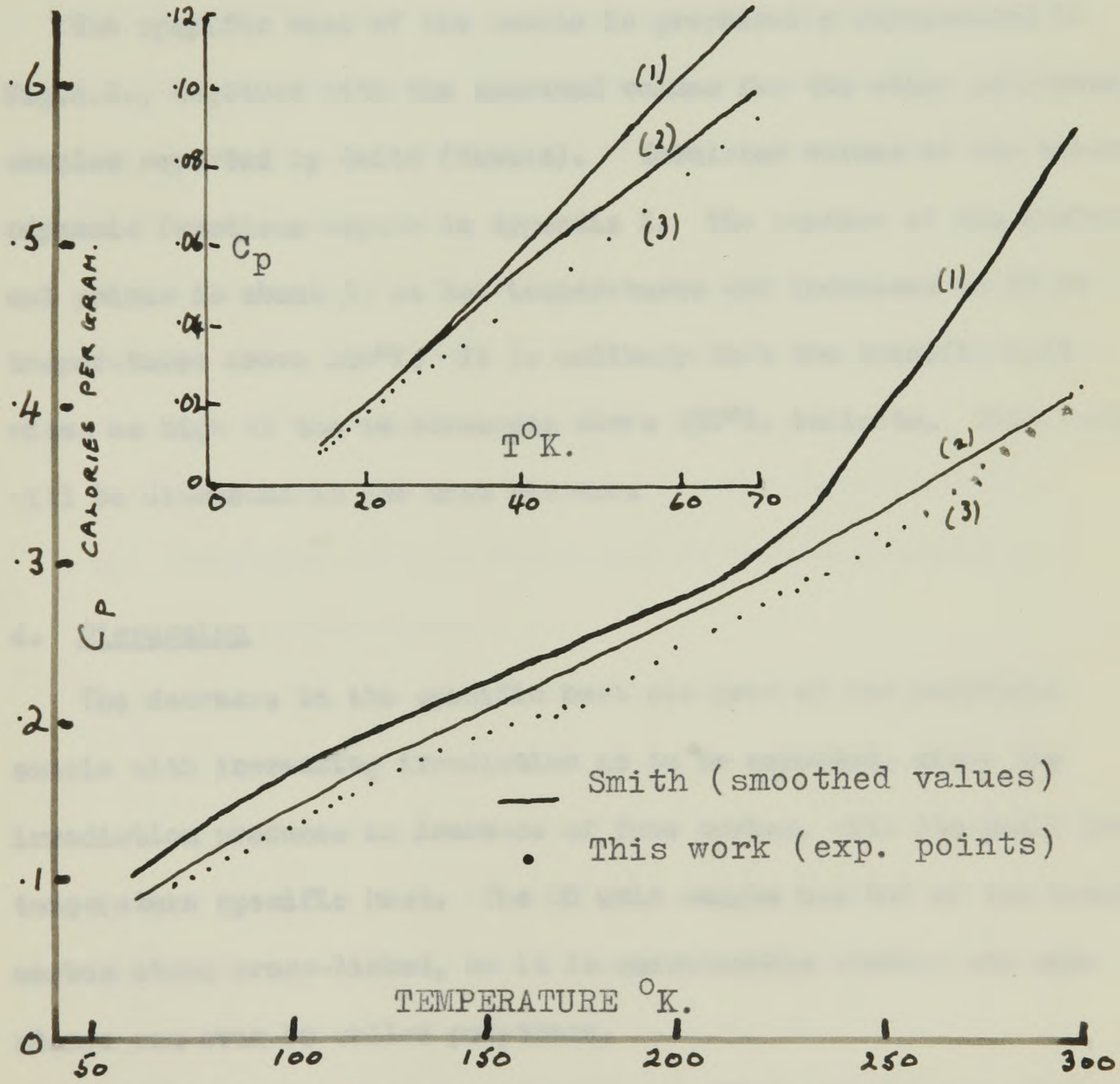


FIG. 4.2 SPECIFIC HEAT OF POLYTHENE

(1) Normal Polythene
(2) Polythene irradiated with 40 units
(3) Polythene irradiated with 80 units

which the temperature of the shield could be changed. In this manner, even though the equilibrium time above 200°K. was about fifteen minutes, the whole experiment was carried out in five days.

3. Results

The specific heat of the sample is graphically represented in Fig.4.2., together with the smoothed values for the other polythene samples reported by Smith (thesis). Tabulated values of the thermodynamic functions appear in Appendix I. The scatter of the individual points is about 3% at low temperatures and increases to 5% at temperatures above 200°K. It is unlikely that the specific heat rises as high as the measurements above 250°K. indicate. This fact will be discussed in the next chapter.

4. Discussion

The decrease in the specific heat per gram of the polythene sample with increasing irradiation is to be expected, since the irradiation produces an increase of free carbon, with its small low temperature specific heat. The 80 unit sample has 60% of the total carbon atoms cross-linked, so it is questionable whether the substance can even be called polythene.

It should be noticed that for the 40 unit sample the specific heat is nearly linear with temperature above 80°K. the mechanism causing the sharp rise in specific heat of the normal polythene having been suppressed by the irradiation. This linearity can now

be seen to be fortuitous, and that further suppression occurs in the 80 unit sample.

5. Discussion on Normal Polythene

The experiments on normal and irradiated polythene carried out by Smith (thesis) showed that the sharp rise in specific heat of normal polythene at about 180°K. could not be attributed to an order-disorder change in the crystallites of the polythene, as had been assumed by previous workers.

His argument was as follows. The specific heat of three samples was measured and they all had the same specific heat over the temperature range 20°K. - 300°K. These samples were:-

(a) Normal polythene, which always contains crystallites.

(b) Polythene slightly irradiated at room temperature and with crystallites.

(c) Polythene, slightly irradiated at a temperature near its melting point, which produces a completely amorphous sample.

As the specific heats of samples (a) and (b) show that no appreciable change has occurred by slightly irradiating the samples, then any difference between the heat capacity of (c) and (a) must be attributed to the amorphous character of (c). But, there is no difference in the heat capacity of (c) and (a) - therefore, the crystallite-amorphous change has little effect on the specific heat.

If this be true, what is the mechanism behind the rise in the specific heat? We will try to show that it is molecular vibration at the natural frequencies of the H-C-H unit of the molecule.

Smith's specific heat curve for normal polythene may be analysed as follows. As we are only interested in the specific heat at the higher temperatures, we will represent the contribution to the specific heat from the low molecular and lattice frequencies by a constant A. Each other frequency we will represent as an Einstein function, $f_E(\frac{\theta}{T})$.

In this manner, giving each f_E a weighting factor B,C,---, we may write:

$$C_v = A + Bf_E\left(\frac{\theta_1}{T}\right) + Cf_E\left(\frac{\theta_2}{T}\right) \text{ ---} \qquad 4.1.$$

A fit may be obtained with the observed specific heat using:

$$C_p = 0.063 + .0366f_E\left(\frac{300}{T}\right) + .0526f_E\left(\frac{1750}{T}\right) \qquad 4.2.$$

A table comparing C_p measured and C_p theoretical is given below.

T °K	C_p (measured)	C_p (theoretical)
50	.083	.082
100	.171	.170
150	.224	.224
200	.276	.280
250	.391	.393
300	.575	.575

(Units - Calories per gram).

The last Einstein function in equation 4.2. is responsible for the rapid rise in specific heat at temperatures above 180°K. A Θ_E of 1750°K. is equivalent to a frequency of 1241 cm^{-1}., which is in the infrared region. Measurements of the characteristic CH_2 frequencies of n-. paraffins have been made by Person and Pementel (1953). Out of six characteristic frequencies, three are very close together. These are:

H-C-H	bend	1459 cm^{-1}.
CH_2	twist	1241 cm^{-1}.
CH_2	wag	1342 cm^{-1}.
	Average	1342 cm^{-1}.

The agreement between our calculated frequency and the average of the frequencies selected would be improved if a $C_p - C_v$ correction were available. The agreement is nevertheless close enough to suggest that the mechanism for the high temperature specific heat of polythene is molecular vibration at the natural CH_2 characteristic frequencies.

CHAPTER 5

POTASSIUM BROMIDE

1. Introduction

This work was carried out as one of a set of experiments to test the constancy of the Gruneisen γ with temperature for an ionic crystal. The work was carried out in collaboration with Dijl, who was measuring the expansion coefficient of the crystal, and it was hoped by comparing both sets of data with the measurements by Galt (1948), on the compressibility to reach a conclusion on the variation of γ with temperature. Unfortunately, unexpected difficulties occurred in the measurement of the dilation of the crystal, so that, at present, it is impossible to report on the variation of γ with temperature.

At the time of making the measurement, only some very early work of Nenst and Lindemann (1911) was known, but it was discovered later that Clusius, Goldman and Perlick (1949) had measured the specific heat of Potassium Bromide, as a sample in a series of measurements on the Alkali Halides. Therefore, these measurements may not be considered as covering new ground.

2. Experimental and Results

Half a mole of Potassium Bromide was placed in the calorimeter described in Chapter 4. The apparatus used was the general purpose machine with extra shield, both described in Chapter 2. The most

exacting test of the constancy of the Gruneisen γ is in the 20°K. to 100°K. region where the specific heat varies rapidly with temperature and the dilation of the crystal is still large enough for measurements to be made with accuracy. However, it was decided to carry out the measurements from 4°K. to 300°K. for the sake of completeness. The results of the measurement are shown as dots in Fig. 5.1. The variation of the Debye θ is shown in Fig. 5.2. Both figures also give the experimental results of Clusius et al (1949). The thermodynamic functions for KBr will be found in appendix II, where the $C_p - C_v$ correction in deriving C_v has been made using values given by Pullin (thesis).

The results between 4°K. and 10°K. are poor, due to a bad vacuum at the time of the measurements. They were not repeated as they were not needed for the calculation of the Gruneisen γ. Nevertheless, there is no indication that the specific heat was not obeying a T^3 law with a $\theta_D = 155$°K. in this region. From 10°K. to 200°K. the specific heat points have a scatter of under 1% about the mean value.

Between 235°K. and 260°K. there are a series of points that are approximately 3% higher than would be expected. This anomalous heat can be associated with some unwanted condensed vapour, as the effect was considerably reduced, though not removed, by pumping the calorimeter for 24 hours at about 300°K. It was possibly due to condensed water vapour on the heater and its surrounds. In this temperature region the vapour pressure of water varies from 10^{-4}mm/Hg to 1mm/Hg.

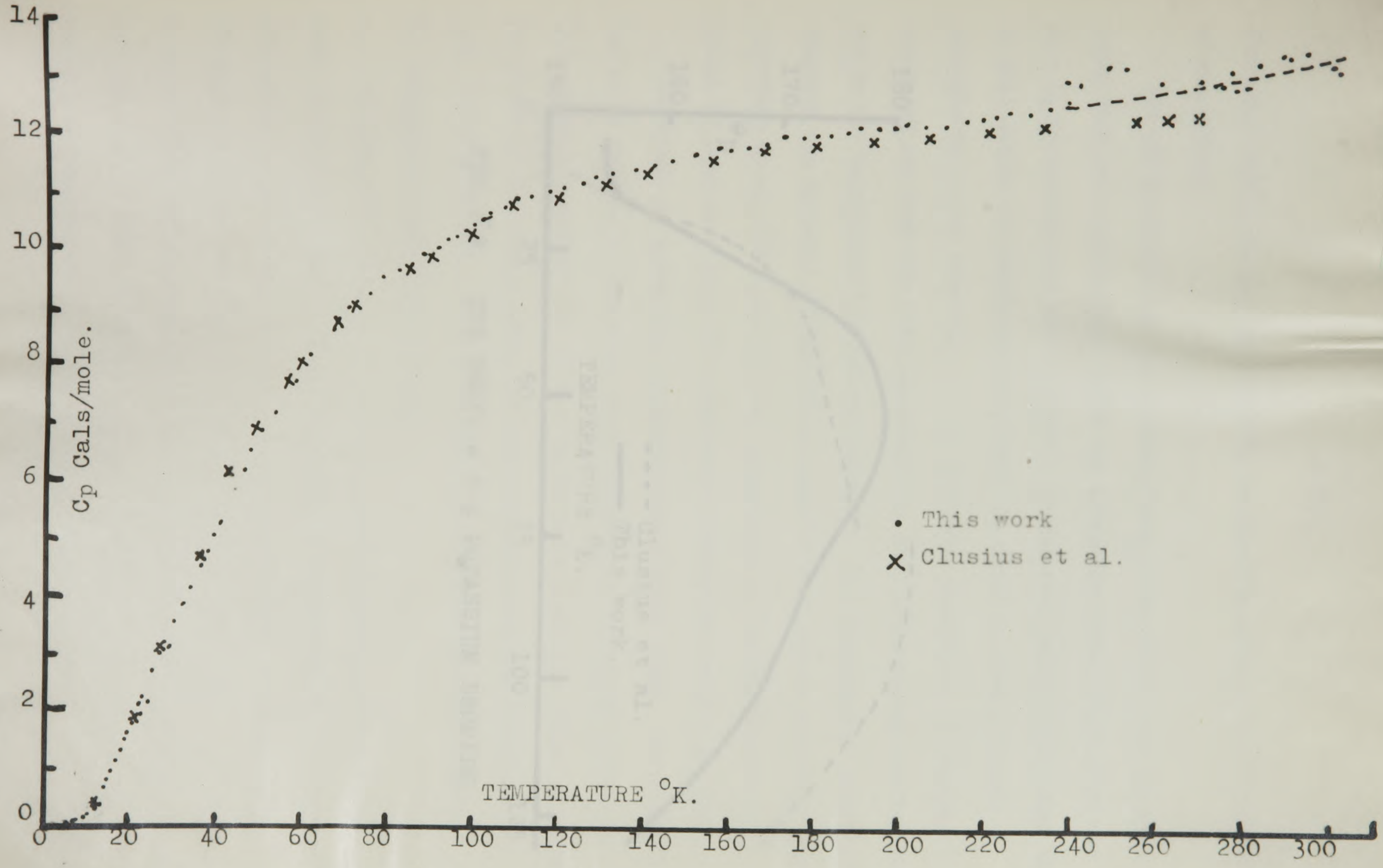


FIG. 5.1 SPECIFIC HEAT OF POTASSIUM BROMIDE.

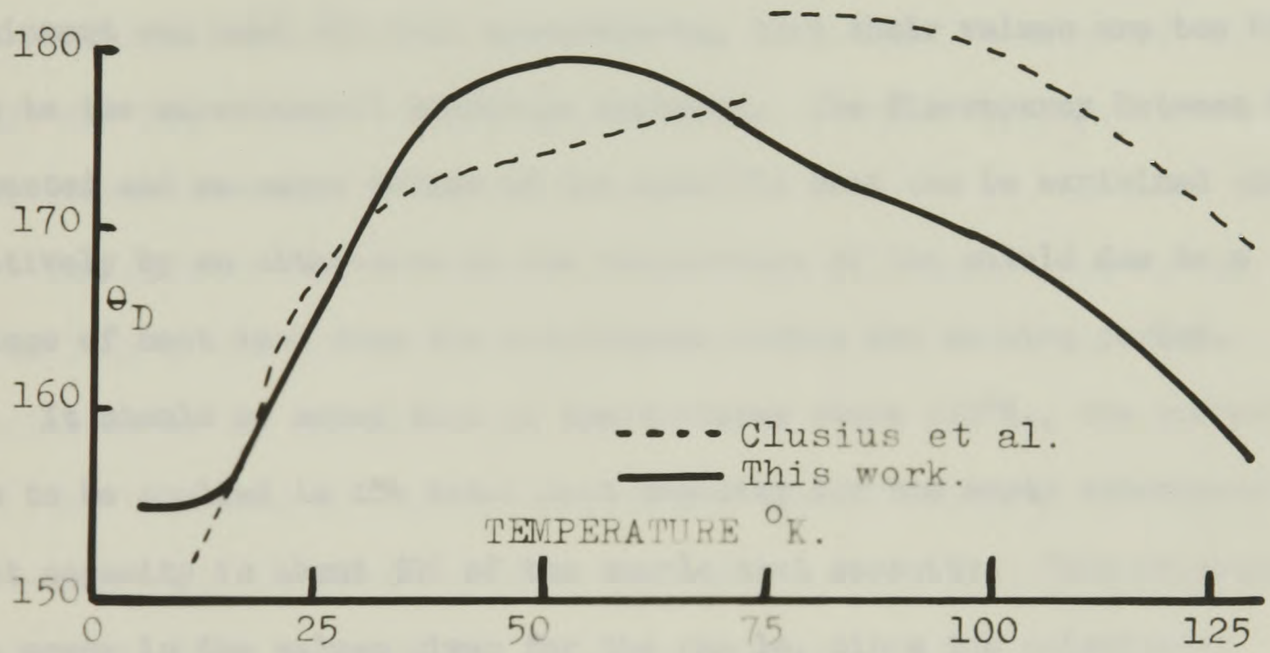


FIG. 5.2. THE DEBYE θ FOR POTASSIUM BROMIDE.

About 0.1 cubic millimetres would be required to explain the magnitude of the effect.

The values found for the specific heat above 260°K. are surprisingly high and considerably above the classical value of 3R after the $C_p - C_v$ correction has been applied. In the same temperature range the 80 unit sample of irradiated polythene was found to have a larger specific heat than expected. It is probable, therefore, as identical equipment was used for both measurements, that their values are too high due to the experimental technique employed. The discrepancy between the expected and measured values of the specific heat can be explained qualitatively by an alteration in the temperature of the shield due to a change of heat leak from the calorimeter during the heating period.

It should be noted that at temperatures above 200°K., the correction to be applied to the total heat capacity for the empty calorimeter heat capacity is about 50% of the sample heat capacity. This increases the error in the values given for the sample, since the calorimeter heat capacity is only known to about 5% in this temperature region.

3. Comparison with Clusius et al.

The agreement between the sets of measurements is within 5% over the whole temperature range. The high values of Clusius et al at about 40°K. are probably due to their use of a lead thermometer. Although this thermometer is accurate, if undisturbed after calibration, it is likely to alter if it receives any mechanical shock. It is interesting to note that there is a break in their θ_D curve at 75°K. This change is only due to a difference of ½% in their specific heat values at this temperat-

ure, but it is probably the temperature at which they changed over from the lead to the platinum thermometer.

The agreement between the two sets of data up to 200°K. is within 2%, that is, within the probable error of these measurements. Above this temperature the Clusius et al data is probably more reliable, due to the reasons given in the previous section.

4. Discussion.

Potassium Bromide is a member of the Alkali Halide group of crystals and has a cubic lattice structure. The atomic weight of the two constituent atoms is in the ratio 1:2.

The general form of the variation of Θ_D with temperature is repeated in many of the Alkali-Halides, Rubidium Bromide having the greatest similarity to the present case.

The behaviour of the low temperature specific heat is in remarkable agreement with Blackman's work on the cubic lattice (1933, 1937). The rapid fall of Θ_D is predicted to occur at about a temperature of $\frac{\Theta_D}{T} = 3.5$., which is 50°K. in the case of Potassium Bromide. The variation of Θ_D with temperature is also of the same form as the theoretical variation, except that the rise of Θ_D predicted by Blackman below $\frac{\Theta}{T} = 16$ does not seem to occur. The possible explanation of this discrepancy is given in the theoretical work by Blackman on one-dimensional lattice specific heats with different mass ratios for the two constituent atoms. When the ratio of the masses is increased, Θ_D at the lower temperatures is decreased, in such a manner that for $\frac{m}{M} = 8$, Θ_D is almost constant below $\frac{\Theta_D}{T} = 12$. The ratio of the masses of Potassium and Bromine

is not 8, but it is possible that the effect of the differences of mass would be greater in the three-dimensional case.

At high temperatures the rise in specific heat above that predicted by a constant Θ_D is probably due to non-central force interaction between the ions. Born and Brody (1921), have shown that potential interaction terms that are cubic in atomic displacements, would increase the specific heat above that calculated from the Debye theory.

APPENDIX I

The Thermodynamic Functions of Irradiated Polythene

(R = 80 Units)

Units - Calories per gram.

T°K.	Cp	S	H-Ho
15	0.010	-	-
20	0.018	0.007	0.11
30	0.032	0.018	0.37
40	0.046	0.029	0.76
60	0.077	0.053	1.98
80	0.105	0.079	3.80
100	0.132	0.106	5.18
150	0.190	0.172	13.2
200	0.248	0.234	24.1
250	0.315	0.297	38.2
300	0.400	0.360	56.1

APPENDIX II

The Thermodynamic Functions of Potassium Bromide

Units - Calories per mole

T°K.	Cp	Cv	S	S-Ho
10	.25		.084	.68
20	1.63		.674	8.70
30	3.56		1.716	34.9
40	5.20	5.19	2.96	79.1
50	6.78	6.76	4.10	139.6
60	7.98	7.93	5.44	213.6
70	8.95	8.87	6.74	298
80	9.62	9.52	7.98	391
90	10.11	9.99	9.14	490
100	10.52	10.37	10.22	593
120	11.10	10.90	12.20	810
140	11.52	11.27	13.94	1036
160	11.85	11.55	15.50	1270
180	12.10	11.75	16.9	1510
200	12.35	11.86	18.2	1750
220	12.41	11.97	19.3	2000
240	12.62	12.11	20.5	2250
260	12.90	12.34	21.5	2510
280	13.21	12.59	22.5	2770
300	13.56	12.92	23.4	3035

APPENDIX XII

Θ_D and γ for the Elements

Introduction

At the request of Mott, N.F., Professor of Physics, Cambridge University, the following compilation of the Debye Characteristic Temperatures for the Elements was undertaken in the Spring of 1954. In the case of metals, the electronic specific heat is indicated by the constant γ, from the equation:

$$C_{electronic} = \gamma T \quad \text{calories/mole/degree.}$$

Only information available in the literature published before December 1953 has been included. It should be made clear that this table is a compilation of experimental data, and not a critical and selective survey.

The explanation of the different columns is as follows:

1st Column (A.N.)

The atomic number of the element. Only elements on which measurements have been made appear in the list.

2nd Column (El)

The international symbol for the element.

3rd Column

The Debye Θ for the temperature range shown in the fourth column. Bracketed - very rough value. When not given refer to the literature.

4th Column (T.R.)

The temperature range over which the Debye Θ given is applicable.

H - The value applicable at high temperatures above the absolute temperature $\frac{\Theta_D}{5}$

L - The value applicable at low temperatures unier the absolute temperature $\frac{\Theta_D}{12}$

5th Column ($\gamma \times 10^4$)

The electronic constant in cals/mole/degree.

6th Column

The accuracy of the Debye Θ for representing the specific heat at constant volume.

If no sign appears, the Θ does not change by more than 10% over the range shown in the fourth column.

X - Θ changes by more than 10% or the specific heat is anomalous.

? - Information available is inconclusive, e.g. Very old work; mean value specific heat, etc.

7th Column

References: when a reference is not given a paper appeared before 1939, and the element is not anomalous. Other references will be found in "Phenomena at Temperatures of Liquid Helium" by Burton, E.F., Grayson Smith, H., and Wilhelm, J.O. (Reinhold Publishing Corporation New York, 1940) page 346.

DEBYE θ TABLES

A.N.	El.	θ	T.R.	Y		
1	H_2	91	H		x	Hill, R.W., Ricketson, B.W.A., Phil.Mag. 45, 277, 1954.
2	He	35	L		x	Kramers, H.C., Wasscher, J.D., Gorter, C.J., Physica 8, 329, 1952.
3	Li	(370)	H		x	Simon, F., Swain, R.C., Z.Phys. Chem. B 28, 189, 1935
		331	L	3.0		Smith, P.L. (Priv.Comm.)
4	Be	925	H	-	)	Hill, R.W., Smith, P.L., Phil.
		1160	L	0.54	)	Mag., 44, 636, 1953.
5	B	1320	H		)	Johnston, H.L., Marsh, H.N.,
		1219	L		x)	Kerr, E.C., J.Amer.Chem.Soc. 73, 1112, 1951.
6	C	1850	H			(Diamond)
		(2300)	H		x)	(Graphite) Gurney, R.W., Phys.
		-	L		x)	Rev. 88, 465, 1952.
7	N_2	(70)	H		x	Giauque, W.F., Clayton, J.O., J.Amer.Chem.Soc. 55, 4875, 1933.
8	O_2	(90)	H		x	Giauque, W.F., Johnston, H.L., J.Amer.Chem.Soc. 51, 2300,1929.
9	F	(80)	H		x	Hu, J., White, D., Johnston, H.L., J.Amer.Chem.Soc. 75, 5642, 1953

A.N.	El.	Θ	T.R.	Y		
10	Ne	63	H			Clusius, K., Z.Phys.Chem. B 31, 459, 1936.
11	Na	159	H	2.7		Smith, P.L. (Priv.Comm.)
12	Mg	320	H			
		375	L	3.26		Smith, P.L., Wolcott, N.M. (to be published)
13	Al	389.1	H			Giauque, W.F., Meads, P.F., J Amer.Chem.Soc. 63, 1897, 1941.
		419	L			
14	Si	(585)	H		x	Anderson, C.T., J.Amer.Chem. Soc. 52, 2301, 1930.
		668	L	31	x	Keesom, P.H., Pearlman, N., Phys.Rev. 85, 730, 1952.
16	S	(300)	H		x)	Eastman, E.D., McCavock, W.C.,
		(180)	L		x)	J.Amer.Chem.Soc. 59, 145, 1937.
17	Cl	115	L		x	Giauque, W.F., Powell, T.M., J.Amer.Chem.Soc., 61, 1970,1939.
18	A	81	H			
19	K	100	H			
20	Ca	230	H			
		220	L			

A.N.	El.	Θ	T.R.	Y		
22	Ti	358	H			Kelley, K.K., Industr.Engng. Chem. 36, 865, 1944.
		280	L	8.00		Estermann, I., Fiedberg, S.A., Goldman, J.E., Phys.Rev. 87, 582, 1952.
23	V	374	H		x	Anderson, C.T., J.Amer.Chem. Soc. 58, 564, 1936.
		326	L	22.2	?	Worley, R.D., Zemansky, M.W., Boorse, H.A., Phys.Rev. 87, 192, 1952.
24	Cr.	485	H			Woertman, J., Burk, D., Goldman, J.E., Phys.Rev. 86, 628, 1952.
		418	L	3.80		Estermann, I., Fiedberg, S.A., Goldman, J.E., Phys.Rev. 87, 582, 1952.
25	Mn	375	H		x)	Armstrong, L.D., Grayson-Smith, H. Canad.J.Res. A 27, 9, 1949.
		410	L	42.1	x)	
26	Fe	420	H			
		462	L	12.0		Keesom, W.H., Kürrelmeyer, B. Physica 6, 364 and 633, 1939.
27	Co	375	H			Clusius, K., Schachinger, L. Z.Naturforsch. A 7, 185, 1952.
28	Ni	375	H			Busey, R.H., Giauque, W.F., J. Amer.Chem.Soc. 74, 3157, 1952.
		413	L	17.4		
29	Cu	312.8	H			Giauque, W.F., Meads, P.F., J. Amer.Chem.Soc. 63, 1897, 1941
		335	L	1.80		Estermann, I., Fiedberg, S.A., Goldman, J.E., Phys.Rev. 87, 582, 1952.

A.N.	El.	Θ	T.R.	Y		
30	Zn	(250)	H		x	Clusius, K., Hartock, P., Z. Phys.Chemie, 134, 243, 1928.
31	Ga	233	H		x)	Adams, C.D., Johnston, H.L.,
		192	L		?)	Kerr, E.C., J.Amer.Chem.Soc. 74, 4784, 1952.
32	Ge	(360)	H		x	Hill, R.W., Parkinson, D.H., Phil.Mag. 43, 309, 1952.
		369	L		x	Keesom, P.H., Pearlman, N., Phys. Rev. 85, 730, 1952.
33	As	275	H			
34	Se	(280)	H		x	Anderson, C.T., J.Amer.Chem. Soc. 59, 1036, 1937.
35	Br	140	H		?	Latimer, W.M., Hoenshil, M.D., J.Amer.Chem.Soc. 48, 19, 1926.
36	Kr	63	H		x	Clusius, K., Kruis, A., Kommerts, F., Ann.Phys.(Leipzig) 33, 642, 1938
40	Zr	235	H			Skinner, G.B., Johnston, H.L., J.Amer.Chem.Soc. 73, 45, 1952.
		265	L	6.92		Estermann, I., Fiedberg, S.A., Goldman, J.E., Phys. Rev. 87, 582, 1952.
41	Cb	280	H		?)	Brown, A., Zemansky, M.W.,
		254	L	21	)	Boorse, H.A., Phys. Rev. 86, 134, 1952.

A.N.	El.	Θ	T.R.	Y		
42	Mo	383	H		)	Horowitz, M., Daunt, J.G., Phys.Rev. 91, 1099, 1953.
		445	L	5.1		
46	Pd	275	L	31		Pickard, G.L., Simon, F.E., Proc.Phys.Soc. 61, 1, 1948.
47	Ag	212.7	H			Meads, P.F., Forsythe, W.R., Giauque, W.F., J.Amer.Chem. Soc. 63, 1902, 1941.
		227	L			Keesom, P.H., Pearlman, N., Phys.Rev. 88, 140, 1952.
48	Cd	(170)	H		x)	Craig, A.S., Krier, C.A.,
		126	L		?)	Coffer, L.W., Bates, E.A., Wallace, W.E., J. Amer.Chem. Soc. 76, 238, 1954.
49	In	109	L	4.33		Clement, J.R., Quinnell, E.H., Phys.Rev. 92, 258, 1953.
50	Sn	(240)	H		x)	Hill, R.W., Parkinson, D.H., Phil.Mag. 43, 309, 1952.
		(150)	L			
51	Sb	201	H			
53	Ir	120	H		x)	Lange, F., Z.Phys.Chem. 110,
		100	L		x)	343, 1924.
54	Xe	55	H			
57	La	140	H		x	Parkinson, D.H., Simon, F.E., Spedding, F.H., Proc.Roy.Soc. A. 207, 137, 1951.
		130	L	16	x	

A.N.	El.	Θ	T.R.	Y		
58	Ce	(70) (110)	H L		x x	Parkinson, D.H., Simon, F.E., Spedding, F.H., Proc.Roy.Soc. A. 207, 137, 1951.
59	Pr	(60) (70)	H L		x x	" " " " "
60	Nd	(100) (40)	H L		x x	" " " " "
72	Hf	213 -	H H		x	Crites[Cu], S., Simon, F.E., Z Phys.Chem. B 25, 273, 1934. Burk, D., Darnell, F., Phys. Rev. 86, 628, 1952.
73	Ta	220	L	12.6	x	Worley, R.D., Zemansky, M.W., Boorse, H.A., Phys. Rev. 91, 1567, 1953.
74	W	380 250	H L	1.8	x x	Lange, Z., Z.Phys.Chem. 110, 343, 1924. Horowitz, M., Daunt, J.G., Phys. Rev., 91, 1099, 1953.
75	Re	277 292	H L		) ?)	Smith, W.T., Oliver, G.D., Cobble, J.W., J.Amer.Chem.Soc. 75, 5785, 1953.
77	Ir	285	H		?	Behn, U.Ann.Phys. (Leipzig) 66, 237, 1898.
78	Pt	225 233	H L	16.07		

A.N.	El.	Θ	T.R.	Y		
79	Au	180	H		)	Geballe, T.H., Giauque, W.F.,
		163	L		x)	J.Amer.Chem.Soc. 74, 2368, 1952.
80	Hg	96	H		x	Simon, F.E., Z.Phys.Chem. 107, 279, 1923.
		-	L		x	Pickard, G.L., Simon, F.E., Proc.Phys.Soc. 61, 1, 1948.
81	Tl	93	H			
		90	L	15.2		
82	Pb	93	H			Meads, P.F., Forsythe, W.R., Giauque, W.F., J.Amer.Chem.Soc. 63, 1902, 1941.
		96.3	L	7.48		Horowitz, M., Silvidi, A.A., Malaker, S.F., Daunt, J.G. Phys.Rev. 88, 1182, 1952.
83	Bi	147	H		x	Anderson, C.T., J.Amer.Soc. 52, 2720, 1930
		100	L		x	Armstrong, L.D., Grayson-Smith, H. Canad. J.Res. A 27, 9, 1949.
90	Th	147	H			Griffel, M., Skochlopole, R.E. J.Amer.Chem.Soc. 75, 5250, 1953
		170	L		x	Smith, P.L. (Priv.Comm.)
92	U	162	H			Jones, W.M., Gordon, J., Long, E.A., J.Chem.Phys. 20, 695, 1952.
		177	L		x	Smith, P.L. (Priv. Comm.)

REFERENCES

Blackman, M., Z. Physik., 86, 421, 1933.

Blackman, M., Proc.Roy.Soc., 159, 416, 1937.

Born, M., and Brody, E., Z.Physik., 6, 132, 1921.

Carlson, D.C., Thesis, Oxford, 1950.

Clusius, K., Goldmann, J., Perlick A., Zeits.fur Naturforschung, A 4, 425, 1949.

Clusius, K., Hiller, K., Zeits.f.Phys.Chem. B 4, 158, 1929.

Cooke, A.H., Duffus, H.J., Wolf, W.P., Phil.Mag. 44, 623, 1953.

Cremer, E., Polanyi, M., Zeits.f.Phys.Chem. B 21, 459, 1933.

Donnison, D.H., Proc.Roy.Soc. A 115, 483, 1927.

Eucken, A., Hiller, K., Zeits.f.Phys.Chem., B 4, 142, 1929.

Galt, J.K., Phys.Rev., 73, 1460, 1948.

Giauque, W.F., J.Amer.Chem.Soc., 52, 4816, 1930.

Grew, K.N., Proc. Roy. Soc., 145, 509, 1934.

Hatton, J., Rollin, B.V., Proc.Roy.Soc., A 199, 222, 1949.

Hill, R.W., Thesis, Oxford, 1952.

Hill, R.W., Journ. of Sci.Instr. 30, 331, 1953

Hund, F., Zeits.f.Phys., 42, 119, 1927.

Loby, T.H., Hercus, E.O., Phil.Trans. A 227, 63, 1927.

Linder, C.T., Westinghouse Res.Rep. R-94433-2-A, 1950

Mendelssohn K., Ruhemann, M., Simon, F.E., Zeits.f.Phys. Chem. B 15, 121, 1931.

Nernst, W., Lindemann, F., Zeits.f.Electrochemie und angewandte Phys.Chemie. 17, 817, 1911

Parkinson, D.H., Quarrington, J.E., Proc.Phys.Soc. A 67, 569, 1954.

Person, W.B., Pomental, G.C., 75, 532, 1953.

Reif, R., Purcell, E.M., Phys.Rev. 91, 631, 1953.

Sadron, C., An.Phys.Soc. A 68, 213, 1955.

Simon, F.E., Mendelssohn K., Ruhemann, M., Naturwissenschaften 18, 34, 1929.

Simon, F.E., Physica 4, 1089, 1937.

Smith, P.L., Thesis, Oxford, 1954.

Sugawara T., Masuda Y., Kanda T., Kanda E., Science Reports of the Research Institutes, Tohoku University, A 7, 67, 1955.

Tomita K., Proc.Phys.Soc., A 68, 213, 1955.

Woolley, H.W., Scott, R.B., Brickwedde, F.G., J.Res.N.B.S., 41, 379, 1948.

ACKNOWLEDGMENTS

In conclusion, the author would like to express his gratitude to:

LORD CHERWELL, for extending to him the facilities of the Clarendon Laboratory.

PROFESSOR SIR FRANCIS SIMON, for his kindness, encouragement, and interest in this work.

DR.R.W.HILL, for his supervision, friendship and skill in teaching to him the art of Low Temperature measurements.

DR.P.L.SMITH, for teaching him the rudiments of calorimetry.

MR.O.LOUNASMA, for his assistance in the construction of the helium apparatus.

DR.W.P.WOLF, for many fruitful discussions.

MR.L.WAINE, for his skill in the construction of the parts for the apparatus.

An Extract from "An Inquiry concerning the Source of the Heat which is Excited by Friction", by Benjamin Count of Rumford, F.R.S., M.R.I.A.

Phil. Trans. Vol. 88, 1798.

"Though there was, in fact, nothing that could justly be considered as surprising in this event, yet I acknowledge fairly that it afforded me a degree of childish pleasure, which, were I ambitious of the reputation of a grave philosopher, I ought most certainly rather to hide than to discover....."