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Fothergill, Derek (1960) *A study of Senftleben's method of determining the heat capacity and thermal conductivity of gases*, Durham theses, Durham University. Available at Durham E-Theses Online: http://etheses.dur.ac.uk/10156/

A STUDY OF SENFTLEBEN'S METHOD OF DETERMINING THE HEAT CAPACITY AND THERMAL CONDUCTIVITY OF GASES

A THESIS SUBMITTED FOR THE DEGREE
OF MASTER OF SCIENCE IN THE
UNIVERSITY OF DURHAM.

by

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ST. CUTHBERTS SOCIETY
1960.

Acknowledgements

I wish to thank Dr. G. Kohnstam and Dr. W.K.R. Musgrave for the help and advice which they gave during the period over which this work was carried out. My thanks are also due to Prof. G.E. Coates whose many comments and discussions were very helpful. I would also like to acknowledge here the generous help and co-operation which I received at various times from several members of the laboratory and workshop staff. Finally, I am indebted to Clarke Chapman & Co.Ltd., for their financial aid without which this work could not have been undertaken.

D. Fothergill.

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SUMMARY

The original intention of this investigation was to determine the heat capacities of several fluorocarbon vapours up to temperatures of about 500°C.

A review of the available methods for doing this showed that a method due to Senftleben (1) was by far the most simple and would probably be easiest to extend over the necessary temperature range. However, it was comparatively untried, and the only investigation to be found in the literature using this method was that of Senftleben himself. A further point was that it was necessary to determine the thermal conductivities of the materials under investigation, using the same apparatus, before their heat capacities could be determined. It was therefore decided to determine whether this method could give reliable heat capacities and thermal conductivities over a range of temperatures.

Early measurements showed that, while reasonable thermal conductivity values could be obtained using this method, this was not the case for heat capacities. Further measurements confirmed that the heat capacity results which were obtained were neither accurate nor consistent. Therefore the emphasis of the investigation turned to the determination of thermal conductivity, and this property was determined for several substances over a temperature range from about 30°C to 100°C.

In the derivation of his expression for heat capacity, Senftleben makes several assumptions. These are reviewed in Section IV. It was concluded that some of these assumptions may not have been valid, and that the method was probably in need of reinvestigation.

SECTION I.

REVIEW OF THE EXPERIMENTAL METHODS FOR DETERMINING THE HEAT CAPACITIES AND THERMAL CONDUCTIVITIES OF GASES.

I.1 HEAT CAPACITIES.

A preliminary survey of the literature revealed four possible methods.

I.1.1. HOT WIRE OR SENFTLEBEN'S METHOD.

The hot wire method, which was eventually used in this investigation, is one quite recently devised by Senftleben(1).

In this method, the gas or vapour under investigation is contained in a horizontally placed glass cylinder with a fine platinum wire stretched along its axis. This wire is heated electrically, and the electrical energy Q, needed to maintain the axial wire at a temperature θ above that of the surrounding thermostat bath is measured at various pressures.

This procedure is repeated for a reference gas of known heat capacity and thermal conductivity, and graphs of Q against pressure are drawn. From the low pressure regions of these graphs values of thermal conductivity are found. These are then used in conjunction with Q values from the high pressure regions of the graphs to calculate Cp values for the material under investigation. In the only experimental investigation using this method, the results obtained by Senftleben were generally within about 1% of the commonly accepted values for the substances investigated at 30°C.

The only drawback to the method appears to be the fact that it is relatively untried and has only been used at 30°C. In the derivation of his final equation for Cp, Senftleben makes several assumptions which may turn out to be unjustified (see Section IV). Also, it is necessary to determine thermal conductivities before heat capacities can be found, which adds a further possible source of inaccuracy. However, Senftleben's results were quite reasonable, and there are several advantages to using the method.

The greatest factor in its favour is its great simplicity. The apparatus is extremely simple when compared with that used in other methods, and only a small part of it need be thermostated. The measurements themselves are quite easy to make and calculation of results from these measurements is very simple. These factors should facilitate the extension of the method to higher temperatures. Furthermore, Senftleben assumes that since this is a comparison method, small errors cancel out to a large extent, rendering the application of corrections unnecessary. With refinement, it is possible that the method could give very accurate results.

I.1.2 CONSTANT FLOW METHOD.

The constant flow method is at present the best known and most accurate method of finding the heat capacities of gases. It was devised by Callendar and Barnes (2) for finding the heat capacities of liquids, then modified by Swann (3) for application to gases. Since then the method has been developed by workers such as Pitzer (4) and De Vries and his co-workers (5) to give very accurate results.

In principle, the method consists of passing the gas or vapour under investigation over a heater at a constant known flow rate. The temperature of the material is measured before and after passing over the heater. From a knowledge of the rate of heat supply to the gas, its rise in temperature and its flow rate, the heat capacity of the gas can be calculated.

The essential part of the apparatus needed in this method is a tube containing two thermocouples for measuring the temperature of the material flowing through the tube. A small heater is situated between the two thermocouples. The tube, which is immersed in a thermostat bath, is generally U shaped and so constructed that direct radiation from the heater to the thermocouples is reduced to a minimum. The incoming gas or vapour is brought first through a long copper or glass spiral so that the material can attain thermostat temperature. The gas is then brought into the tube containing the thermocouples and heater, and its initial temperature is measured using the first thermocouple. It is then warmed slightly by passage over the heater and its final temperature measured using the second thermocouple. The flow rate is adjusted so that the rise in temperature is constant and small, after which the flow rate itself must be kept constant.

The practical difficulties of this method are enumerated below.

I. 1.2.1. After passing over the heater, the temperature of the gas stream tends to fall before reaching the thermocouple where its final temperature is measured. This must either be prevented or correction made for the effect. Two methods have been used.

(a) Sinke and De Vries (5e) prevented this effect by placing the heater and thermocouple in a very thin walled glass tube which thus had a very low thermal capacity. As further precautions, the walls of this tube were silvered and the whole tube surrounded by a vacuum jacket. However, at higher temperatures, use of a very thin walled glass tube under pressure would be impossible. This sets a limit on the use of this method.

(b) Pitzer (4) used a silvered U tube of normal glass. This was surrounded by a vacuum jacket. However, he measured the final temperatures of the gas using two thermocouples at different distances from the heater. Apparent heat capacities were calculated from both measurements and an extrapolation procedure used to find the true heat capacity.

I. 1.2.2. Achievement of constant gas flow rate is difficult and once more, several different methods have been used.

(a) Several workers (4. 5a.b.c. 6) have used a method where the liquid under investigation was boiled at a constant rate, providing a constant stream of vapour. Electrical heating was used for the boiler in all cases. Since mains voltages are not steady, Waddington, Todd and Huffmann (6) used high capacity batteries to provide a constant voltage for the heaters. To ensure steady conditions, the boiler was surrounded by an evacuated jacket which was further surrounded by a thermostat bath at the boiling point temperature of the material under investigation.

(b) De Vries and his co-workers (5d.e) placed the liquid under investigation in a hypodermic syringe. The plunger was then depressed by a constant speed electric motor to which it was connected by a screw arrangement. Drops of liquid from the syringe fell into a flash boiler where they were vapourised, the vapour then passing into the measuring system. A drawback to this method was that at low flow rates, surges of vapour were obtained instead of a constant stream.

I. 1.2.3. Initially, inefficient heat exchange between the gas stream and the heater and the thermocouples caused some trouble. This was overcome by more efficient heater and thermocouple design. (5).

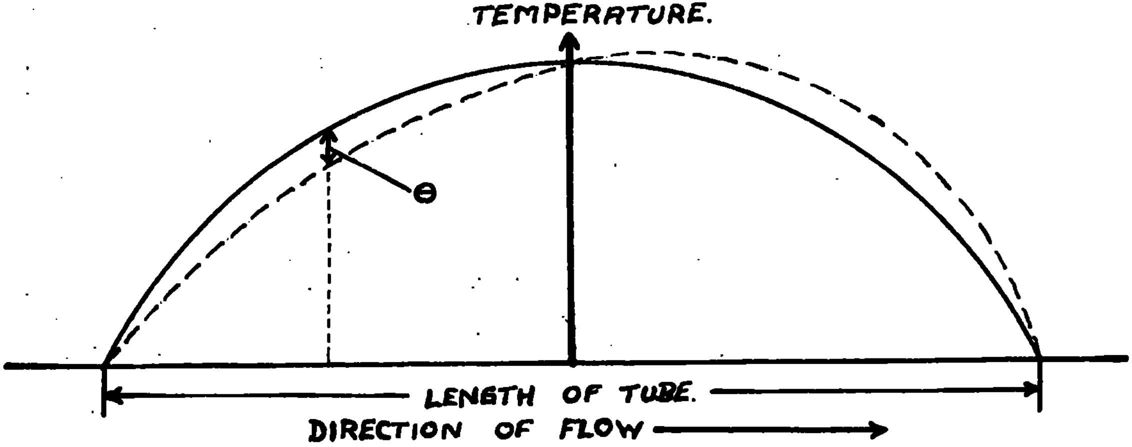
I. 1.2.4. A correction must be made for radiation from the heater. To do this, Sinke and De Vries (5) made measurements at different flow rates but with the same heater temperature. From the measurements, apparent heat capacities were calculated and an extrapolation procedure used to obtain the true heat capacity.

The constant flow method has been used up to about 170°C by De Vries and his co-workers (5e.). Weltner and Pitzer (7) have used the method up to 250°C and they claim an accuracy of about 0.3% at room temperature changing to about 1% at 200°C. This accuracy is quite good, but the practical difficulties are considerable and could prove to be insuperable at high temperatures.

I. 1.3. METHOD DUE TO BLACKETT, HENRY AND RIDEAL. (8).

Blackett, Henry and Rideal devised a constant flow comparison method, and used it at around room temperature. It has also been used by other workers (9) both in the original and in modified forms, with varying degrees of success.

The method consists of heating a fine iron tube electrically in such a way that symmetrical temperature gradients are set up from the middle of the tube to its ends. When the materials under investigation is passed through the tube, the symmetry of these temperature gradients is destroyed. The situation is illustrated diagrammatically below where the full line shows the symmetrical temperature gradients and the broken line represents the situation when a gas is passing through the tube.



The change in temperature, θ, at any point can be measured by thermocouples welded to the tube. The heat capacity, Cp, of the gas under investigation is proportional to θ and inversely proportional to the flow rate F.

i.e. $Cp \propto \theta/F$

The procedure is repeated for a reference gas of known heat capacity (subscript $_o$) and the equation

$$\frac{Cp}{Cp_o} = \frac{(\theta/F)}{(\theta/F)_o}$$

used to find Cp, which is the only unknown.

To achieve constant gas flow, Blackett, Henry and Rideal used a constant speed electric motor to drive a piston along a cylinder containing the gas under investigation. This system was improved by Henry (9a.). Eucken and Sarstedt (9b) and Potop (9c.) passed the material through fine capillaries or a membrane across which was maintained a constant pressure gradient.

An extension of this method has been suggested by

Chapman (10). His suggestion was that two fine iron tubes as nearly identical as possible be used. The material under investigation is passed through one of these tubes while a reference gas of known heat capacity is passed through the other. Their flow rates are adjusted so that the temperature at the middle of each tube is the same. When this condition is attained, the ratio of the two flow rates is equal to the ratio of the heat capacities of the two gases. In practice, it would almost certainly be impossible to obtain two identical tubes. This difficulty can be overcome either by interchanging the gases in the two tubes or by passing the same gas through both tubes. In this way, the necessary correction factor can be evaluated. The method does not seem to have been used in practice.

Another adaptation of this method was devised by Bennewitz and Schulze (9a). A uniform temperature gradient was established along the length of a glass tube. The disturbance of this temperature gradient when a gas is passed through the tube is compensated by electrical heating. However, it was only after a long and difficult investigation that Bennewitz and Schulze obtained any reasonable results. On the other hand, Dailey and Felsing (9f.), using the same adaption, claim that results can be obtained fairly easily and accurately up to 100°C.

The original method was used successfully by its authors at around room temperature. It has also been used fairly successfully up to about 200°C. by Eucken and Sarstedt (9b.) and up to 370°C by Henry (9g.). However, after a very extensive investigation up to 600°C, Potop (9c.) concluded that the method could not be relied upon to give accurate results. The reasons which he put forward were that it is impossible to obtain steady conditions, especially at higher temperatures, where it is difficult to measure temperature accurately. Also, the welding of thermocouples to the delicate iron tube upset the conditions necessary for obtaining accurate heat capacities.

There is a certain amount of disagreement between the various authors as to the value of this method. Building and developing the necessary apparatus would almost certainly prove to be a long and difficult process and even then, accurate results may not be obtained. The Chapman method has not been investigated experimentally, but the difficulties would probably be much the same as those in the original method. Such an investigation would therefore probably prove to be unfruitful.

I. 1.4. REGNAULTS METHOD.

This method was not actually devised by Regnault, but he was the first worker to use this method to obtain results of any accuracy (11). The method consists simply of passing the preheated gas or vapour into a calorimeter containing a liquid of known heat capacity. From the rise in temperature of the calorimeter liquid, the heat capacity of the gas or vapour can be calculated.

There are, however, several difficulties for which accurate corrections cannot be made.

(a) Only the mean heat capacity of a gas over a range of temperature can be found. This is highly undesirable for compounds whose heat capacities are strongly temperature dependent.

(b) There can be considerable heat loss from the tube along which the gas passes into the calorimeter. This can be partly overcome by heating this tube to the same temperature as that of the furnace which is heating the gas.

Unfortunately, this causes the supply of a considerable amount of heat directly to the calorimeter besides the heat supplied to it by the gas in cooling.

(c) Some of the compounds in which we are interested are liquid at room temperature. Unless the calorimeter is initially at a temperature above their boiling point (which would involve further heat loss errors) the final calculation of the heat capacity will be complicated by latent heat effects. Unfortunately, the latent heats are very large compared with the other quantities measured, and accurate correction is almost impossible.

Despite these difficulties, the method was used by Holborn and Austin (12) to measure mean heat capacities up to 800°C. An accuracy of 1% is claimed for these results. Holborn and Hanning (13) extended the method to 1400°C, but the results were not so accurate as the previous ones.

CONCLUSION.

From this review, it can be seen that, while the difficulties in the other methods are not insuperable, Senftlebens method is experimentally by far the simplest and it appeared that there would be no difficulty in employing this method for determining heat capacities at elevated temperatures.

I. 2. THERMAL CONDUCTIVITY.

There appear to be two general methods of determining gaseous thermal conductivities.

I. 2.1. PARALLEL PLATE METHOD.

I. 2.2. HOT WIRE METHOD.

The two methods are very similar in principle, the difference between them being that in the first method the rate of heat transfer between two parallel plates is measured, while in the second method measurement is made of the radial heat transfer from a hot wire surrounded by the gas under investigation.

I. 2.1. PARALLEL PLATE METHOD.

The parallel plate method was devised by Stefan (14) then developed and improved by several workers although it is not now in common use.

One of the earliest developments of this method was due to Winkelman (15) who used concentric cylinders instead of parallel plates. The annulus between the cylinders was filled with the gas under investigation at a known temperature. The outer cylinder was then cooled to $0^{\circ}C$ by plunging the apparatus into ice water. From the rate of cooling of the inner cylinder under these conditions, the thermal conductivity of the gas could be calculated. The method can be used as a comparison method or to make absolute determinations in which case corrections for radiation and conduction along the gas inlet lead are necessary.

Hercus and Laby (16) used two horizontal parallel plates of silvered copper with a guard ring. The top plate was heated electrically while the bottom plate was cooled with running water. With this arrangement, heat transfer is in a downward direction and convection effects are eliminated. Above the top plate and guard ring was placed another plate at the same temperature as the top plate. This ensured that all the heat loss from the top plate was in a downward direction. From the rate of heat supply to the top plate and the dimensions of the apparatus it was possible to calculate the thermal conductivity of the gas between the plates. Again, a radiation correction was applied.

However, it proved difficult to obtain consistent results using this method mainly because of the difficulty in keeping the conditions steady over a long enough period of time to complete the necessary measurements.

I. 2.2. HOT WIRE METHOD.

This is generally known as the Schleiermacher method although the principle was used before Schleiermacher himself used it to measure thermal conductivity (17). It is now the most commonly used method of determining gaseous thermal conductivities.

The apparatus consists essentially of a narrow tube with a fine platinum wire stretched along its axis. The gas or vapour under investigation is passed into this cell at fairly low pressures as this reduces convection effects. The axial wire in the cell is heated electrically and a known temperature gradient established between it and the walls of the cell. From a knowledge of the energy dissipated in the wire, the temperature gradient between the wire and the walls of the cell and the dimensions of the cell, the thermal conductivity of the gas or vapour can be calculated.

This method requires very careful attention to detail when making absolute determinations of thermal conductivity, and the original method has been very much improved by the work of various investigators (18). Some of the improvements in design of the apparatus and application of corrections are enumerated below.

I. 2.2.1. A correction for the radiation of heat from the axial wire must be made, although this can be reduced by using a very fine platinum wire with a small radiating surface.

I. 2.2.2. A small correction must be made for the temperature drop across the walls of the vessel, the inner surface of the wall being at a slightly higher temperature than the outer surface.

I. 2.2.3. A further correction must be made for the effects which arise at the ends of the cell due to non-uniformity of the cell itself, and to the conduction of heat from the axial wire through the metal electrical leads which are much better conductors than the gases in the cell. Three different types of cell have been used to eliminate or to allow for correction of these effects.

(a) Compensating cells as used by Dickins (18d). This method involves the use of two cells which differ only in length, so that by a process of subtraction, measurements are obtained which refer effectively only to the uniform central portion of the longer tube.

(b) The thick wire cell which was developed by Kannuluik and Martin (18c.). In this method, no attempt is made to minimise conduction of heat along the leads, but the cell is so constructed that end effects can easily be corrected for by a mathematical treatment.

(c) The potential lead cell which was used in gradually improving forms by Schleiermacher (17), Weber (18a) and by Johnston and his co-workers (18b.c). In this type of cell, very fine potential leads to the axial wire are used. They are attached to this wire in such positions that measurements are effectively made only on the central portion of the wire which is in the uniform part of the tube. In this way, conduction along the electrical leads is cut down because of their extreme fineness, and the end correction is very small.

<u>I. 2.2.4.</u> The last important correction is for the effect of accommodation and the temperature discontinuity which accompanies it. According to Knudson (19), when a molecule of a gas at temperature θ strikes a hot surface at temperature θ'', the final temperature of the gas molecule θ', lies between θ and θ''. This gives rise to the relationship

$$\theta' - \theta = \alpha(\theta'' - \theta)$$

where α is called the accomodation coefficient.

From this it can be seen that there will be a small temperature discontinuity at any solid-gas interface where the solid and the gas are at different temperatures. For the purpose of the hot wire method, Dickins (18d) has shown that the effect is more important at the hot wire than at the wall of the vessel, where the effect is negligible. The effect is also more important at low pressures than at high pressures.

In the hot wire method, the measurements for the determination of thermal conductivity are made at low pressures to eliminate convection effects. The resulting thermal conductivity values show a dependence on pressure due to the effect of temperature discontinuity. High pressure measurements which would eliminate temperature discontinuity effects are impossible because of convection effects. These difficulties are overcome by an extrapolation procedure. Conductivity measurements are made at several different low pressures where convection effects are negligible. These results are then extrapolated to give an effective conductivity at infinite pressure where the temperature discontinuity is zero. In this way, both convection and temperature discontinuity errors are eliminated.

Despite the fact that the hot wire method is the most commonly used method for the determination of thermal conductivity and has been used in many very careful investigations, values of thermal conductivity found by different authors for the same substance may vary quite widely, this being especially so at high temperatures. Even for such common substances as AIR, ARGON and CO_2, no consistent figures are available as can be seen by reference to Figures 4, 5 and 6, and references (20), (21) and (22). For CO_2 at about 100°C, values quoted by various authors cover a range of about 7% of the values themselves, although this variation is much less near room temperature. for AIR, the values found in the literature cover a range of 2 to 3% over the whole temperature range from 0°C to 100°C. The values available for ARGON are slightly more consistent than for AIR or CO_2, but even so, the variation is still appreciable.

It is obvious from these remarks then that all of the difficulties in this method have not been removed, but despite this, it remains the best method of obtaining absolute values of the thermal conductivities of gases.

I. 2.3. SENFTLEBEN'S METHOD.

Senftleben's method, which is described in the previous section on methods of determining heat capacity, is only a simple variation on the above hot wire method.

Measurements are made on two substances under absolutely identical conditions, and from these measurements, the ratio of the conductivities of the two gases can be found. To find an unknown thermal conductivity from this ratio, the thermal conductivity of one of the gases must be known. As pointed out earlier, it is virtually impossible to find a substance whose thermal conductivity can be said to be accurately known. However, thermal conductivity ratios found by Senftleben agree very well with the ratios of values found in the literature for the common gases.

Thus the method would appear to be quite valid, and once more, it is much simpler experimentally than the other methods described above.

SECTION II

SENFTLEBEN'S METHOD FOR DETERMINING THE THERMAL CONDUCTIVITY AND HEAT CAPACITY OF GASES.

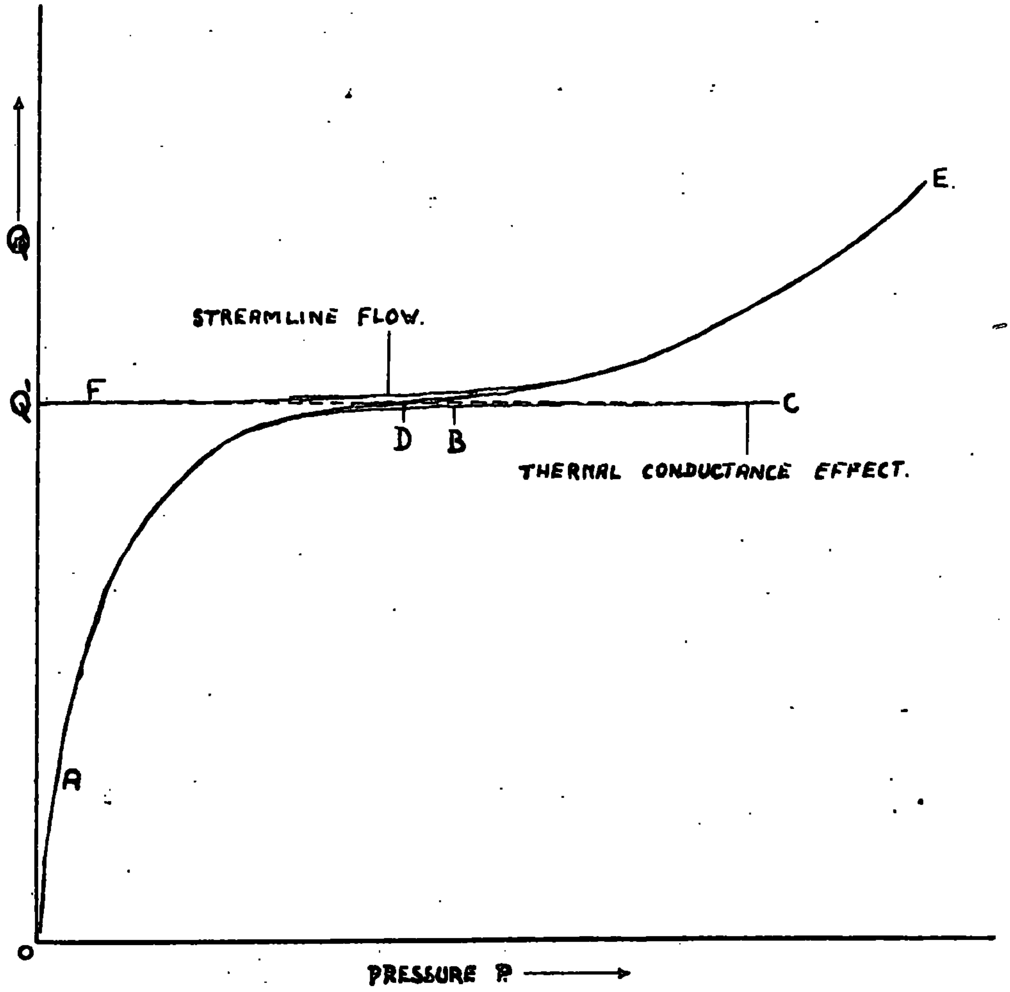
The gas or vapour under investigation is contained in a horizontally placed glass cylinder with a fine platinum wire stretched along its axis. This wire is heated electrically. From the electrical energy Q, needed to maintain the axial wire at a temperature θ° above that of the surrounding thermostat bath at various pressures, first the thermal conductivity λ, then the heat capacity Cp of the material under investigation can be found.

II. 1.1. DETERMINATION OF THERMAL CONDUCTIVITY.

In this method, thermal conductivities are determined by comparison of the low pressure regions of two Q against P graphs, one for the material under investigation and the other for a gas of known thermal conductivity. A diagrammatic Q against P curve of the type which might be obtained for any gas or vapour is shown in Figure 1.

At low pressures, there is no convection, and ignoring the small corrections for radiation and conduction of heat along the electrical leads, energy is transferred from the hot wire to the walls of the vessel by conduction only. If this state of affairs persists, Q eventually becomes independent of pressure (curve ABC, Figure 1), and its value Q' is then directly

FIG. 1. DIAGRAMMATIC LOW-PRESSURE $Q \sim P$ CURVE.



proportional to the thermal conductivity of the gas in the tube. In practice, however, convection effects always appear before the horizontal portion of the curve is realised. These effects are shown in Figure 1 by the curve EF which has its zero at $Q = Q'$. Since the conduction and convection effects are additive, experimentally the composite curve ADE in Figure 1 is obtained. However, this curve always shows a point of inflexion at $Q = Q'$ so that there is no difficulty in obtaining values of Q' from the experimental curves.

To determine an unknown thermal conductivity, Q' values are obtained from the Q against P curves for the gas under investigation and for a comparison gas of known thermal conductivity. Since these Q' values are proportional to the thermal conductivities of the respective gases (see section II.1b), one arrives at the expression

$$\frac{Q'}{Q'_o} = \frac{\lambda}{\lambda o} \qquad \text{or} \qquad \lambda = \frac{\lambda o . Q}{Qo.}$$

where the subscript o refers to the comparison gas of known thermal conductivity, λo.

Since λo, Q and Q_o are all known, the unknown thermal conductivity λ, is easily evaluated.

II. 1.2. THEORY OF THE DETERMINATION OF THERMAL CONDUCTIVITY.

Let L be the length of the axial wire, r_1 its radius and T_1 its temperature. T_2 is the temperature of the wall of the glass tube, and r_2 its radius. The temperature gradient at any point between the walls of the axial wire and the walls of the tube is $\frac{dT}{dr}$.

Assuming that all the energy is transferred from the axial wire by conduction, the amount of energy passing per second through the surface of a cylinder of radius r is given by the expression

$$Q' = - \lambda . 2\pi r L . \frac{dT}{dr} \quad \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_(1).}$$

For this particular case, the total heat loss per second, Q', can be found by integrating equation (1) between the limits of r_1 and r_2, and T_1 and T_2.

$$Q' \int_{r_1}^{r_2} \frac{dr}{r} = -2\pi L \lambda . \int_{T_1}^{T_2} dT$$

$$Q'(\ln r_2 - \ln r_1) = - 2\pi L \lambda (T_2 - T_1).$$

$$= 2\pi L \lambda (T_1 - T_2).$$

Therefore, writing $T_1 - T_2 = \theta$,

$$\lambda = Q' \left(\frac{\ln r_2 - \ln r_1}{2\pi L \theta} \right) \quad \text{\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_(2).}$$

In experiments to find thermal conductivities, r_1, r_2 and $2\pi L$ remain constant and measurements on different gases are all done under identical conditions, so that T_1 and T_2 also remain constant. In equation (2) then, the expression inside the brackets remains constant, and the equation can be written

$$\lambda = Q'B.$$

where $B = \left(\frac{\ln r_2 - \ln r_1}{2\pi L(T_1 - T_2)} \right)$ and is constant.

The value of λ therefore is directly proportional to the value of Q!

It is obvious that by combining the expressions for the two substances, one of which is designated by the subscript o, one arrives at the expression

$$\frac{\lambda}{\lambda o} = \frac{Q!B.}{Q'_{o}.B} \quad \text{or} \quad \frac{\lambda}{\lambda o} = \frac{Q}{Qo}$$

From this, $\lambda = \lambda o. \frac{Q}{Qo}$ ______________ (3).

This equation is used as described earlier to find an unknown thermal conductivity.

II. 2.1. DETERMINATION OF HEAT CAPACITY Cp.

The heat capacity of the gas under investigstion can be obtained from the expression

$$Cp = Cpo. \frac{\lambda}{\lambda o} \frac{p^{o}}{p} \sqrt{Am.}$$

where the subscript o again refers to a reference substance of known heat capacity and thermal conductivity, Cp is the molar heat capacity, p is the gas pressure and Am can be evaluated from the experimental data from the high pressure regions of the Q against P curves (see Section II.2b). The term $\lambda / \lambda o$ is obtained as shown in the previous section. Cp can therefore be evaluated if Cp_o and λo are known.

II. 2.2. THEORY OF THE DETERMINATION OF HEAT CAPACITY Cp.

It is convenient at this point to set out the meanings of the symbols used in the following discussion:-

q	Energy lost per unit area per unit time from the platimum wire.
Q.	Total energy lost per unit time from the platimum wire.
F.	Surface area of the platimum wire.
θ	Temperature difference between the wire and the walls of the cell.
l.	Diameter of the platimum wire, $= 2r_1$.
ρ	Density of the gas.
δ	Coefficient of thermal expansion of the gas (1/T for gases).
g	Gravitational constant.
λ	Thermal conductivity of the gas.
η	Viscosity of the gas.
C_p	Molar heat capacity of the gas at constant pressure.
c_p	Heat capacity per gram of gas at constant pressure.

In an earlier paper (23), Senftleben has discussed the problem of heat transfer under the conditions prevailing in this investigation, i.e. between horizontal coaxial cylinders where $r_1 \ll r_2$. At higher pressures where heat transfer takes place both by conduction and convection, Senftleben assumes that in the convective movement of the gas, only streamline flow of the gas is operative and there is no turbulent flow.

For a discussion of heat transfer under these conditions, it is convenient to define three dimensionless quantities. They are: -

The Nusselt number, $Nu = \frac{Q.1}{\lambda F \theta}$ (4a).

The Grashof number, $Gr = \frac{1^3 \rho^2 g \delta \theta}{\eta^2}$ (4b).

The Prandtl number, $Pr = \frac{cp.\eta}{\lambda}$ (4c).

These three quantities are related by the expression

$$Nu = f\,(Gr.Pr).$$

The precise nature of the function involved in this expression cannot be found on a theoretical basis. From an analysis of many experimental observations however, Senftleben showed that the relationship between Nu and the product Gr.Pr. was best expressed by the equation

$$Nu = f(Gr.Pr) = \frac{2}{\ln \frac{s}{r}} \left[1 - \frac{.033}{\ln\frac{s}{r}(Gr.Pr)^{\frac{1}{4}}} \left(\sqrt{1 + \frac{\ln\frac{s}{r}(Gr.Pr)^{\frac{1}{4}}}{.033}} - 1\right) \right] - (5)$$

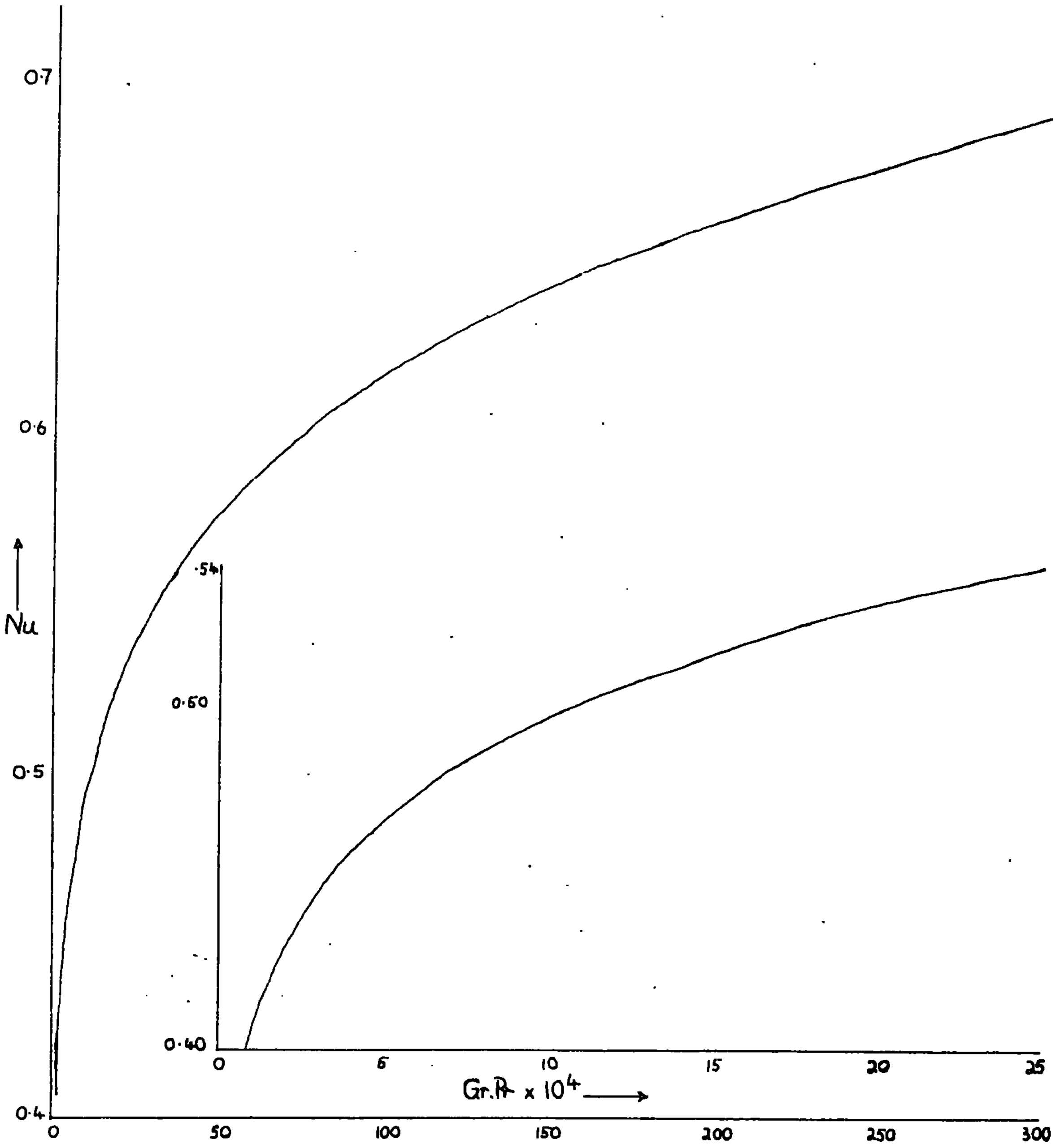
where $\frac{s}{r} = 1 + \frac{4.5}{(Gr.Pr)^{\frac{1}{4}}}$

For a wire of surface area F, length L and diameter 1, equation (4a) can be written

$$Nu = \frac{Q}{\pi L \lambda \theta} \qquad (4a)$$

Q values are obtained from the high pressure regions (50 - 80 cms) of the Q against P curves for the gases involved. π, L, and θ are known, and λ has been previously determined. Thus, using equation (4a), Nu values can be found. For each value of Nu, a corresponding value of Gr.Pr can be found using equation (5). For practical use, equation (5) is expressed

FIG. 2. GRAPH OF Nu AGAINST Gr. Pr.



graphically (see figure 2), and the graphs drawn in large scale sections.

In this way, experimental Gr.Pr values for the gas under investigation and the reference gas are obtained. Senftleben uses these to define a quantity Am.

$$Am = \frac{(Gr.Pr)}{(Gro.Pro)} \text{ (Experimental)} \qquad (6).$$

where once more the subscript o refers to the comparison gas of known thermal properties.

For any arbitrary set of conditions which are identical for both gases, theoretical values of Gr.Pr and $Gr_o.Pr_o$. can be found by inserting the appropriate values of λ, Cp, η etc. in the definitions of these quantities (equations (4b) and (4c)). These are used to define a quantity A.

$$A = \frac{(Gr.Pr)}{(Gr_o.Pr_o)} \text{ (Theoretical)} \qquad (7).$$

According to Senftleben, the experimental conditions in the determination of the experimental values of Gr.Pr and $Gr_o.Pr_o$ are not identical. This is attributed to differences in the thermal properties of the two gases, these differences causing differences in the flow conditions of the two gases when convection takes place. As a result, experimental Gr.Pr and $Gr_o.Pr_o$ values are not exactly equal to the theoretical values as defined using equations (4b) and (4c). Therefore Am is not equal to A which was defined for absolutely identical conditions of measurement on the two gases.

Senftleben proposes that Am and A are related by the expression

$$Am = A.a. \tag{8}$$

where $a = Pr/Pr_o$. (9)

The value of a will generally be close to unity, since for most gases, the values of Pr only vary between about .7 and .9. The value of Pr involves the three thermal properties, Cp, η and λ. Since the difference between Am and A is said to be caused by differences in these thermal properties for the two gases, it seems likely that the ratio of these properties, i.e. the ratio of the Pr values, will be some measure of the difference between Am and A. In any case, Cp values obtained in this manner by Senftleben were very reasonable, so it seems that the assumption is quite valid.

Combination of equations (7) and (9) gives

$$\frac{Gr_o}{Gr} A = a \tag{10}$$

and use of equation (8) to substitute for A in equation (10) gives

$$\frac{Gr_o \cdot Am.}{Gr \quad a} = a \quad \text{or} \quad \frac{Gr_o}{Gr} = \frac{a^2}{Am} \tag{11}$$

Substitution for Gr and Gr_o using equation (4b) gives

$$\frac{\rho_o^2 . \eta^2}{\rho^2 . \eta_o^2} = \frac{a^2}{Am} \tag{12}$$

From Boyles Law,

$$P = \frac{\rho RT}{\mu}$$

where ρ is the gas density and μ its molecular weight. This expression is used to substitute for ρ in equation (12), and taking square roots,

$$\frac{a}{\sqrt{Am}} = \frac{\rho_o . \mu_o . \eta}{\rho . \mu . \eta_o} \qquad (13)$$

In this equation, we now substitute for a from equations (7) and (4c), and obtain

$$\frac{\mu . cp}{\mu_o . cp_o} = \frac{\lambda .}{\lambda o} \, \frac{Po .}{P} \sqrt{Am}$$

Since $\mu . cp = Cp$, the equation finally becomes

$$Cp = Cp_o . \frac{\lambda}{\lambda o} . \frac{Po .}{P} \sqrt{Am} \qquad (14).$$

Using equation (14), an unknown heat capacity Cp, can be determined in the manner outlined at the beginning of this section on heat capacities. If, at the beginning of the calculation of $\sqrt{Am}$, Q values are chosen for the two gases at the same pressure, equation (14) is further simplified by the removal of the term Po/P.

SECTION III

RESULTS.

In this section, the final thermal conductivity and heat capacity values obtained from this investigation are set down, together with the experimental conditions under which the measurements were made.

Three cells were used to make the measurements. These cells are numbered I, II and III in the tables in this section and they are shown diagramatically in figures 7, 8 and 9. The actual experimental results obtained from these cells are shown later in appendix I.

III. 1. THERMAL CONDUCTIVITY RESULTS.

Due to the inconsistency of thermal conductivity results found in the literature, the results quoted here are obtained from comparisons with three of the more common gases, AIR, ARGON and CO_2. The thermal conductivity values for these three gases were taken from the tables in the National Bureau of Standards Circular Number 564. (24).

These values are shown in Table I, together with the conductivity values obtained in this investigation for AIR, ARGON and CO_2.

The thermal conductivity values shown in these tables apply at a temperature intermediate between the thermostat temperature and the temperature of the hot wire. Thus, in the first column for example, the thermostat temperature is 25°C and θ is 10.67°C, so that the thermal conductivities apply at a temperature of 30°C.

Besides AIR, ARGON and CO_2, the other substances investigated were CH_3Br, $CClF_2.CClF_2$, CF_4, $CCl_3.CF_3$ and $CFCl_2.CClF_2$. The thermal conductivity values found for these compounds are set out in Table II, together with values found in the literature for some of the substances.

FIG. 3. GRAPHS OF THERMAL CONDUCTIVITY, λ, (CALS/CM/SEC/°C AGAINST TEMPERATURE (°C) FOR CF_4, $CFCl_2.CClF_2$ AND $CCl_3.CF_3$.

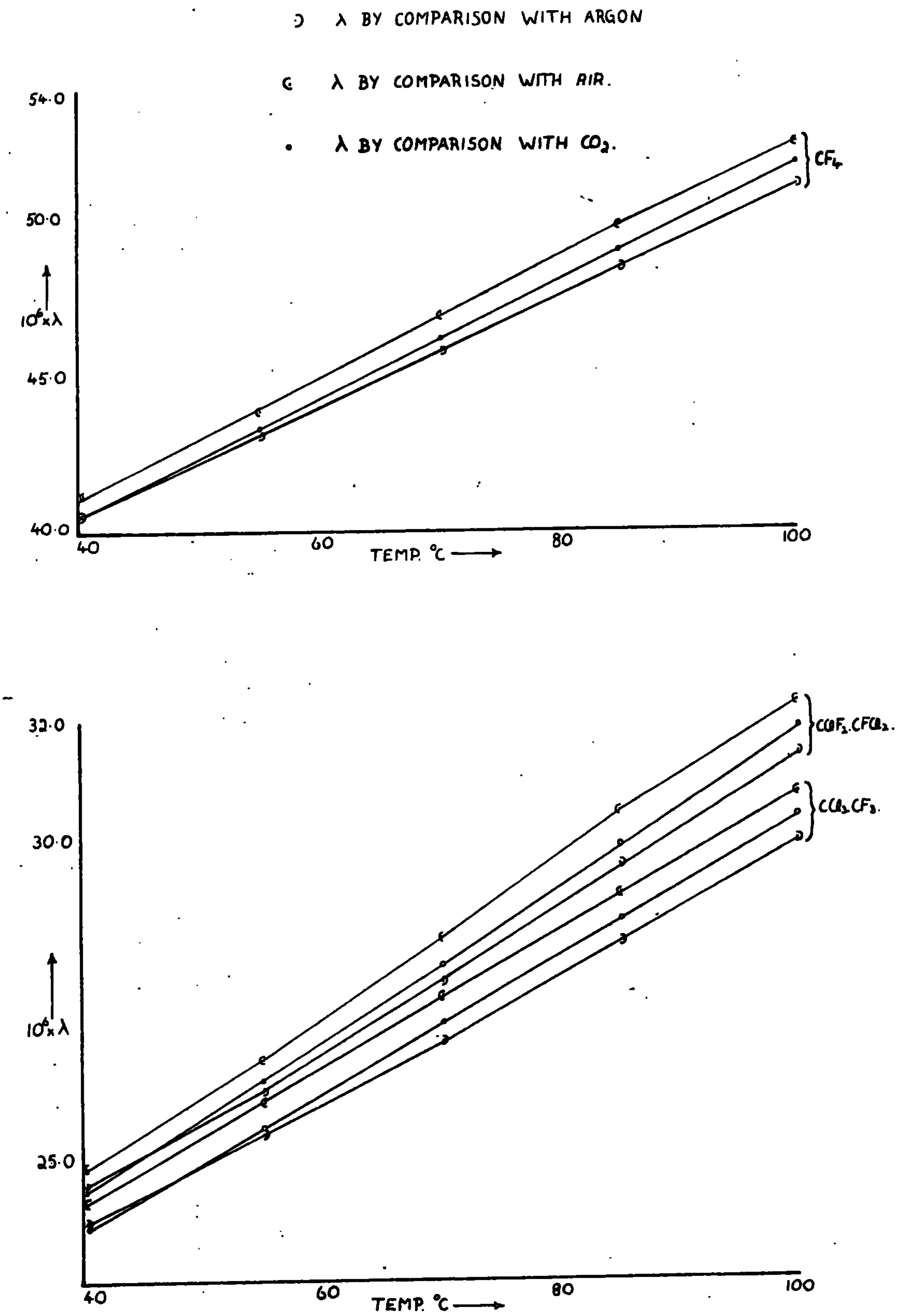


TABLE I THERMAL CONDUCTIVITIES OF AIR, ARGON AND CO_2 IN CALS/CM/SEC/°C.

Cell Number		I	II	III	III	III	III	III	III
Thermostat Temperature °C.		25	35	35	35	50	65	80	95
Θ°C.		10.67	13.0	9.3	12.1	12.1	12.1	12.1	12.2
$10^6 \times \lambda(\text{AIR})$	(By comp. with ARGON)	-	63.65	-	64.22	66.61	68.65	71.11	73.78
	(By comp with CO_2)	62.33	67.01	-	64.09	66.95	69.37	71.92	74.97
	(N.B.S.).	63.25	65.15	-	65.15	67.87	70.51	73.20	75.85
$10^6 \times \lambda(\text{ARGON})$	(By comp. with AIR)	-	44.83	-	44.39	46.30	48.40	50.23	51.74
	(By comp. with CO_2)	-	46.11	44.20	43.66	45.67	47.62	49.36	51.14
	(N.B.S.)	-	43.80	43.75	43.80	45.44	47.13	48.80	50.43
$10^6 \times \lambda(CO_2)$	(By comp. with AIR)	40.72	40.74	-	42.59	45.37	48.43	51.44	54.14
	(By comp. with ARGON)	-	39.81	41.50	41.98	44.53	47.16	49.98	52.66
	(N.B.S.)	40.13	41.90	41.90	41.90	44.75	47.65	50.55	53.40

TABLE II THERMAL CONDUCTIVITIES OF CH_3Br, CF_4, $CClF_2$. CCl_3.CF_3 and $CFCl_2$.$CClF_2$. FOUND BY COMPARISON WITH ARGON, AIR AND CO_2. THERMAL CONDUCTIVITIES IN CALS/SEC/CM/°C.

Cell Number		I	III	III	III	III	III	III
Thermostat Temperature °C.		25	35	35	50	65	80	95
θ°C.		10.57	9.3	12.1	12.1	12.1	12.1	12.2
$10^6 x \lambda(CH_3Br)$	(By comp. with ARGON)	-	-	-	-	-	-	-
	(By comp. with AIR)	20.79	-	-	-	-	-	-
	(By comp. with CO_2)	20.49	-	-	-	-	-	-
	(Literature)	18.6^x	-	-	-	-	-	-
$10^6 x \lambda(CClF_2)_2$	(By comp. with ARGON)	-	28.10	-	-	-	-	-
	(By comp. with AIR)	27.83	-	-	-	-	-	-
	(By comp. with CO_2)	27.42	28.40	-	-	-	-	-
	(Literature)	25.10^+	26.40^+	-	-	-	-	-
$10^6 x \lambda(CF_4)$	(By comp. with ARGON)	-	40.40	40.66	43.06	45.62	48.28	50.90
	(By comp. with AIR)	-	-	41.19	43.87	46.85	49.70	52.22
	(By comp. with CO_2)	-	40.80	40.53	43.27	46.09	48.84	51.61
$10^6 x \lambda(CCl_3CF_3)$	(By comp. with ARGON)	-	-	23.95	25.36	26.84	28.38	30.02
	(By comp. with AIR)	-	-	24.27	25.83	27.56	29.22	30.81
	(By comp. with CO_2)	-	-	23.88	25.48	27.11	28.71	30.44
$10^6 x \lambda(CCl_2F.-CF_2Cl)$.	(By comp. with ARGON)	-	-	25.54	26.05	27.76	29.65	31.41
	(By comp. with AIR)	-	-	24.86	26.55	28.50	30.52	32.22
	(By comp. with CO_2)	-	-	24.47	26.18	28.04	29.90	31.84

x Ref. (25) + Ref. (26)

The thermal conductivity values from TABLE II for CF_4, CCl_3CF_3 and $CClF_2CFCl_2$ are also shown graphically in Fig. 3.

III. 2. HEAT CAPACITY RESULTS.

In contrast to their thermal conductivities, the heat capacities of the common gases are accurately known. The results quoted here are calculated by comparison with ARGON only, and from Q values for each substance at 76 cms pressure.

The compounds investigated were AIR, CO_2, N_2, CH_3Br, CF_4 and $CClF_2.CClF_2$ and the heat capacity values found for these compounds are shown in Table III, together with other heat capacity values found in the literature.

The heat capacity values in this table once more apply at a temperature intermediate between the thermostat temperature and the temperature of the hot wire. Due to the large errors in most of the values quoted in Table III, and to the small temperature coefficient of Cp of most of the gases, a single value of Cp from the literature is sufficient for comparison purposes.

TABLE III

HEAT CAPACITIES OF AIR, CO_2, N_2, CH_3Br, CF_4 AND $CClF_2$ $CClF_2$ IN CALS/MOLE/°C CALCULATED BY COMPARISON WITH ARGON.

Cell Number	I	II	II	III	
Thermostat temperature °C	25.05	25.05	35.00	35.00	Literature
θ°C	29.10	10.67	17.00	20.00	values
Cp (AIR)	6.48^x	-	6.36	-	6.97 (27)
Cp (CO_2)	9.95	11.56	9.66	-	9.30 (27)
Cp (N_2)	6.17^x	6.93	-	-	6.96 (28)
Cp (CH_3Br)	10.80	14.99	-	-	10.53 (29)
Cp ($(CClF_2)_2$)	24.83	31.87	-	-	-
Cp (CF_4)				$15.09^‡$	15.27 (30)

[x] These results for AIR and N_2 are calculated for 59.64 and 62.81 cms respectively. Due to the limitations of the potentiometer, voltage readings could not be made at any higher pressures.

[‡] Calculated by comparison with CO_2, NOT ARGON.

The figures in parentheses are the numbers of the references from which these heat capacity values were obtained.

FIG. 4. GRAPHS OF THERMAL CONDUCTIVITY, λ, OF AIR IN CALS/CM/SEC/°C AGAINST TEMPERATURE IN °K

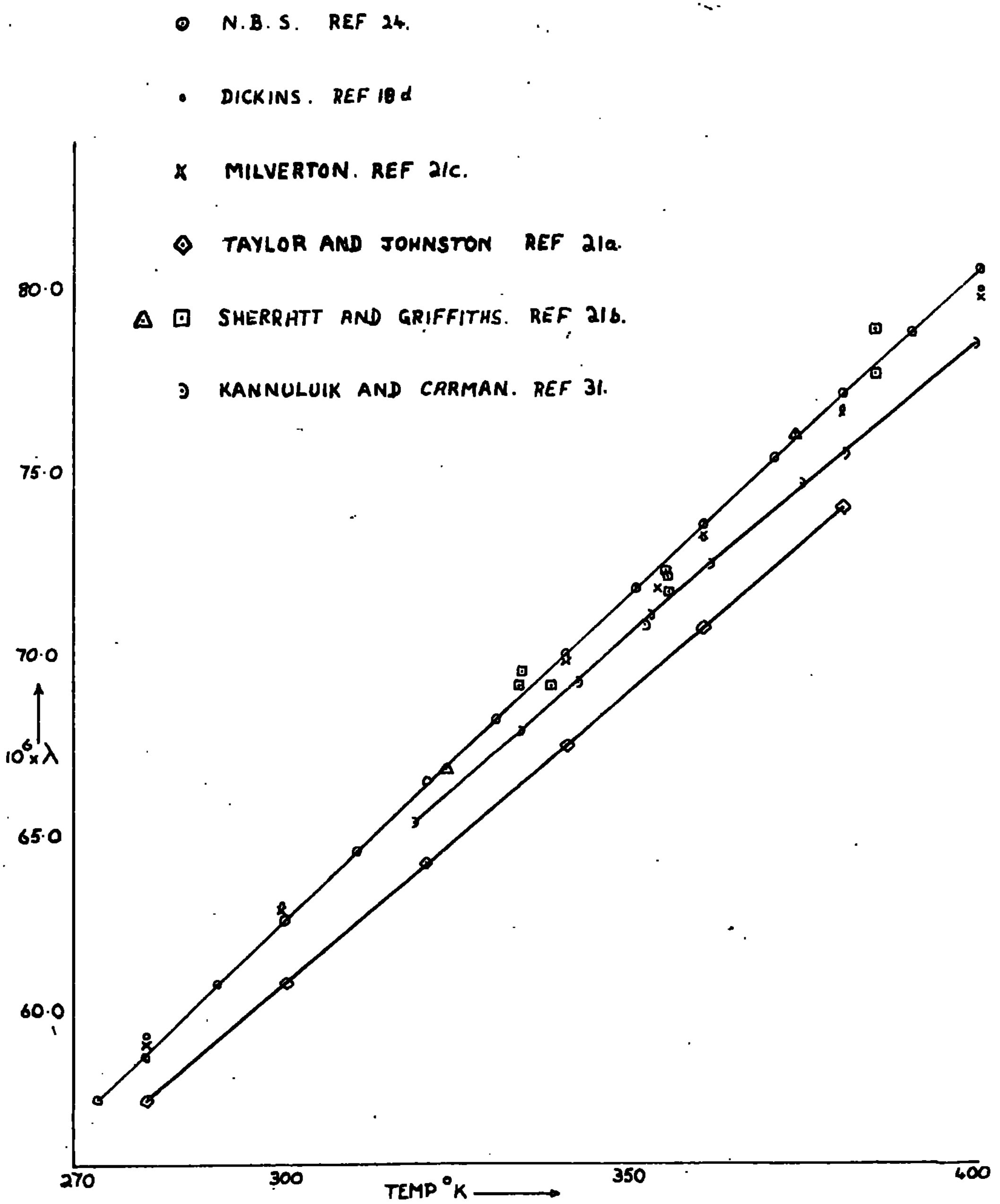


FIG. 5. GRAPHS OF THERMAL CONDUCTIVITY, λ, OF CO_2 (CALS|CM|SEC|°C) AGAINST TEMPERATURE IN °K.

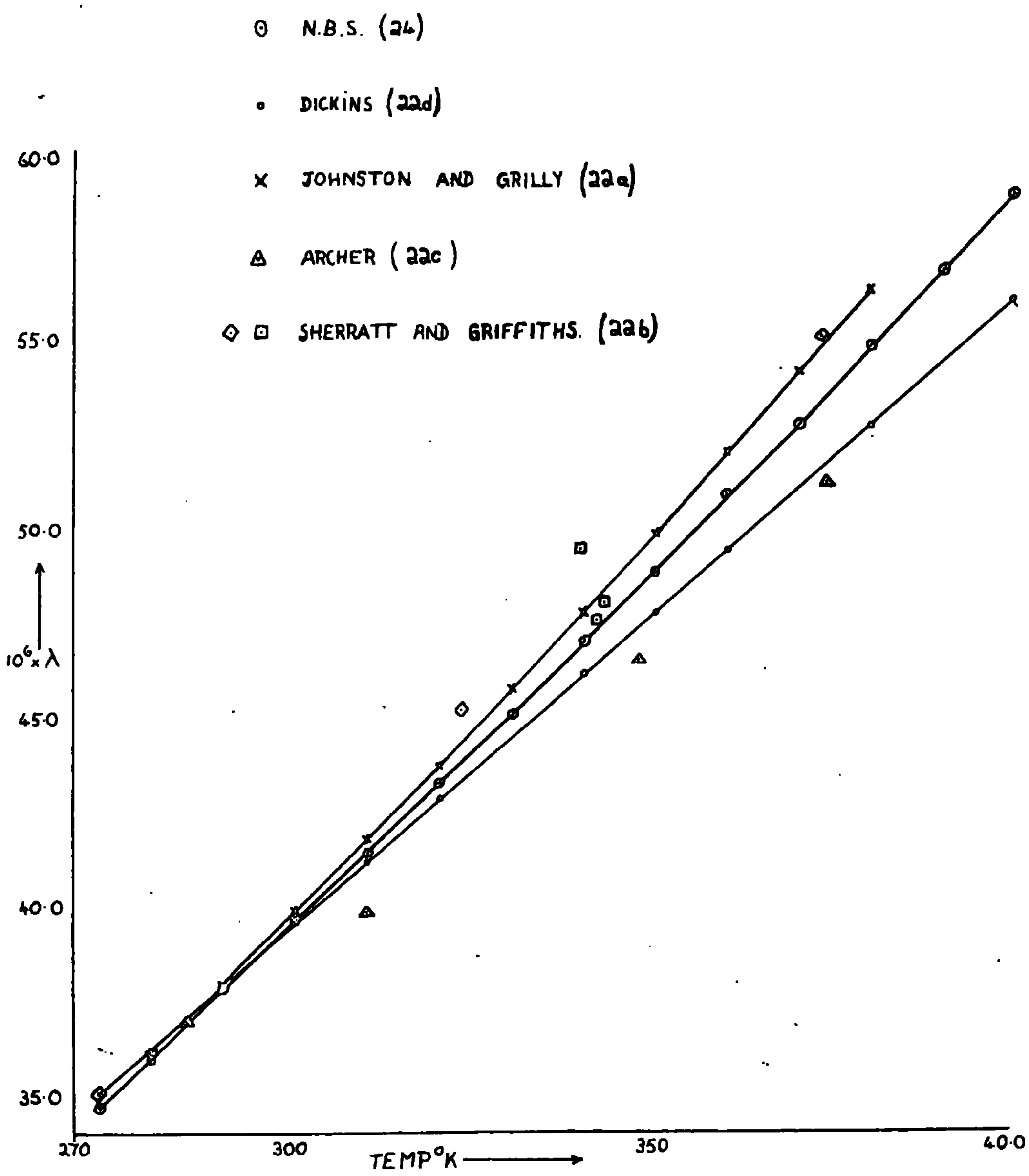
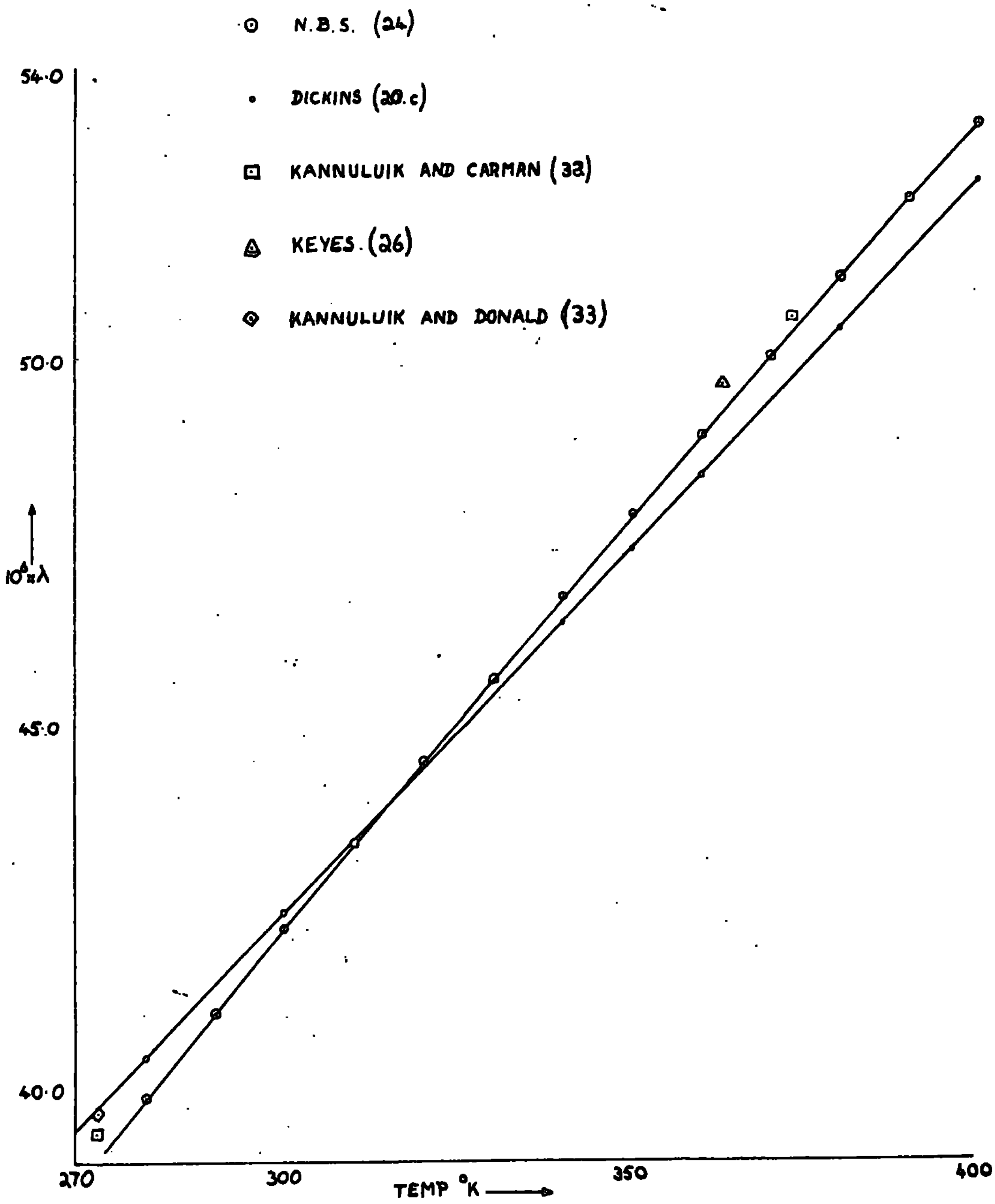


FIG. 6. GRAPHS OF THERMAL CONDUCTIVITY, λ, OF ARGON (CALS/CM/SEC/°C) AGAINST TEMPERATURE IN °K.



SECTION IV

DISCUSSION OF RESULTS

IV. 1. THERMAL CONDUCTIVITY RESULTS.

Thermal conductivity results from this investigation are obtained by comparison with values for reference gases of known thermal conductivity. The accuracy and reliability of these reference values must be examined before discussing any results.

The reference gases used in this investigation are ARGON, AIR and CO_2 and the thermal conductivity values assumed for these gases are taken from the National Bureau of Standards Circular Number 564. (24). These values are the results of an analysis by the National Bureau of Standards of experimental values obtained by many different workers (20, 21, 22). The experimental results are fitted to an empirical equation (see Appendix V) which gives the best possible expression of the variation of thermal conductivity with temperature. The reference values are set out graphically in Figures 4, 5 and 6 which also show several sets of experimental results obtained by previous workers.

It is at once obvious that these experimental values frequently show considerable divergences from the National Bureau of Standards values. For AIR and CO_2 the experimental values may vary by as much as 3½% from the National Bureau of

Standards values. Values for ARGON are more consistent, but the variation is still about 1% at the higher temperatures. Comparison of an unknown substance with only one of these gases is obviously insufficient to obtain results for which accuracy can be claimed. Unknown substances are therefore compared with all three gases, ARGON, AIR and CO_2, giving three values for each unknown gas. The true thermal conductivities can be expected to be inside the range of the values obtained in this way.

It is of interest however, first to look at an intercomparison of the three reference gases. The results of such an intercomparison from this investigation are shown in Table I, together with thermal conductivity values from the National Bureau of Standards Circular.

The results from cell II do not fit in well with the general pattern and should be regarded with some suspicion. Unfortunately, these results were not confirmed because cell II was accidentally broken while being inspected for faults. It was suspected that one of the pyrex-Platinum seals was faulty (see section V, description of cell II) but the cell was broken before this could be ascertained or the readings confirmed.

Generally however, when compared with values obtained by previous workers, the early results of this investigation in the first three columns of Table I are quite good.

Measurements were therefore made on several substances using cell III over a range of temperature from about 40°C to 100°C. The results for ARGON, AIR and CO_2 are shown in the last five columns of Table I.

The values of λCO_2 calculated by comparison with ARGON agree quite well with the National Bureau of Standards values for λCO_2, being slightly smaller. The difference between the two is about 0.2% at 40°C, increasing to just over 1% at about 100°C. The λCO_2 values from this investigation fall well within the range of values obtained by previous workers.

Values of λARGON calculated by comparison with CO_2 are conversely greater than the National Bureau of Standards values for ARGON by the same percentages as the CO_2 values were low. These values of λARGON also compare very well with the results obtained by previous workers (20).

However, values of λARGON and λCO_2 calculated by comparison with AIR are found to be 2-3% greater than the National Bureau of Standards values. Similarly, when ARGON and CO_2 are used as reference gases to determine λAIR, the results are 2-3% lower than the National Bureau of Standards values for λAIR. It is significant that the more recent investigations of AIR by Kannuluik and Carman (31) and Taylor and Johnston (18b) give values of λAIR which are respectively about 2% and 3% lower than the National Bureau of Standards values. This confirms the trend in the results of the present investigation. The National Bureau of Standards values are computed mainly from earlier results which are probably less accurate than the more modern ones. Therefore, thermal conductivities calculated by comparison with the National Bureau of Standards values for λAIR are probably too high.

Recent measurements of λARGON by Kannuluik and Carman (32), Kannuluik and Donald (33) and Keyes (26) give values which are about 0.5% greater than the National Bureau of Standards values. Thermal conductivity values calculated by comparison with these values then are likely to be slightly small.

Thermal conductivity values obtained by Johnston and Grilly (18c) for CO_2 are 1-3% higher than the National Bureau of Standards values over the temperature range from 40°C to 100°C. However, this trend is not supported by any other recent results. The National Bureau of Standards values are a good average of all the results, and thermal conductivities calculated by comparison with these are probably fairly accurate.

From these remarks, it seems that the most accurate thermal conductivity values are probably between those obtained by comparison with ARGON and those obtained by comparison with CO_2. However, an average of the three results obtained should not involve more than about 0.5% error at the lower temperatures, and about 1% at the most at the higher temperatures where the spread is greater.

Besides AIR, ARGON and CO_2, the other substances investigated were CH_3Br, $CClF_2.CClF_2$, CF_4, $CCl_3.CF_3$ and $CClF_2.CFCl_2$. The results obtained for these substances are shown in Table II. Measurements on CH_3Br and $CClF_2.CClF_2$ were made only at low temperatures, and, of the five substances, these are the only two for which thermal conductivity values are available in the literature.

In both cases, the thermal conductivity values from this investigation are much greater than the literature values. The values of λCH_3Br from this investigation are about 10% greater than the value obtained by extrapolation of the results of Vines and Bennett (25) to the same temperature. The results obtained in this investigation are perfectly reproducible, and there does not seem to be any reason for such large errors, especially since the results were obtained by comparison with two reference gases. Unfortunately, no other values for could be found in the literature, but further measurements would probably clarify the situation.

The thermal conductivity values for $CClF_2.CClF_2$ obtained in this investigation are about 7% higher than those found by F.G. Keyes (26) at the same temperatures. Since Keyes results are the only ones to be found in the literature for $CClF_2.CClF_2$, the same remarks apply here as were made about CH_3Br.

For the remaining substances, i.e. CF_4, $CF_3.CCl_3$ and $CClF_2.CFCl_2$, no results could be found in the literature for comparison with the results from this investigation. The values found for CF_4 are of the same order of magnitude as those for CO_2 and the ratio of their thermal conductivities remains fairly constant over the temperature range of the measurements made here. The thermal conductivity of CF_4 is consistently just over 3% lower than that of CO_2.

The thermal conductivity values obtained for CH_3Br and CF_4 can be compared with those for other halogenated methanes. Some approximate thermal conductivity values for some of these compounds are set out in Table IV to facilitate this comparison.

TABLE IV

APPROXIMATE THERMAL CONDUCTIVITY VALUES IN CALS/CM/SEC/°C FOR SOME HALOGENATED METHANES.

COMPOUND	CH_4	CF_4	CCl_2F_2	CH_3Cl	CH_3Br
$10^6 \times \lambda$	75(18c)	38	28(26)	26(1)	20

The figures in parentheses are the numbers of the references from which the values were obtained.

The thermal conductivity of methane is greater than that of AIR, and the substitution of halogen atoms for hydrogen atoms lowers the thermal conductivity. The amount of the lowering seems to depend on the size of the substituents, and the lowering effect is in the order $Br > Cl > F$. However, substitution of a Br or a Cl atom for a hydrogen atom seems to completely swamp the effect of the remaining hydrogens, and the thermal conductivities of CH_3Br and CH_3Cl are only about $\frac{1}{4}$ and $\frac{1}{3}$ respectively of that of pure methane. The effect of F atoms is much smaller, and the substitution of four F atoms for four hydrogen atoms only lowers the thermal conductivity of pure methane by about $\frac{1}{2}$.

A further illustration of the effect of substitution is given by Keyes results for CCl_2F_2 (26). It can be seen from these that substitution of two F atoms of CF_4 by two Cl atoms lowers the thermal conductivity considerably. However, this compound with two Cl and two F atoms has a thermal conductivity of the same order of magnitude as that of methyl chloride with only one Cl and three hydrogen atoms.

It seems then that the presence of F atoms in the molecule gives rise to anomalous thermal conductivity results when compared with other substituted methanes. It is difficult to correlate these substitution effects, but they appear to depend on the relative changes in the size and weight of the molecules and of the substituents.

The same trends are shown in the substituted ethanes as can be seen from Table V.

TABLE V

APPROXIMATE THERMAL CONDUCTIVITY VALUES IN CALS/CM/SEC/°C FOR SOME HALOGENATED ETHANES.

COMPOUND	C_2H_6	C_2H_5Cl	$CClF_2.CClF_2$	$CClF_2.CFCl_2$	$CCl_3.CF_3$
$10^6 x\ \lambda$	52(1)	28(1)	27	25	24

The figures in parentheses are the numbers of the references from which the values were obtained.

As can be seen from the table, the thermal conductivity of methane is lowered by about $\frac{1}{3}$ by the substitution of CH_3 for a hydrogen atom. The effect of substituting a hydrogen atom by a chlorine atom in ethane is much smaller than the corresponding effect in methane, the thermal conductivity of ethane being lowered by just less than $\frac{1}{2}$.

The two compounds of molecular formula $C_2Cl_3F_3$ have almost the same thermal conductivity. This is of the same order of magnitude as, but slightly smaller than that of C_2H_5Cl. Between these two comes $CClF_2.CClF_2$, having a slightly higher thermal conductivity than the two compounds of molecular formula $C_2Cl_3F_3$. This is in accordance with the fact that it contains one less Cl and one more F atom.

We have here once more the anomalous effect where compounds containing several F and Cl atoms have thermal conductivities of the same order of magnitude as that of C_2H_5Cl with only one Cl atom. The relative differences in thermal conductivity caused by substitution of hydrogen atoms by halogens are much smaller in the ethanes than in the lighter methanes.

In conclusion, it might be said that the intercomparison of AIR, ARGON and CO_2 gives quite reasonable thermal conductivity results, so that there does not seem to be any reason why the extension of the method to other compounds should not be successful. In support of this, the thermal conductivity values found for halogenated methanes and ethanes in this investigation fit in quite well with results obtained by other authors for similar compounds.

IV. 2. HEAT CAPACITY RESULTS.

Heat capacities can be determined very accurately and reproducibly so that there is no difficulty in finding a suitable reference gas. The reference gas used in this investigation was ARGON whose heat capacity is very well known both from experimental and theoretical determinations. A further advantage of using ARGON is that its temperature coefficient of heat capacity is negligible.

The heat capacity results from this investigation are shown in TABLE III, and it can easily be seen that these results are extremely unpredictable. One or two of the individual values are quite reasonable but others vary by as much as 20-30% from reliable values found in the literature. What is worse, the results are not reproducible from one cell to another

Heat capacity values are calculated using equation (14)

$$Cp = Cp_o . \frac{\lambda .}{\lambda_o} \frac{p_o}{p} \sqrt{Am.} \qquad (Am).$$

The values in Table III are calculated from Q values such that $p_o = p = 76$ cms. pressure. However, Q values were determined for the various gases over a pressure range from

50 to 80 cms. pressure. Cp values were calculated using several Q values in this range, always keeping p_o equal to p. (see Appendix II). The values calculated in this way showed too great a dependence on pressure, besides which, this variation with pressure was not always in the correct direction. For some gases, Cp seemed to increase with increasing pressure while for others, Cp seemed to decrease with increasing pressure Also, Cp values for one substance might increase with increasing pressure using Q values from one cell, but decrease with increasing pressure using Q values from another cell. Neither the individual results nor the average of the results over the whole pressure range were found to be any improvement on the values in Table III.

Other Cp values were calculated from Q values which corresponded to keeping the term p_o in equation (14) constant at 76 cms. pressure and varying only p, but the values obtained suffered from the same defects as those above.

Calculation of the term $\sqrt{Am}$ in equation (14) involves the use of absolute values of λ and λo. The ratio $\lambda / \lambda o$ is found experimentally with reasonable accuracy, but a value for λ_o must be assumed in order to calculate a value for λ. In this case, values of λ_o for ARGON were taken from the National Bureau of Standards Circular Number 564 (24) but these values are not necessarily correct. Small variations in the values of λ and λ_0 can cause variations in the values of Cp calculated from them. By varying λ however, while some Cp values are improved, others are made worse so that this cannot by itself be responsible for the errors in the Cp values.

The Cp values in Table III are all calculated using ARGON as the reference gas. However, values of Cp calculated by comparison with other gases such as AIR and CO_2 are subject to errors of the same order of magnitude as those in Table III.

In the experimental section (Section V.11) describing the apparatus, it is mentioned that the axial wires in the cells are not accurately centred. This might be expected to cause some systematic error in the results. However, the errors in the results are absolutely unpredictable, so it seems unlikely that they are caused by some constant fault in the apparatus such as this inaccurate centering of the axial wire.

The last possible source of experimental error seems to be the pressure and voltage measurements, but these are completely reproducible. Therefore, an examination of some of the assumptions made by Senftleben in deriving his expression for Cp may be profitable. One of the weakest points in Senftlebens derivation of an expression for Cp is the assumption that

$$Am = A.a \qquad (10).$$

where $Am = \frac{(Gr.Pr)}{(Gr_o.Pr_o)}$ (Experimental), $A = \frac{(Gr.Pr)}{(Gr_o.Pr_o)}$ (Theoretical)

and $a = \frac{Pr.}{Pr_o}$

Senftleben does not give any adequate experimental or theoretical justification for assuming that A is not equal to Am, or that the relationship between them is Am = A.a as he proposes. It is however, quite easy to investigate the accuracy of this relationship for two common gases such as ARGON and CO_2.

First, using equations (4b) and (4c), which are expressions for Gr and Pr, an expression for A can be worked out. This is the ratio of the theoretical Gr.Pr values for the two gases.

$$Gr = \frac{l^3\rho^2 g\delta\theta}{\eta^2} \qquad (4b).$$

$$Pr = \frac{cp.\eta}{\lambda} \qquad (4c)$$

From these expressions, we have

$$A = \frac{(Gr.Pr)}{(Gr_0.Pr_0)}\,(Theor.) = \frac{\rho^2.\eta o.cp.\lambda o}{\rho_0^2.\eta.\ cpo.\lambda}$$

The gas density, ρ, is given by the expression

$$\rho = \frac{\mu.p}{RT}$$

where μ is the molecular weight and p the gas pressure. Working with both gases at the same temperature and pressure, ρ is proportional to μ, and can be replaced by it in the expression for A. Also, since $\mu.cp = Cp$, we have finally

$$A = \frac{Cp.\mu.\eta o.\lambda o.}{Cp_0.\mu o.\eta.\lambda.}$$

For a comparison of CO_2 with ARGON (subscript o) at 30^oC, values of Cp, η and λ are taken from the National Bureau of Standards Circular Number 564 (24). From these values,

$$\frac{Cp}{Cp_o} = 1.87, \quad \frac{\mu}{\mu_o} = 1.15, \quad \frac{\eta_o}{\eta} = 1.74 \text{ and } \frac{\lambda_o}{\lambda} = 1.06$$

$$\text{therefore,} \quad A = 3.96$$

From experimental measurements on ARGON and CO_2, values of Am are found to vary from about 4.5 to 6.0. It is obvious then that Am and A are not identical.

To find a value for a, Pr values for ARGON and CO_2 are taken from the National Bureau of Standards Circular Number 564.

$$Pr(\text{ARGON}) = 0.677 \qquad Pr(CO_2) = 0.770$$

$$\text{Therefore,} \quad a = \frac{Pr.}{Pr_o} = 1.14$$

From the figures hitherto obtained,

$$a.A = 4.5$$

This corresponds very well with the experimental value of Am of about 4.5. Unfortunately, values of Am varied from cell to cell, and in some cases were as high as 6. It is obvious then that for ARGON and CO_2, Senftlebens assumption that Am = a.A is not consistently aaccurate.

A further source of inconsistency in the results of this investigation was variation in the experimental values of Am which should be reasonably constant for any two substances. When Am values for the same substance in the same cell were calculated for different pressures, the variation in these Am values was totally unpredictable and led to the apparent variation of Cp with pressure (see Appendix II). Besides this, Am values for the same two substances but from different cells were usually quite different.

Possible sources of this inconsistency are Senftlebens initial equations and the relationship connecting Nu and Gr.Pr. This relationship was apparently arrived at after an examination of many data, but reference to Senftlebens paper (23) shows that all the results for the various gases did not fit this relationship which was merely the best possible expression connecting all the results. It may be that it is impossible to find a single expression connecting Nu and Gr.Pr for all gases.

Another assumption made by Senftleben when working out his theory was that at higher pressures where heat is removed from the hot wire by convection, only streamline flow of the gas from the hot wire takes place. Again, this is possibly not quite accurate, and it is possible that some turbulent flow may occur.

In its present state, Senftlebens method is certainly not capable of giving accurate heat capacity results. It seems probable that the errors in the results arise because the various assumptions made by Senftleben in the derivation of his theory are not completely valid. If this is so, then the whole method needs a thorough theoretical and experimental re-investigation, a matter far beyond the scope of this thesis.

SECTION V

EXPERIMENTAL WORK

This section is most conveniently broken down into three sub-sections as follows:-

V.1. APPARATUS

V.2. PROCEDURE BEFORE MAKING MEASUREMENTS ON GASES.

V.3. MEASUREMENTS ON GASES.

V.1. APPARATUS.

V.11. CELLS ON WHICH MEASUREMENTS WERE MADE.

Three different cells were used in the course of this investigation. They are shown diagrammatically in Figures 7, 8 and 9.

CELL I.

This cell (see Figure 7) consisted of a glass tube of internal diameter 2 cms. with a gas inlet lead inserted in the middle of its length. Two narrow tubes were attached to the ends of this wide tube and electrical leads made from 0.5 mm. tungsten rod sealed through the ends of these. A fine platinum wire of diameter 0.005 cms. and length 11.195 cms. was attached at one end direct to the thick tungsten lead then connected to the other thick tungsten lead via a fine tungsten spiral spring to keep it taut. Several loose strands of platinum wire were passed through the spring and attached to the axial platinum

FIG.7. CELL I.

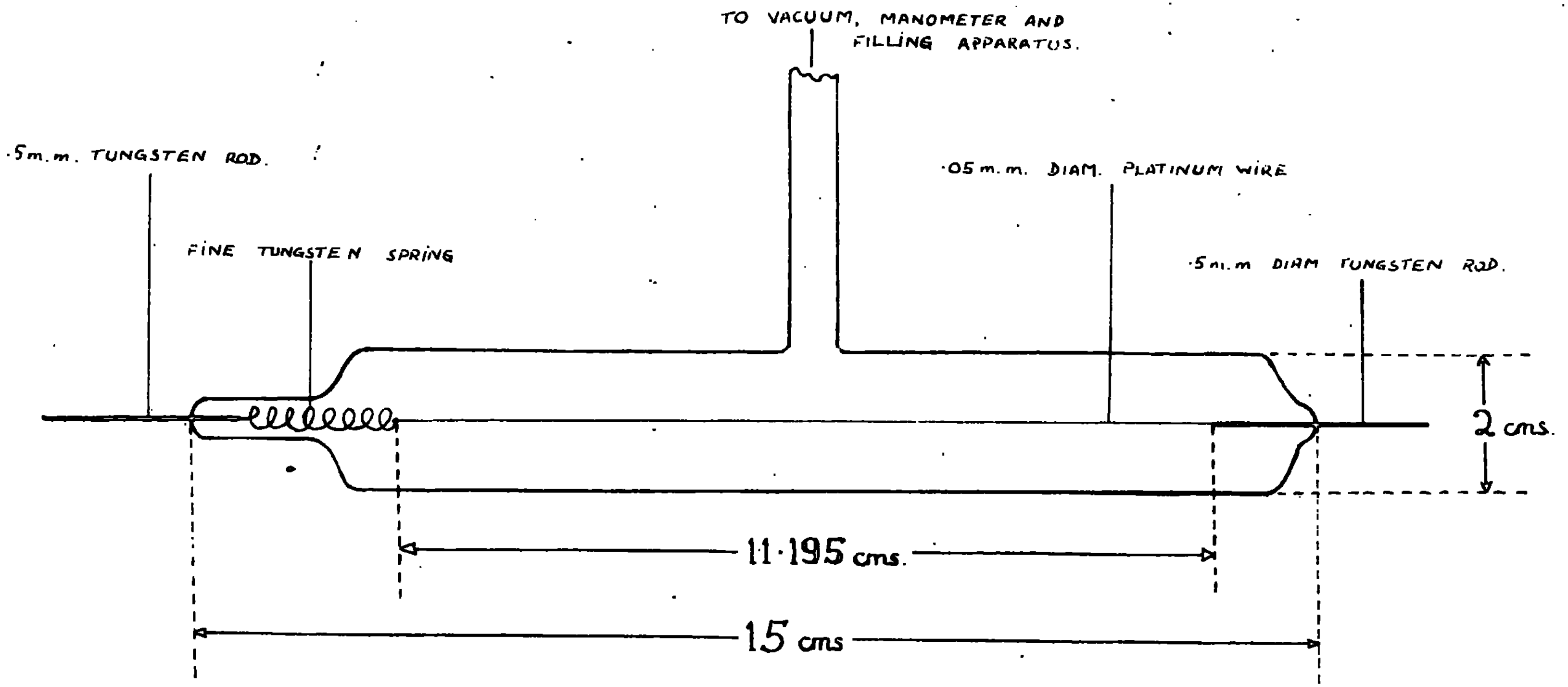
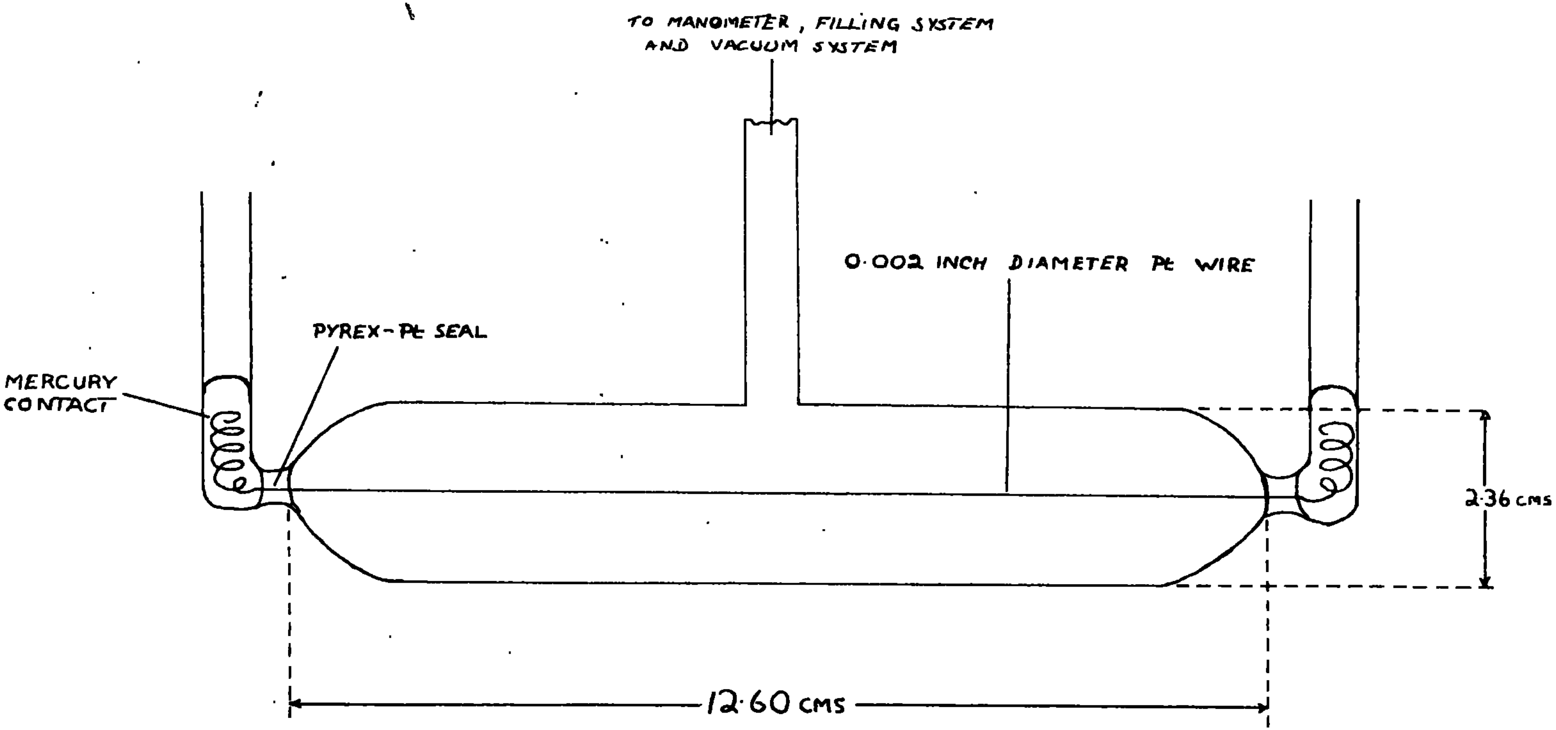

TO VACUUM, MANOMETER AND FILLING APPARATUS.
·5m.m. TUNGSTEN ROD.
FINE TUNGSTEN SPRING
·05 m.m. DIAM. PLATINUM WIRE
·5 m.m DIAM TUNGSTEN ROD.
2 cms.
11·195 cms.
15 cms

FIG. 8. CELL II.


TO MANOMETER, FILLING SYSTEM
AND VACUUM SYSTEM
0·002 INCH DIAMETER Pt WIRE
PYREX-Pt SEAL
MERCURY
CONTACT
2·36 CMS
12·60 CMS

wire and the thick tungsten lead. These ensured that the current through the spring was never large enough to heat it.

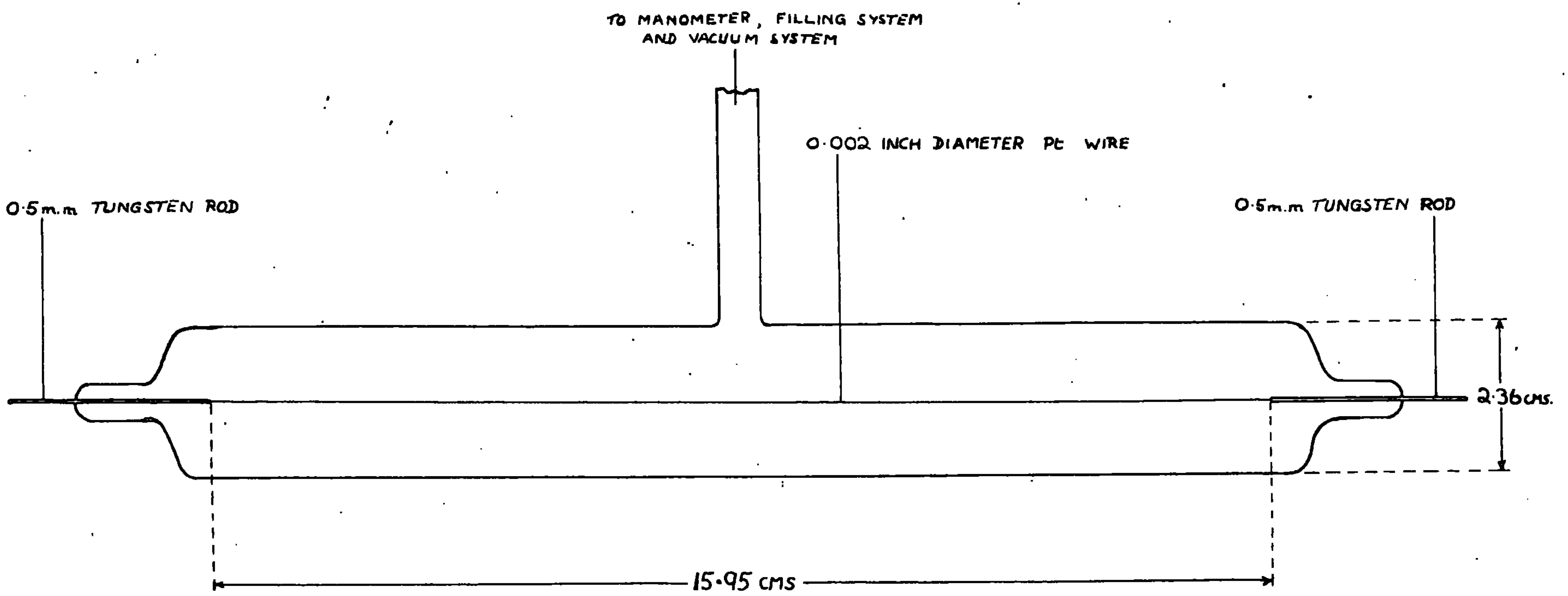
All the platinum-tungsten and tungsten-tungsten connections were silver soldered and the tungsten leads were passed through the walls of the cell by means of tungsten-pyrex seals. Electrical leads of thick copper wire were silver soldered to the outer ends of the thick tungsten leads.

CELL II.

This cell (see Figure 8) was of length 12.60 cms. and internal diameter 2.36 cms. The platinum wire (diamter 0.002 ins.) was stretched along the full length of this cell and brought out, by means of platinum-pyrex seals, into two narrow side arms which were attached to the ends of the cell. The platinum wire was connected to the electrical supply and measuring circuits by copper wires via mercury contacts in the two side arms of the cell.

It must be mentioned here that the platinum-pyrex seals are not perfectly vacuum tight. In this case, the mercury in the side arms completed the seals quite effectively, and there was no noticeable leak when the apparatus was evacuated. While in use however, one of the platinum-pyrex seals seemed to come loose, resulting in a slight movement of the platinum wire in the seal (see Section IV). The measurements made using this cell are therefore not very reliable.

FIG. 9. CELL III



CELL III.

The wide glass tube from which this cell (see Figure 9) was made was of length about 16 cms. and internal diameter 2.36 cms. The platinum wire (length 15.95 cms. and diameter 0.002 cms.) was held between two leads made from 0.5 mm. tungsten rod to which the platinum wire was silver soldered. The tungsten leads were brought out of the ends of the cell via tungsten-pyrex seals and the connections to the electrical supply and measuring circuits were silver soldered to the outer ends of these leads.

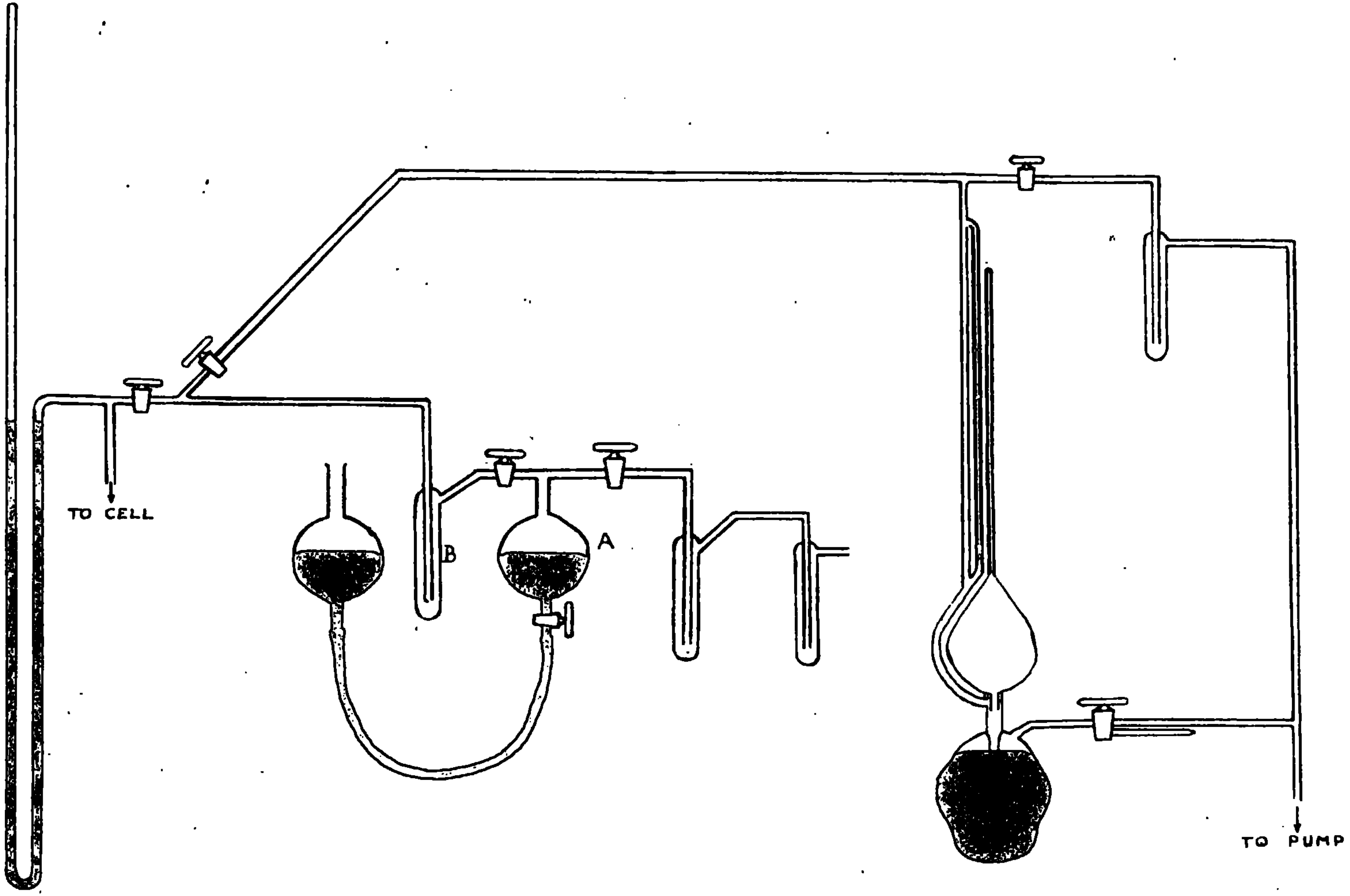
In none of the cells was the wire accurately centred along the axis. Centring was merely done visually when the wire was sealed through the ends of the cell.

V. 1.2. FILLING AND VACUUM SYSTEMS.

The filling and vacuum systems are shown diagrammatically in Figure 10. The filling system consisted of a mercury manometer for measuring the gas pressure in the cell, a trap B for the introduction and removal of condensable vapours and a storage reservoir A, to which was connected a moveable bulb containing mercury. The pressure in the system could be varied by raising and lowering this bulb.

Trap B was later replaced by a large glass bulb which was attached to the apparatus by means of a ground glass joint. This bulb could be closed to the rest of the apparatus by the

FIG. 10. CELL, MANOMETER, FILLING AND VACUUM SYSTEMS.



use of a tap between the bulb and the ground glass joint. This was more useful than the trap in that it could be filled with pure gas from say a gas chromatography apparatus before being attached to the apparatus used in this investigation.

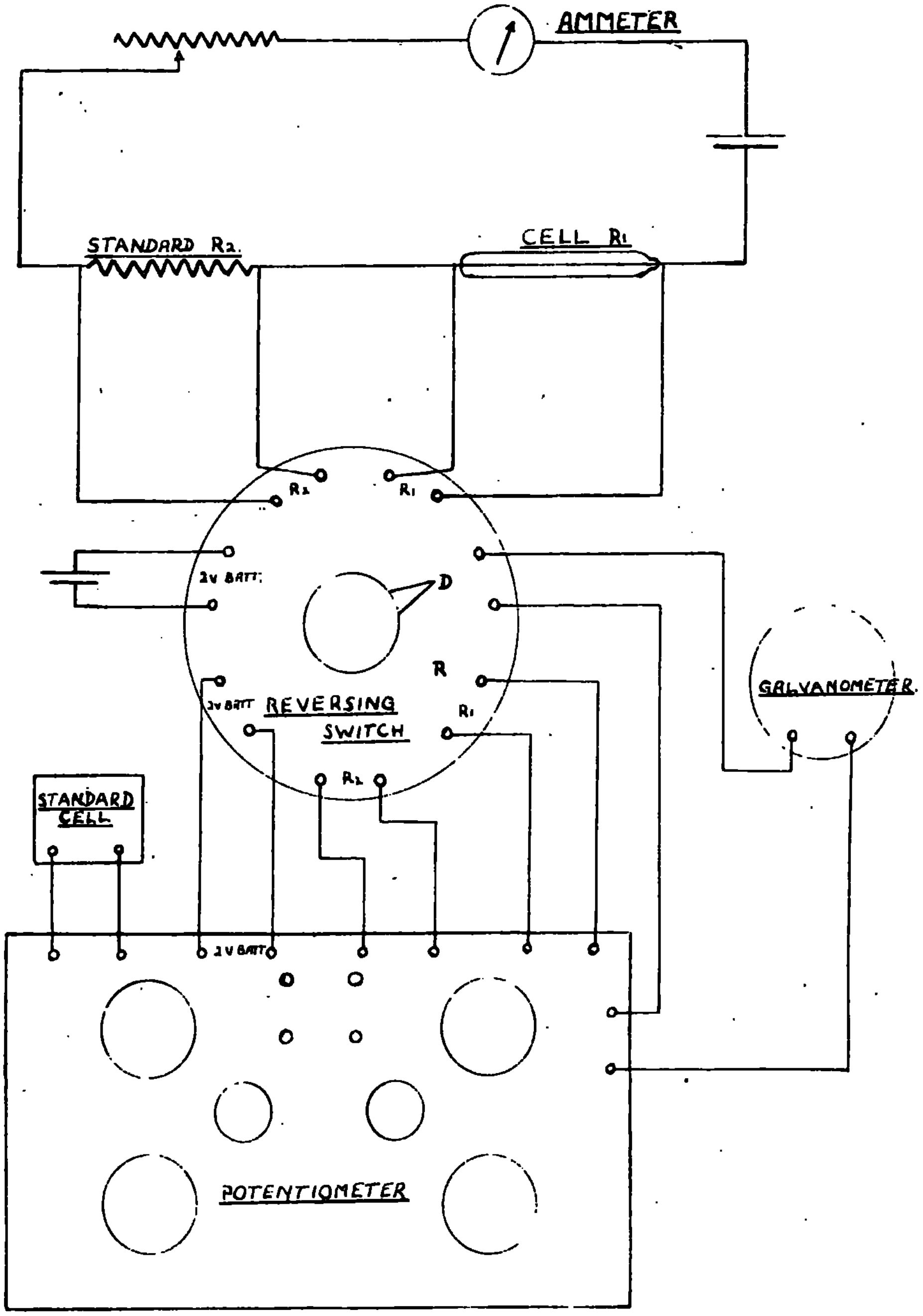
The whole of the glass apparatus was attached to a vacuum system which was used for the complete removal of gases from the apparatus when measurements on them were completed. This system consisted of a two stage mercury diffusion pump with a rotary oil filled backing pump (Metrovac). Using this system, the pressure in the apparatus could be reduced to about 10^{-4}mm. of mercury.

Such low pressures were at first measured using a McCleod Gauge which could be used for pressure measurements down to 10^{-4}mm. of mercury. Later it was realised that such accurate measurement of pressure was unnecessary, and the McCleod Gauge was replaced by an Edwards Vacustat which gave sufficient indication of the pressure in the system for the purposes of this investigation.

V. 1.3. ELECTRICAL SUPPLY AND MEASURING SYSTEMS.

The electrical supply and measuring systems are shown diagrammatically in Figure 11. The electrical supply to the cell was obtained from two 2 volt cells connected in parallel. Connected in series with this two volt source were a standard resistance R_2, a series of variable resistances to vary the current through the cell, and an ammeter to give an indication

FIG II: CELL CIRCUIT AND MEASURING INSTRUMENTS



of this current. The standard resistance R_2 was kept in an oil filled Dewar Flask to keep its temperature fairly constant. However, in a rough investigation it was found that variations in temperature of the same order of magnitude as variations in room temperature had negligible effect on this resistance.

A Tinsley potentiometer (type 4025) was used to measure the voltage drops across the cell and standard resistance R_2. A Tinsley Oil filled reversing switch (type 4092) was used in conjunction with the potentiometer to eliminate the effect of stray voltages. At its maximum sensitivity the potentiometer can detect and measure a difference of one microvolt. On its least sensitive range, it can be used to measure voltages of up to one volt accurately to four decimal places, with a possible estimation of the fifth. A Tinsley Weston Cadmium cell was used to standardise the measured voltages.

On the most sensitive potentiometer range, a Tinsley galvanometer with a sensitivity of one large scale division (1 cm.) per microvolt was used, while on the less sensitive potentiometer ranges, a Cambridge Scalamp galvanometer was used. The sensitivity of this galvanometer could be varied, but its maximum sensitivity was four large scale divisions (4 cms.) per 10^{-4} volts.

Sheathed cable was used for all the electrical connections, and the sheaths were earthed to prevent the picking up of stray voltages.

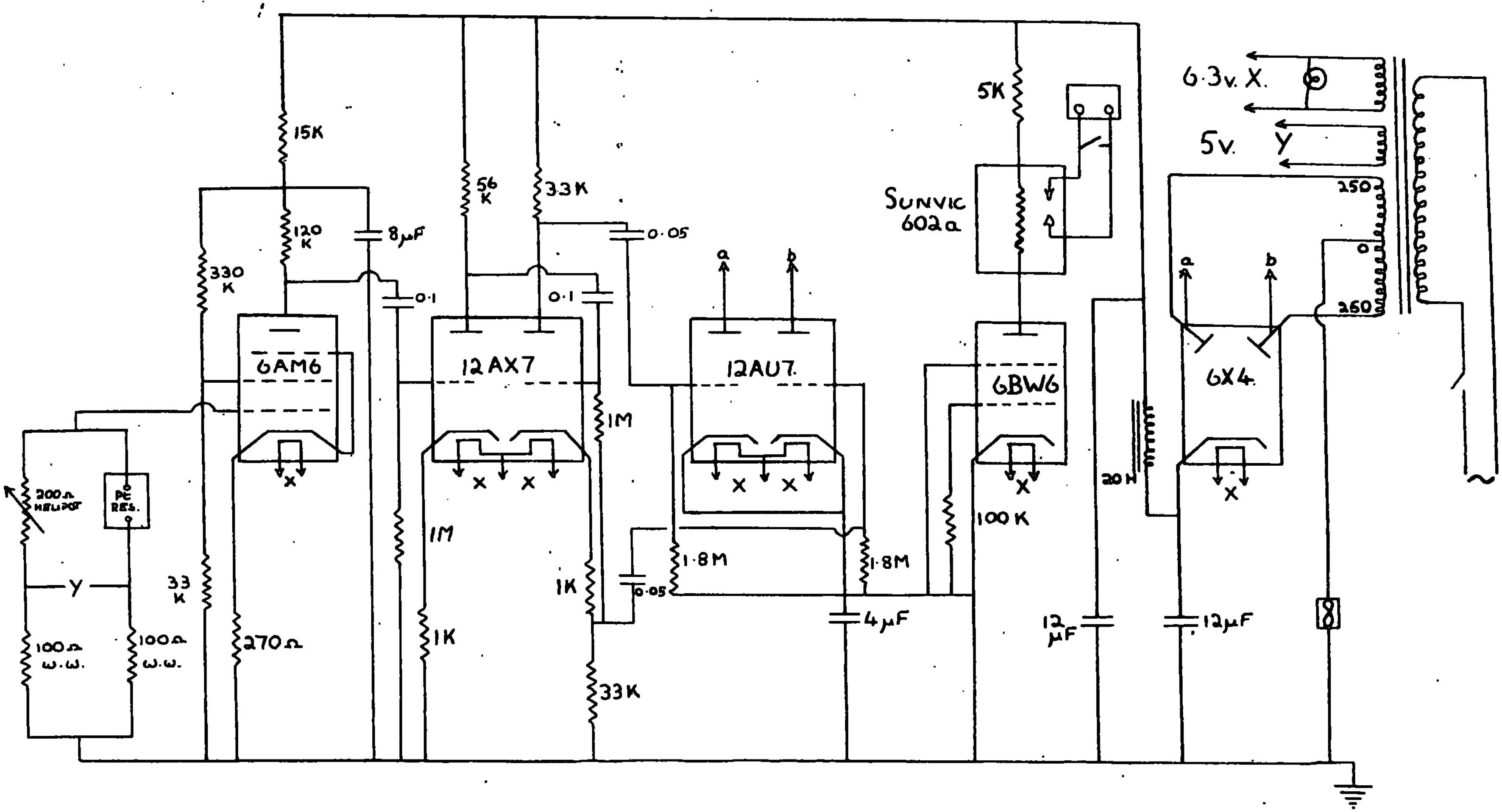
V. 1.4. THE THERMOSTAT AND THERMOREGULATOR.

The liquid used in the thermostat bath was heavy white oil. This proved to be quite satisfactory up to about 100°C but above this temperature the fumes became rather unpleasant and there was a small amount of charring.

The thermoregulator used to control the bath temperature was one designed by Coates and Ricketts (34) and was an improved version of an earlier design by Coates (35). The thermoregulator circuit is shown in Figure 12. The thermoregulator consists of a platinum resistance thermometer which is placed in one arm of an A.C. bridge circuit, the other arms consisting of a 200 ohm helical potentiometer and two 100 ohm wire wound resistances. A 5 volt A.C. supply is connected across the bridge.

When the A.C. bridge is out of balance, a small voltage is set up across it. This voltage is applied to the grid of a valve (6 Am 6) (see Figure 12). The working of the thermoregulator depends on the change of phase of this voltage in going from one side to the other of the balance point of bridge. The thermoregulator is so designed that when the thermostat temperature is low, this small applied voltage is used to enhance the current through the Sunvic relay switch. Thus the heaters are switched on and the temperature rises. When the thermostat temperature is too high, due to the phase change at the balance point of the bridge, the current through the

FIG. 12. THERMOREGULATOR CIRCUIT.



relay is reduced and the heaters switch off. Further detail can be obtained by reference to the original paper (35).

The temperature at which the bath is kept can be varied by adjusting the helical potentiometer. The platinum resistance thermometer has a resistance of about 75 ohms at room temperature. Thus, the 200 ohms of the helipot are quite sufficient to cover the increase in this resistance over the temperature range from 25 to 100°C. The thermoregulator behaved in a satisfactory fashion over this range, regulating the temperature to within the necessary limits i.e. ± 0.005°C. Apart from some isolated disturbances, the variation was generally much smaller than this.

V.2. PROCEDURE BEFORE MAKING MEASUREMENTS ON THE GASES.

This procedure can be dealt with in three sections.

V. 2.1. ANNEALING OF THE WIRE IN THE CELL.

V. 2.2. STANDARDISATION OF THE 'STANDARD' RESISTANCE, R_2.

V. 2.3. DETERMINATION OF THE TEMPERATURE COEFFICIENT OF RESISTANCE OF THE WIRE IN THE CELL.

V. 2.1. ANNEALING OF THE WIRE IN THE CELL.

This annealing is carried out to remove from the cell wire any stresses or strains which might affect its resistance. At first, the annealing was carried out simply by evacuating the cell and passing a fairly large current through the wire, thus heating it to a fairly high temperature. However, with cells annealed in this way, some trouble was encountered due to a slow drift in the cell-wire resistance with time, implying that annealing was incomplete.

This was overcome by enclosing the cell in a furnace at about 450°C and, at the same time, passing a current through the wire to heat it to an even higher temperature. After being treated in this way for about two days, further variation in the resistance of the cell-wire was within the limits of experimental accuracy.

V. 2.2. STANDARDISATION OF THE 'STANDARD' RESISTANCE, R_2.

Two 'standard' resistances were used in the course of this work, the experimental results of which a re shown in Appendix III. The first was standardised by comparison with a primary standard resistance of 1 ohm (manganin coil, 1 ohm at 17°C.) The second was standardised by comparison with a standard 10 ohm resistance (Cambridge and Paul Instrument Co. Ltd., Manganin coil, No. L-9426. 10 ohms at 20°C). The two resistances i.e. R_2 and the true standard, were connected in series and the same current passed through each. The potential drops across the two were measured using the Tinsley potentiometer, the ratio of these two voltages being equal to the ratio of the two resistances. Knowing this ratio, the value of R_2 is easily found. The measurements were repeated for several different values of the current and the results averaged, although the variation was small. The actual results can be seen in Appendix III.

V. 2.3. DETERMINATION OF THE TEMPERATURE COEFFICIENT OF RESISTANCE OF THE CELL WIRE.

After being annealed, the cell was placed in the thermostat bath and connected to the supply and measuring circuits by soldered connections. The cell was left open to the atmosphere so that it was filled with air and the wire could easily assume the temperature of the thermostat bath.

Current was then passed through the cell-wire and standard resistance R_2, which were connected in series, and the voltage drops across the two were measured. This procedure was repeated for several different small current values. If the cell-wire resistance is R_1 and the standard resistance R_2, and the respective voltage drops across them are V_1 and V_2, then

$$\frac{V_1}{V_2} = \frac{R_1}{R_2}$$

Thus, from the measurements of V_1 and V_2, the ratio R_1/R_2 can be found. Since R_2 is known, the value of R_1 at the temperature of the thermostat bath can then be found. This procedure was repeated at several different thermostat temperatures to cover the desired range of temperature. The relevant measurements and graphs are shown in Appendix IV.

The temperature of the thermostat bath was measured using a standard thermometer graduated in tenths of degrees, which could be read to $\pm$ 0.01°C with the aid of a burette reader.

Since the value of R_2 is constant and R_1 is constant at constant temperature, the value of the ratio R_1/R_2 is characteristic of the temperature of the cell-wire. When experiments are being carried out on gases, it is the ratio R_1/R_2 which is in fact measured, so that it is more convenient to draw the calibration curve as a graph of temperature against ratio R_1/R_2. Values of R_1 can be found quite easily from this graph if required, since the value of R_2 is known.

The currents used in this calibration naturally had to be extremely small to avoid heating the wire and thus increasing its resistance. It was found, however, that no appreciable heating effect was obtained until the current through the cell-wire was several times greater than the maximum current used in the above calibration. There should therefore be no error in the results arising from this source.

V. 3. MEASUREMENTS ON GASES.

The apparatus is now in a state where it can be used to determine the thermal properties of gases and vapours. Determination of these properties requires a knowledge of the energy Q which it is necessary to dissipate in the cell-wire at various pressures to maintain this wire at a constant temperature θ^{o}C above that of the inner wall of the cell. For our purposes, this is assumed to be at thermostat temperature. The following procedure was used for the determination of Q values.

The whole apparatus was evacuated then the storage bulb, A, filled with the pure gas under investigation. (For a note on the purity of the gases, see Appendix VI). This was then used to fill the cell to the required pressure, and a heating current passed through the cell-wire. The voltage drops across the cell-wire and the standard resistance were measured and the ratio R_1/R_2 found, from which the temperature of the cell-wire was determined. The heating current was varied using rheostats until the temperature of the cell-wire remained steady at some pre-determined value i.e. until the ratio R_1/R_2 remained steady at the value corresponding to this temperature.

This procedure was repeated at various pressures until the necessary pressure ranges were covered. The ratio R_1/R_2 was adjusted to the same value at each pressure by use of the rheostats to adjust the heating current.

To eliminate the effect of stray voltages, the polarities of the measured voltages were reversed using the Tinsley reversing switch, and then remeasured. However, in no case was there an appreciable difference between the original voltage and the reversed voltage.

These voltage measurements were also quite reproducible when repeat readings were made on the same compound under the same conditions. When Q values were calculated from the repeat readings and these Q values plotted on the original pressure, P, against Q graphs, then the error involved was usually no greater than the experimental error involved in the original readings.

Values of Q can easily be calculated from the voltage measurements using the expressions

$$Q = \frac{(V_1)^2}{R_1} \text{ watts} \quad \text{or } Q = \frac{(V_1)^2}{R_1 . J} \text{ cals/sec.}$$

where R_1 is the resistance of the cell-wire and V_2 the voltage across it.

Alternatively, the expressions

$$Q = \frac{V_1V_2.}{R_2.} \text{ watts} \quad \text{or } Q = \frac{V_1V_2.}{R_2J} \text{ cals/sec}$$

can be used, where R_2 is the standard resistance and V_2 the voltage across it.

The gas pressure in the cell was originally measured using a cathetometer to measure the difference in the mercury levels in the two arms of the manometer. However, the variation of Q with pressure is not very great, and the results are plotted on graphs where the second decimal place in the value of the pressure can only be estimated roughly. Therefore, it was later found sufficient to measure pressures with a metre rule which could be read to about the nearest 0.05 cms.

From the information now available, it is possible to draw the appropriate graphs for the determination of λ and Cp values. These graphs were actually drawn in two portions, one covering a low pressure range for the determination of λ and the other covering a high pressure range for evaluation of Cp.

As can be seen from the section on the theory of the determination of thermal conductivity (Section II.1b), the low pressure regions of the graphs for the substance under investigation and the reference substance are used to find the ratio of two Q' values. However, examination of the above expressions for Q shows that Q is directly proportional to V_1^2, so that we have the expression

$$\frac{Q'}{Q'_o} = \frac{(V_1^2)'}{(V_1^2)'_o}$$

Since $\frac{Q'}{Q'_o} = \frac{\lambda}{\lambda_o}$, then $\frac{(V_1^2)'}{(V_1^2)'_o} = \frac{\lambda}{\lambda_o}$

Thus, for the low pressure regions it is sufficient to draw graphs of pressure against V_1^2. From these graphs, the ratio $(V_1^2)'/(V_1^2)'_o$ can be found, and knowing λ_o, λ can then be found.

The pressure at which the point of inflexion occurs varies from gas to gas and also depends on the dimensions of the cell and on the temperature gradient between the axial wire and the walls of the cell. The temperature gradient used in this investigation was usually about 10°C. The pressure ranges covered varied between about 0 to 10 cms. for vapours such as $CCl_3.CF_3$ and $CFCl_2.CClF_2$, and 0 to 35 cms. for permanent gases such as ARGON and AIR.

In the high pressure range, measurements were made from about 50 to 80 cms. pressure, and Q against pressure graphs drawn from the results. Several temperature gradients between 10°C and 30°C were used for these measurements.

Cp and λ values were calculated using these graphs in the manner described earlier in Section II.

APPENDIX I

DETAILED EXPERIMENTAL RESULTS

(a) THERMAL CONDUCTIVITY RESULTS.

The procedure for making measurements for the determination of thermal conductivities has been described earlier in Section V.3. The necessary pressure and voltage measurements can be made very accurately, and errors in these measurements are negligible compared with the possible errors in the thermal conductivity values assumed for the reference gases. The pressure and voltage measurements made on the three cells are set out in Tables VI to X. Also in these tables are values of V_1^2 at each pressure. V_1^2 is proportional to Q, the energy dissipated per second in the cell wire for constant R_1.

The thermal conductivity values calculated from the initial results from the three cells (Tables VI, VII and VIII) are quite good, and the temperature range of the measurements is then extended using cell III. However, when attempting to make measurements at higher temperatures, some of the results could not be reproduced. The cell-wire was then thoroughly annealed and its temperature coefficient of resistance re-determined. The resistance of the wire was found to have changed. Further readings were found to be reproducible, so measurements were then made on ARGON, AIR, CO_2 and CF_4 at five temperatures from 35 to 95°C. These measurements are shown in Table IX.

When beginning to make further measurements, a fault developed in one of the cell connections. The repair of this connection involved a small but significant change in the resistance of the cell wire. Since an exact knowledge of the temperature of the cell wire is not necessary for the determination of thermal conductivities, the temperature coefficient of resistance of the cell wire was not re-determined. Measurements were then made on $CCl_3.CF_3$, $CFCl_2.CClF_2$ and CO_2, which was used as the reference gas. Using these results, plus the previous results for ARGON, AIR and CO_2, $CCl_3.CF_3$ and $CFCl_2.CClF_2$ could effectively be compared with AIR and ARGON as well as CO_2.

Reference to the pressure against V_1^2 graphs for CO_2 (Figure 16) shows that at each temperature, the point of inflexion occurs at the same pressure to within fairly narrow limits. Also, the slope of these graphs is very small at the point of inflexion. Therefore, a single measurement made at the pressure where the point of inflexion usually occurs ought to be sufficient to give a value for $(V_1^2)'$ directly. Any error involved should be quite small since a 2 cm. error in the position of the point of inflexion only involves about 0.3% error in the value of $(V_1^2)'$.

To confirm the validity of this idea, single measurements were made on ARGON, AIR and CO_2, and the results were found to be good. In this series of results therefore, only single measurements were made on CO_2 at the various temperatures. However, a full series of pressure-voltage measurements were made on $CCl_3.CF_3$ and $CFCl_2.CClF_2$ and these are shown in Table X.

Graphs of pressure against V_1^2 are drawn from the pressure-voltage data which have now been obtained. From these graphs are obtained values of $(V_1^2)'$, i.e. values of V_1^2 at the points of inflexion. These are used to calculate thermal conductivities as outlined in Section V.3. Some of the pressure against V_1^2 graphs are shown in Figures 13, 14, 15, 16 and 17, and the $(V_1^2)'$ values from these graphs are shown in Table XI.

The following abbreviations and symbols are used in the tables:-

P. - gas pressure in cms. of mercury.

V_1.- voltage drop across the cell wire.

V_2.- voltage drop across the standard resistance R_2.

$(V_1^2)'$ value of V_1^2 at the point of inflexion of the pressure against V_1^2 graphs.

TABLE VI.

EXPERIMENTAL RESULTS FROM CELL I.

Thermostat Temperature = 25.05°C. Under experimental conditions $R_1/R_2 = 1.2500$

Wire Temperature = 35.72°C $\Theta = 10.67°C$. $R_2 = 6.1068$ ohms.

CO_2.

P	V_1	V_2	V_1^2
1.65	0.44006	0.35205	0.1937
3.02	0.44181	0.35345	0.1952
4.28	0.44512	0.35609	0.1981
5.69	0.44580	0.35669	0.1987
7.15	0.44606	0.35685	0.1990
9.12	0.44609	0.35687	0.1990
10.22	0.44716	0.35772	0.1999
15.21	0.44882	0.35906	0.2014

AIR

P	V_1	V_2	V_1^2
1.33	0.54042	0.43232	0.2921
2.95	0.55140	0.44111	0.3040
4.21	0.55550	0.44440	0.3086
5.75	0.55580	0.44464	0.3089
7.99	0.55600	0.44480	0.3091
10.25	0.55650	0.44520	0.3097
12.46	0.55736	0.44589	0.3107
16.82	0.55779	0.44623	0.3111

TABLE VI (Continued)

$CClF_2.CClF_2$

P	V_1	V_2	V_1^2
1.69	0.36185	0.28948	0.1309
2.36	0.36355	0.29084	0.1322
3.57	0.36615	0.29294	0.1341
4.74	0.36889	0.29511	0.1361
5.88	0.37205	0.29764	0.1384
7.11	0.37506	0.30004	0.1407
8.69	0.38024	0.30420	0.1446
10.12	0.38527	0.30822	0.1484
11.98	0.39205	0.31364	0.1537
14.93	0.40158	0.32124	0.1613

CH_3Br

P	V_1	V_2	V_1^2
0.97	0.30832	0.24666	0.0951
1.90	0.31150	0.24920	0.0970
3.68	0.31257	0.25010	0.0977
7.03	0.31871	0.25497	0.1016
8.74	0.31873	0.25503	0.1016
10.44	0.31906	0.25524	0.1018
12.33	0.32067	0.25654	0.1028
15.70	0.32420	0.25936	0.1051
18.85	0.32770	0.26216	0.1074

TABLE VII

EXPERIMENTAL RESULTS FROM CELL II

Thermostat temperature = 35.00°C. R_2 = 10.119 ohms.

Under experimental conditions, $R_1/R_2 = 0.8500$.

Wire temperature = 48.00°C and $\theta = 13.00$°C.

(a) AIR

P	V_1	V_2	V_1^2
0.90	0.68828	0.80976	0.4737
2.05	0.71340	0.83929	0.5089
3.15	0.71867	0.84550	0.5165
4.35	0.72211	0.84952	0.5214
5.85	0.72360	0.85131	0.5236
7.15	0.72526	0.85329	0.5260
10.55	0.72667	0.85491	0.5280
12.05	0.72749	0.85585	0.5292
15.05	0.72760	0.85605	0.5294
19.55	0.72858	0.85712	0.5308

TABLE VII (continued).

(b) ARGON

P.	V_1	V_2	V_1^2
1.05	0.58600	0.67764	0.3318
2.35	0.59238	0.69689	0.3509
3.45	0.59655	0.70182	0.3559
4.30	0.59821	0.70378	0.3579
5.10	0.59920	0.70493	0.3590
6.25	0.60049	0.70646	0.3606
7.55	0.60170	0.70788	0.3620
9.05	0.60230	0.70856	0.3628
10.55	0.60297	0.70937	0.3636
11.85	0.60330	0.70977	0.3640
14.75	0.60346	0.70995	0.3642
19.05	0.60426	0.71087	0.3651

TABLE VII. (continued).

(c). CO_2.

P	V_1	V_2	V_1^2
1.00	0.55842	0.65697	0.3118
1.90	0.56638	0.66633	0.3208
2.90	0.56853	0.668866	0.3232
4.00	0.57052	0.67120	0.3255
5.20	0.57170	0.67257	0.3268
7.40	0.57262	0.67368	0.3279
8.70	0.57300	0.67412	0.3284
10.00	0.57386	0.67512	0.3291
11.50	0.57415	0.67547	0.3296
13.00	0.57445	0.67583	0.3300
14.50	0.57517	0.67668	0.3308
15.90	0.57510	0.67658	0.3307
17.30	0.57585	0.67747	0.3316
19.50	0.57677	0.67854	0.3327

TABLE VIII

EXPERIMENTAL RESULTS FROM CELL III

Thermostat temperature = 35.00°C. R_2 = 10.119 ohms.

Under experimental conditions, $R_1/R_2 = 1.0000$

Wire temperature = 44.33°C and θ = 9.33°C.

(a) CO_2.

P	V_1	V_2	V_1^2
2.00	0.55006	0.55006	0.3026
4.10	0.55443	0.55443	0.3074
6.10	0.55565	0.55565	0.3087
8.10	0.55700	0.55700	0.3102
10.10	0.55739	0.55739	0.3107
12.10	0.55788	0.55788	0.3112
14.00	0.55848	0.55848	0.3119
16.20	0.55906	0.55906	0.3125
18.00	0.55970	0.55970	0.3133
20.05	0.56000	0.56000	0.3136
22.00	0.56057	0.56057	0.3142
24.10	0.56177	0.56177	0.3156
26.00	0.56304	0.56304	0.3170

TABLE VIII. (continued).

(b) ARGON.

P	V_1	V_2	V_1^2
0.55	0.52160	0.52160	0.2721
1.00	0.54663	0.54663	0.2988
2.05	0.56157	0.56157	0.3154
4.10	0.56799	0.56799	0.3226
6.10	0.57036	0.57036	0.3253
8.10	0.57106	0.57106	0.3261
10.00	0.57163	0.57163	0.3268
12.15	0.57211	0.57211	0.3273
14.10	0.57252	0.57252	0.3278
16.15	0.57299	0.57299	0.3283
18.10	0.57312	0.57312	0.3285
20.20	0.57328	0.57328	0.3286
22.20	0.57348	0.57348	0.3289
24.00	0.57368	0.57368	0.3291
26.40	0.57392	0.57392	0.3294
29.00	0.57420	0.57420	0.3297
31.10	0.57430	0.57430	0.3298
33.10	0.57467	0.57467	0.3302

TABLE VIII. (continued).

(c) CF_4.

P	V_1	V_2	V_1^2
0.60	0.51720	0.51720	0.2675
1.10	0.53288	0.53288	0.2840
2.10	0.54207	0.54207	0.2938
4.10	0.54763	0.54763	0.2999
6.10	0.54988	0.54988	0.3024
8.00	0.55120	0.55120	0.3038
10.15	0.55254	0.55254	0.3053
12.10	0.55399	0.55399	0.3069
14.15	0.55583	0.55583	0.3089
16.10	0.55764	0.55764	0.3110
18.05	0.55986	0.55986	0.3134
20.15	0.56252	0.56252	0.3164

TABLE VIII. (continued)

(d) $CClF_2.CClF_2$.

P	V_1	V_2	V_1^2
0.65	0.43935	0.43935	0.1930
1.10	0.44423	0.44423	0.1973
2.10	0.44972	0.44972	0.2022
4.10	0.45648	0.45648	0.2084
6.10	0.46162	0.46162	0.2131
8.10	0.46743	0.46743	0.2185
10.00	0.47400	0.47400	0.2247
12.00	0.48204	0.48204	0.2324
14.10	0.48958	0.48958	0.2397

TABLE IX

EXPERIMENTAL RESULTS FROM CELL III AT VARIOUS TEMPERATURES, ARGON, AIR, CO_2 AND CF_4.

(a) Thermostat Temperature = 35.00°C. Θ = 12.10°C. Ratio R_1/R_2 = 1.0000

CO_2

P	V_1	V_2	V_1^2
2.00	0.59401	0.59401	0.3528
4.10	0.59879	0.59879	0.3585
6.00	0.60061	0.60061	0.3607
8.00	0.60172	0.60172	0.3621
10.10	0.60232	0.60232	0.3628
12.15	0.60298	0.60298	0.3636
13.95	0.60350	0.60350	0.3642
16.00	0.60441	0.60441	0.3653

AIR

P	V_1	V_2	V_1^2
3.90	0.73580	0.73580	0.5414
8.10	0.74130	0.74130	0.5495
11.95	0.74324	0.74324	0.5524
16.10	0.74399	0.74399	0.5535
20.05	0.74492	0.74492	0.5549
24.00	0.74570	0.74570	0.5561
28.00	0.74654	0.74654	0.5573

TABLE IX.a. (Continued)

CF$_4$

P	V_1	V_2	V_1^2
2.00	0.58240	0.58240	0.3392
4.00	0.58840	0.58840	0.3462
6.00	0.59100	0.59100	0.3493
7.90	0.59240	0.59240	0.3509
10.00	0.59380	0.59380	0.3526
12.00	0.59537	0.59537	0.3545
14.00	0.59762	0.59762	0.3571

ARGON

P	V_1	V_2	V_1^2
8.10	0.62100	0.62100	0.3856
12.10	0.62230	0.62230	0.3873
16.00	0.62314	0.62314	0.3883
20.00	0.62372	0.62372	0.3890
24.00	0.62378	0.62378	0.3891
28.00	0.62410	0.62410	0.3895
32.10	0.62470	0.62470	0.3903

TABLE IX (Continued)

(b) Thermostat Temperature = 50.00°C. θ = 12.10°C. Ratio R_1/R_2 = 1.0428

CO$_2$

P	V_1	V_2	V_1^2
2.00	0.62037	0.59491	0.3849
4.00	0.62527	0.59961	0.3910
6.10	0.62722	0.60147	0.3935
8.10	0.62822	0.60243	0.3947
10.10	0.62897	0.60316	0.3956
12.00	0.62980	0.60393	0.3966
14.00	0.63056	0.60467	0.3976
16.00	0.63130	0.60538	0.3985

AIR

P	V_1	V_2	V_1^2
4.00	0.75711	0.72603	0.5732
8.10	0.76290	0.73157	0.5820
12.00	0.76452	0.73312	0.5845
16.10	0.76582	0.73438	0.5865
20.10	0.76712	0.73562	0.5885
24.00	0.76805	0.73652	0.5899
28.05	0.76870	0.73715	0.5909
32.10	0.76903	0.73746	0.5914
36.00	0.76975	0.73815	0.5925

TABLE IX.b.(Continued)

CF_4

P	V_1	V_2	V_1^2
2.00	0.60596	0.58109	0.3672
4.00	0.61311	0.58795	0.3759
6.00	0.61557	0.59030	0.3789
8.00	0.61710	0.59177	0.3808
10.00	0.61830	0.59292	0.3823
12.10	0.62015	0.58470	0.3846
14.00	0.62202	0.59648	0.3869

ARGON

P	V_1	V_2	V_1^2
8.00	0.63496	0.60890	0.4032
12.10	0.63650	0.61038	0.4051
15.90	0.63782	0.61164	0.4068
20.10	0.63863	0.61241	0.4078
24.00	0.63901	0.61278	0.4083
28.00	0.63942	0.61327	0.4090
32.10	0.64018	0.61390	0.4098

TABLE IX (Continued)

(c) Thermostat Temperature = 64.90°C. Θ = 12.10°C. Ratio R_1/R_2 = 1.0850

CO$_2$

P	V_1	V_2	V_1^2
2.10	0.64430	0.59383	0.4151
4.00	0.64980	0.59890	0.4222
6.00	0.65230	0.60120	0.4255
8.00	0.65355	0.60235	0.4271
10.10	0.65430	0.60302	0.4281
12.00	0.65510	0.60377	0.4292
14.10	0.65600	0.60461	0.4303

AIR

P	V_1	V_2	V_1^2
4.10	0.77794	0.71698	0.6052
8.00	0.78344	0.72224	0.6141
12.00	0.78580	0.72423	0.6175
16.20	0.78750	0.72581	0.6202
20.00	0.78790	0.72617	0.6208
24.10	0.78848	0.72670	0.6217
28.30	0.78883	0.72703	0.6223
32.10	0.78902	0.72721	0.6226

TABLE IX.c.(Continued)

CF_4

P	V_1	V_2	V_1^2
2.00	0.62995	0.58060	0.3968
4.00	0.63778	0.58781	0.4068
6.00	0.64054	0.59035	0.4103
8.00	0.64267	0.59233	0.4130
10.10	0.64427	0.59379	0.4151
12.10	0.64619	0.59557	0.4176
14.10	0.64830	0.59751	0.4203

ARGON

P	V_1	V_2	V_1^2
8.00	0.64935	0.59848	0.4217
12.10	0.65134	0.60032	0.4242
16.10	0.65244	0.60133	0.4257
20.00	0.65310	0.60194	0.4265
24.00	0.65353	0.60234	0.4271
28.10	0.65379	0.60257	0.4274
32.00	0.65430	0.60303	0.4281
36.00	0.65510	0.60378	0.4292

TABLE IX (Continued)

(d) Thermostat Temperature = 80.00°C. θ = 12.10°C. Ratio R_1/R_2 = 1.1280.

CO_2

P	V_1	V_2	V_1^2
2.00	0.66850	0.59266	0.4469
4.00	0.67586	0.59917	0.4568
6.00	0.67796	0.60102	0.4596
8.00	0.67963	0.60251	0.4619
10.10	0.68071	0.60346	0.4634
12.10	0.68143	0.60410	0.4643
14.00	0.68236	0.60492	0.4656

AIR

P	V_1	V_2	V_1^2
4.00	0.79970	0.70897	0.6395
8.00	0.80632	0.71482	0.6502
12.00	0.80910	0.71728	0.6546
16.10	0.81803	0.71882	0.6574
20.00	0.81177	0.71965	0.6590
24.00	0.81221	0.72004	0.6597
28.00	0.81254	0.72033	0.6602
31.90	0.81318	0.72090	0.6613
35.90	0.81377	0.72142	0.6622

TABLE IX.d.(Continued)

CF_4

P	V_1	V_2	V_1^2
2.00	0.65440	0.58015	0.4282
4.00	0.66360	0.58829	0.4404
6.00	0.66654	0.59090	0.4443
8.00	0.66840	0.59255	0.4468
10.10	0.66983	0.59382	0.4487
12.10	0.67156	0.59535	0.4510
14.10	0.67333	0.59691	0.4534

ARGON

P	V_1	V_2	V_1^2
8.00	0.66830	0.59247	0.4466
12.10	0.67066	0.59455	0.4498
16.10	0.67170	0.59548	0.4512
20.00	0.67273	0.59639	0.4526
24.10	0.67290	0.59650	0.4528
28.00	0.67340	0.59699	0.4535
32.10	0.67380	059734	0.4540
36.00	0.67440	0.59787	0.4548

TABLE IX (Continued)

(e) Thermostat Temperature = 95.00°C. Θ = 12.20°C Ratio R_1/R_2 = 1.1707

CO_2

P	V_1	V_2	V_1^2
2.00	0.69960	0.59758	0.4894
4.00	0.70670	0.60365	0.4994
6.00	0.71010	0.60658	0.5042
8.00	0.71150	0.60776	0.5062
10.00	0.71245	0.60857	0.5076
12.00	0.71353	0.60949	0.5091

AIR

P	V_1	V_2	V_1^2
8.10	0.83783	0.71567	0.7020
12.10	0.84162	0.71889	0.7083
16.00	0.84240	0.71955	0.7096
20.00	0.84300	0.72008	0.7106
23.90	0.84350	0.72050	0.7115
28.20	0.84404	0.72097	0.7124
32.00	0.84437	0.72125	0.7130
35.90	0.84570	0.72187	0.7142

TABLE IX.e.(Continued).

ARGON

P	V_1	V_2	V_1^2
8.00	0.69157	0.59074	0.4783
12.00	0.69435	0.59310	0.4821
16.10	0.69553	0.59411	0.4838
20.00	0.69642	0.59487	0.4850
24.00	0.69677	0.59516	0.4855
28.00	0.69712	0.59545	0.4860
32.10	0.69748	0.59578	0.4865
35.90	0.69810	0.59632	0.4873

CF_4

P	V_1	V_2	V_1^2
4.00	0.69330	0.59220	0.4807
6.00	0.69720	0.59555	0.4861
8.00	0.69929	0.59732	0.4890
10.00	0.70090	0.59870	0.4913
12.00	0.70217	0.59978	0.4930
14.10	0.70339	0.60082	0.4948

TABLE X

EXPERIMENTAL RESULTS FROM CELL III AT VARIOUS TEMPERATURES.

$CCl_3.CF_3$ AND $CFCl_2.CClF_2$.

(a) Thermostat temperature = 35.00°C. Θ = 12°C.

Ratio R_1/R_2 = 1.0000 R_2 = 10.119 ohms.

$CCl_3.CF_3$.

P	V_1	V_2	V_1^2
1.60	0.45160	0.45160	0.2039
2.75	0.45601	0.45601	0.2079
3.60	0.45910	0.45910	0.2108
4.60	0.46212	0.46212	0.2135
5.40	0.46581	0.46581	0.2170
7.80	0.47820	0.47820	0.2287
9.80	0.48940	0.48940	0.2395

$CFCl_2.CClF_2$.

P	V_1	V_2	V_1^2
2.10	0.45860	0.45860	0.2103
2.90	0.46223	0.46223	0.2137
4.00	0.46604	0.46604	0.2172
5.00	0.46983	0.46983	0.2208
6.00	0.47426	0.47426	0.2249
7.00	0.47920	0.47920	0.2296

TABLE X. (continued).

(b) Thermostat temperature = 50.00°C. θ = 12°C.

Ratio R_1/R_2 = 1.0428 R_2 = 10.119 ohms.

$CCl_3.CF_3$.

P	V_1	V_2	V_1^2
2.60	0.47570	0.45618	0.2263
3.40	0.47850	0.45886	0.2290
4.00	0.47951	0.45981	0.2299
4.50	0.48024	0.46052	0.2307
5.20	0.48269	0.46286	0.2330
6.00	0.48530	0.46539	0.2355

$CFCl_2.CClF_2$.

P	V_1	V_2	V_1^2
2.10	0.47850	0.45887	0.2290
3.00	0.48261	0.46281	0.2329
4.00	0.48627	0.46630	0.2365
5.00	0.48940	0.46931	0.2395
6.00	0.49325	0.47300	0.2433
7.00	0.49701	0.47660	0.2470
7.95	0.50138	0.48080	0.2514

TABLE X. (continued).

(c) Thermostat temperature = 64.90°C. Θ = 12°C.

Ratio R_1/R_2 = 1.0850 R_2 = 10.119 ohms.

$CCl_3.CF_3$.

P	V_1	V_2	V_1^2
2.55	0.49280	0.45420	0.2429
3.55	0.49516	0.45637	0.2452
4.15	0.49690	0.45797	0.2469
3.95	0.49607	0.45717	0.2461
4.95	0.49900	0.45989	0.2490
5.75	0.50122	0.46192	0.2512

$CFCl_2.CClF_2$.

P	V_1	V_2	V_1^2
2.50	0.49842	0.45938	0.2484
3.85	0.50371	0.46425	0.2537
5.50	0.50926	0.46936	0.2593
7.00	0.51444	0.47413	0.2646
8.60	0.51984	0.47911	0.2702

TABLE X. (continued).

(d) Thermostat temperature = 80.00°C. θ = 12°C.

Ratio R_1/R_2 = 1.1280 R_2 = 10.119 ohms.

$CCl_3.CF_3$.

P	V_1	V_2	V_1^2
2.70	0.51376	0.45546	0.2640
3.60	0.51671	0.45805	0.2670
4.30	0.51850	0.45966	0.2688
5.00	0.52047	0.46141	0.2709
5.80	0.52247	0.46318	0.2730
7.00	0.52265	0.46654	0.2770

$CFCl_2.CClF_2$.

P	V_1	V_2	V_1^2
2.45	0.52241	0.46313	0.2729
4.05	0.52911	0.46907	0.2800
5.70	0.53423	0.47360	0.2854
7.35	0.53890	0.47774	0.2904
8.90	0.54330	0.48165	0.2952
10.70	0.54900	0.48670	0.3014

TABLE X. (continued).

(e) Thermostat temperature = 95.05°C. Θ = 12°C.

Ratio R_1/R_2 = 1.707 R_2 = 10.119 ohms.

$CCl_3.CF_3$.

P	V_1	V_2	V_1^2
2.70	0.53793	0.45950	0.2894
3.55	0.54063	0.46180	0.2923
4.00	0.54178	0.46278	0.2935
4.60	0.54345	0.46421	0.2953
5.40	0.54571	0.46614	0.2978

$CFCl_2.CClF_2$.

P	V_1	V_2	V_1^2
2.40	0.54722	0.46743	0.2994
5.00	0.55350	0.47278	0.3064
5.50	0.55809	0.47672	0.3115
7.00	0.56262	0.48058	0.3165
8.60	0.56699	0.48432	0.3215

TABLE XI $(V_1^2)'$ VALUES USED IN CALCULATION OF THERMAL CONDUCTIVITIES.

Cell Number	I	II	III	III	III	III	III	III	III	III	III	III	III
Thermostat Temperature °C.	25.05	35.00	35.00	35.00	50.00	64.90	80.00	95.00	35.00	50.00	64.90	80.00	95.05
θ°C	10.67	13.00	9.33	12.1	12.1	12.1	12.1	12.1	12	12	12	12	12
ARGON	-	.3640	.3286	.3890	.4080	.4272	.4860	-	-	-	-	-	-
AIR	.3091	.5290	-	.5550	.5913	.6224	.6598	.7125	-	-	-	-	-
CO_2	.1990	.3308	.3115	.3629	.3955	.4275	.4635	.5075	.3720	.4040	.4323	.4720	.5148
CH_3Br.	.1016	-	-	-	-	-	-	-	-	-	-	-	-
$CClF_2CClF_2$	.1360	-	.2110	-	-	-	-	-	-	-	-	-	-
CF_4	-	-	.3035	.3510	.3825	.4135	.4480	.4905	-	-	-	-	-
CCl_3CF_3	-	-	-	-	-	-	-	-	.2120	.2300	.2460	.2680	.2935
$CFCl_2CClF_2$	-	-	-	-	-	-	-	-	.2173	.2364	.2544	.2800	.3070

FIG. 13. P AGAINST V_1^2 CURVES. CELL I.

THERMOSTAT TEMP. = 25·05°C θ = 10·67°C

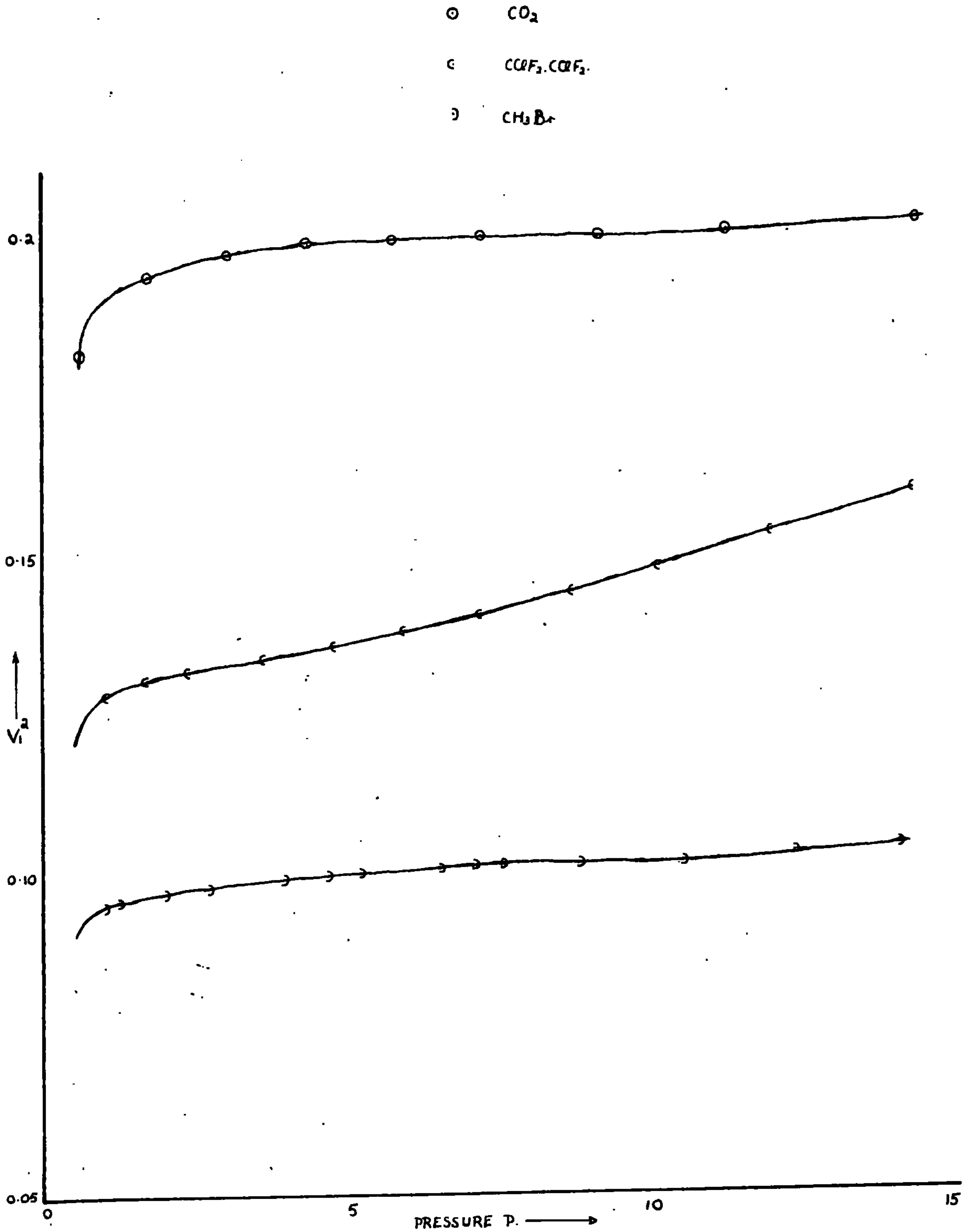
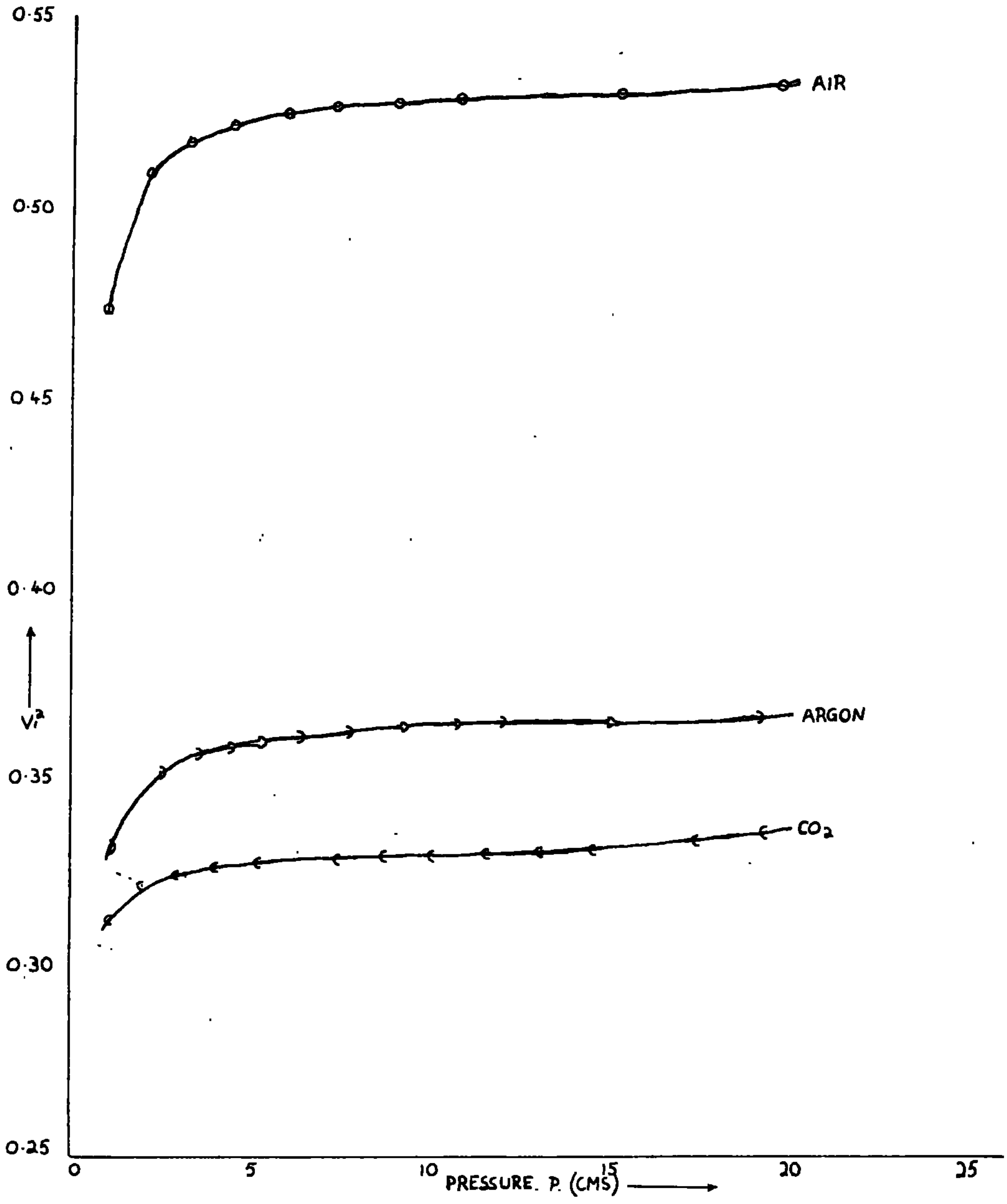


FIG. 14. P AGAINST V_i^2 CURVES. CELL II

THERMOSTAT TEMP. = 35·00°C θ = 13·00°C.



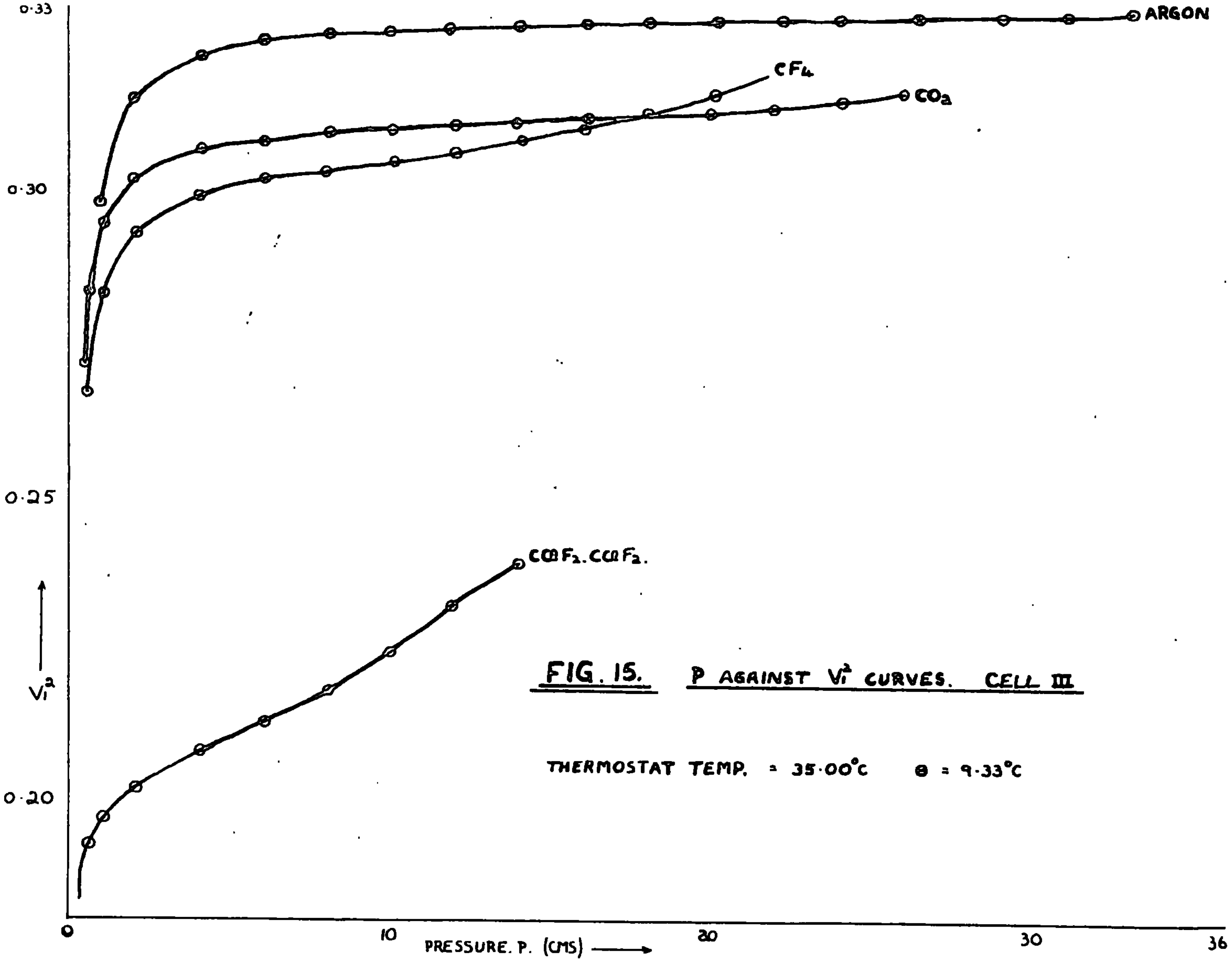
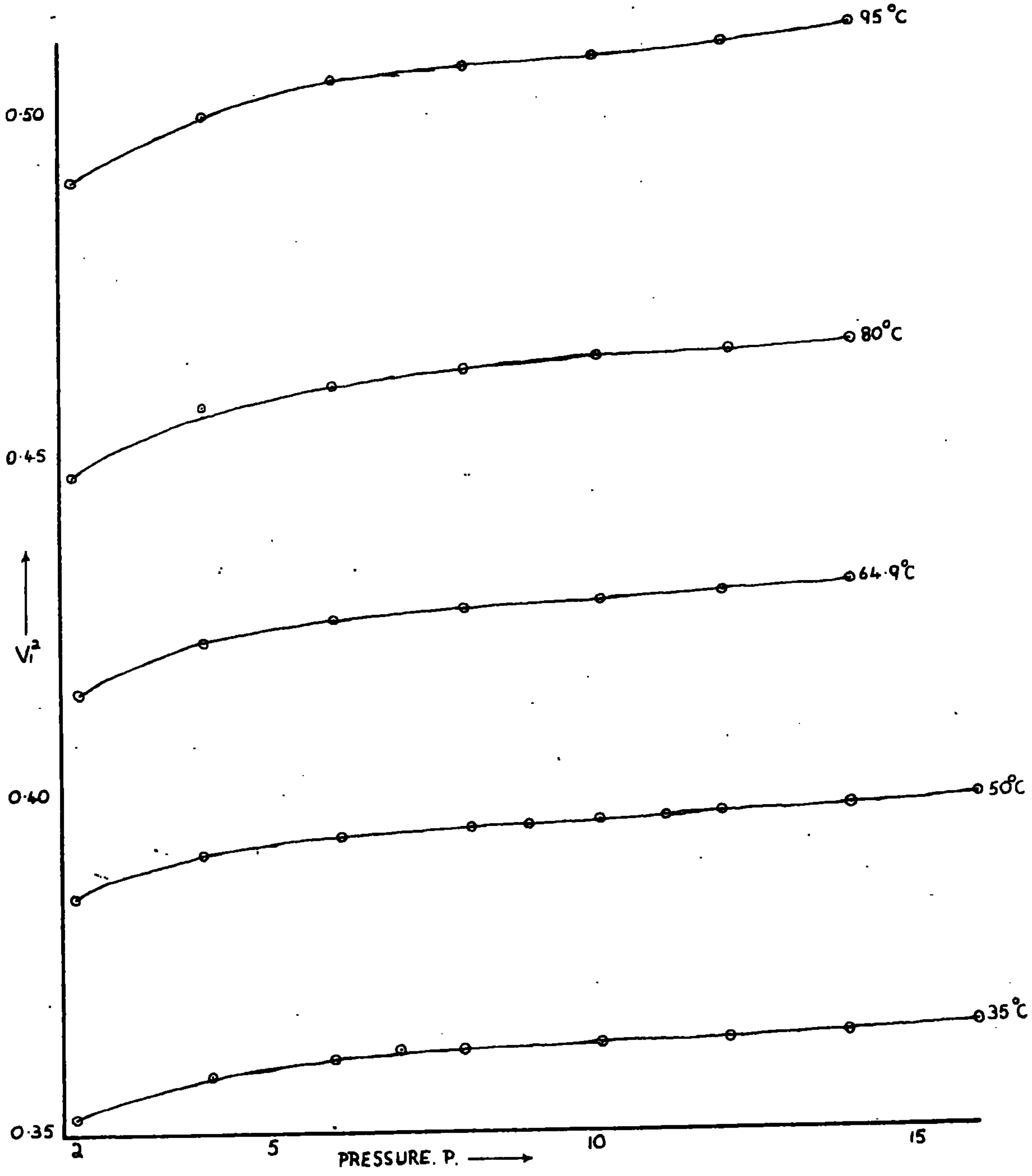


FIG. 15. P AGAINST V_1^2 CURVES. CELL III

THERMOSTAT TEMP. = 35·00°C   θ = 9·33°C

FIG. 16 P AGAINST V_1^2 CURVES FOR CO_2 AT VARIOUS TEMPS. CELL III

THERMOSTAT TEMPS. MARKED ON CURVES
FOR ALL CURVES, $\theta \simeq 12 \cdot 1^\circ C$



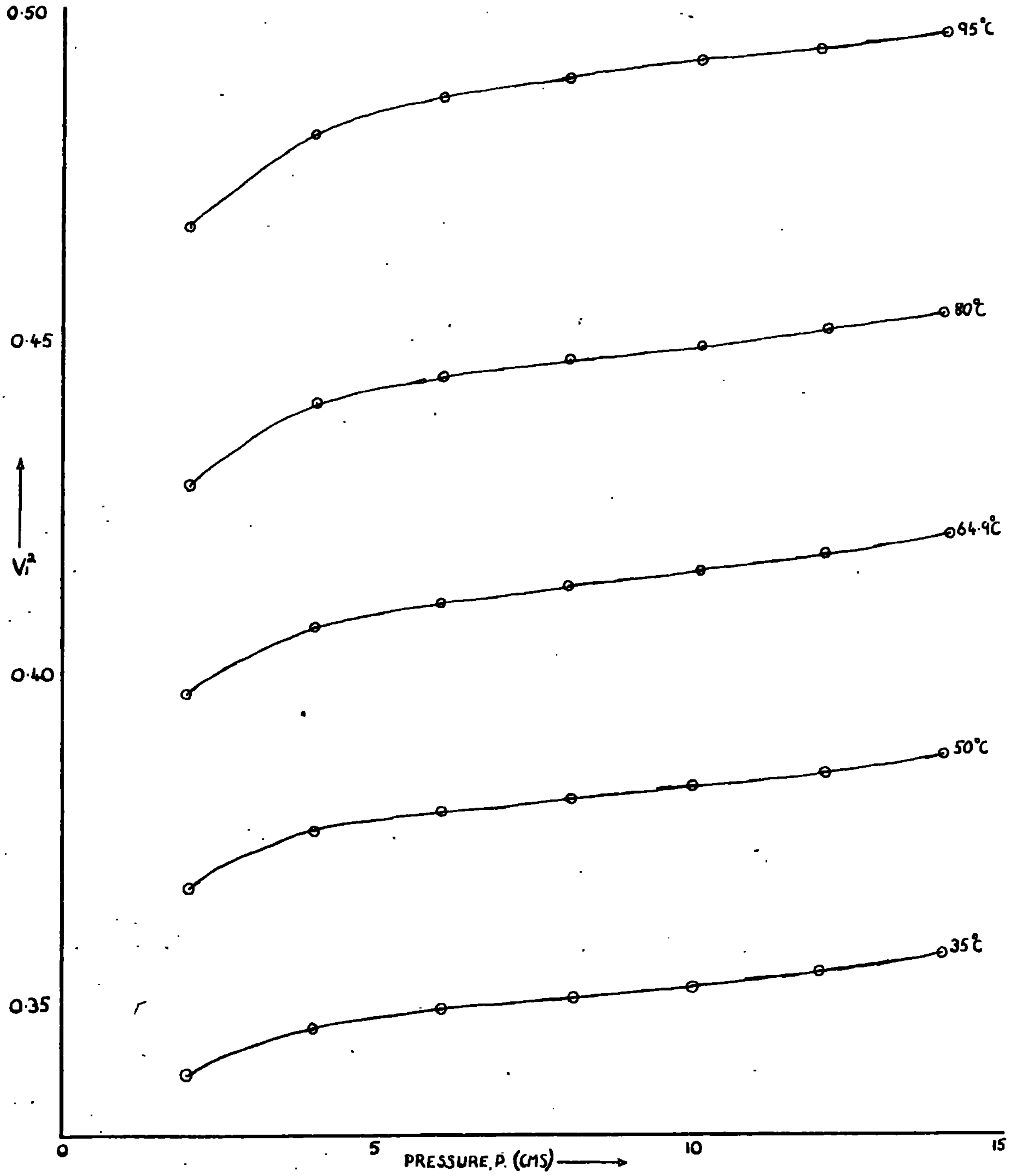


FIG. 17. P AGAINST V_i^2 CURVES FOR CF_4 AT VARIOUS TEMPS. CELL III.

THERMOSTAT TEMPS. MARKED ON CURVES.
FOR ALL CURVES $\theta \simeq 12{\cdot}1°C$

(b). HEAT CAPACITY RESULTS.

Pressure-voltage measurements for the determination of heat capacities are made in the pressure range 45 to 80 cms. pressure. From these measurements, graphs of Q against pressure are drawn, and these are used in the calculation of heat capacities as described in Section II.2. The pressure-voltage measurements from which these graphs are obtained are shown in Tables XII to XV, and the graphs themselves can be seen in Figures 18, 19, 20 and 21.

The following abbreviations and symbols are used in Tables XII to XVI:-

P. - gas pressure in cms. of mercury.

V_1. - voltage drop across the cell wire.

V_2. - voltage drop across the standard resistance R_2.

Q. - rate of energy dissipation in the cell wire in Cals/second.

TABLE XII

EXPERIMENTAL RESULTS FROM CELL I

Thermostat temperature = 25.05°C. Θ = 29.10°C.

Ratio R_1/R_2 = 1.3200 R_2 = 6.1068 ohms.

	P	V_1	V_2	10^2 x Q
ARGON	50.19	0.83050	0.62916	2.045
	60.46	0.84820	0.64250	2.133
	67.87	0.86037	0.65179	2.194
	76.18	0.87410	0.66219	2.265
AIR	51.31	0.99836	0.75633	2.954
	55.04	1.00530	0.76159	2.995
	59.64	1.01499	0.76894	3.053
CO_2.	57.67	0.88210	0.66826	2.307
	63.63	0.89582	0.67865	2.379
	71.55	0.90711	0.68720	2.439
	78.28	0.91795	0.69541	2.498
$(CClF_2)_2$.	49.98	0.82364	0.62397	2.011
	57.57	0.83539	0.63287	2.069
	67.32	0.84832	0.64266	2.133
	76.54	0.85850	0.65038	2.185

TABLE XIII

EXPERIMENTAL RESULTS FROM CELL I

Thermostat temperature = 25.05°C. Θ = 10.67°C.

Ratio R_1/R_2 = 1.2500 R_2 = 6.1068 ohms.

	P	V_1	V_2	10^3 x Q
ARGON	46.90	0.46533	0.37226	6.777
	60.10	0.47020	0.37615	6.921
	67.00	0.47358	0.37885	7.021
	75.70	0.47808	0.38246	7.155
N_2.	47.11	0.55928	0.44739	9.792
	60.03	0.56384	0.45107	9.952
	67.00	0.56743	0.45394	10.079
	75.70	0.57234	0.45790	10.254
CO_2.	48.48	0.47202	0.37762	6.974
	59.83	0.48366	0.38692	7.323
	67.04	0.49155	0.39324	7.563
	75.90	0.49904	0.39923	7.696

TABLE XIII (continued)

	P	V_1	V_2	10^3x Q
$(CClF_2)_2$.	47.65	0.45000	0.36000	6.339
	56.70	0.45712	0.36569	6.541
	66.85	0.46592	0.37274	6.795
	75.52	0.47292	0.37834	7.001
CH_3Br.	47.80	0.37033	0.29626	4.293
	56.50	0.37706	0.30165	4.450
	66.80	0.38424	0.30737	4.621
	75.50	0.38987	0.31189	4.758

TABLE XIV

EXPERIMENTAL RESULTS FROM CELL II

Thermostat temperature = 35.00°C. θ = 17.00°C.

Ratio R_1/R_2 = 0.8600 R_2 = 10.119 ohms.

	P	V_1	V_2	10^{2}x Q
ARGON	50.75	0.71139	0.82720	1.390
	59.05	0.71966	0.83683	1.422
	67.70	0.72990	0.84870	1.462
	75.90	0.73939	0.85976	1.501
AIR	50.35	0.85134	0.98994	1.989
	54.15	0.85602	0.99536	2.012
	58.35	0.86050	1.00060	2.033
	66.95	0.87134	1.01319	2.083
CO_2.	50.50	0.72262	0.84024	1.434
	59.30	0.73655	0.85647	1.490
	68.10	0.74843	0.87027	1.538
	76.20	0.75825	0.88168	1.579

TABLE XV

EXPERIMENTAL RESULTS FROM CELL III

Thermostat temperature = 35.00°C. θ = 20.00°C.

Ratio R_1/R_2 = 1.0300 R_2 = 10.119 ohms.

	P	V_1	V_2	$10^2 x\ Q$
ARGON	50.10	0.85300	0.82815	1.667
	55.10	0.85907	0.83405	1.692
	60.10	0.86624	0.84100	1.720
	65.25	0.87365	0.84820	1.750
	70.25	0.88084	0.85518	1.778
	75.20	0.88745	0.86159	1.805
CO_2.	50.10	0.88800	0.86213	1.807
	55.10	0.89790	0.87175	1.848
	60.00	0.90659	0.88020	1.883
	64.90	0.91553	0.88886	1.921
	70.00	0.92351	0.89661	1.955
	75.00	0.93080	0.90368	1.985
CF_4.	50.00	0.93026	0.90316	1.983
	55.00	0.93916	0.91199	2.023
	60.10	0.94720	0.91964	2.057
	64.00	0.95328	0.92552	2.083
	68.10	0.95936	0.93140	2.110
	72.10	0.96473	0.93663	2.133
	76.10	0.96989	0.94163	2.156

FIG. 18. Q AGAINST P CURVES FROM CELL I.

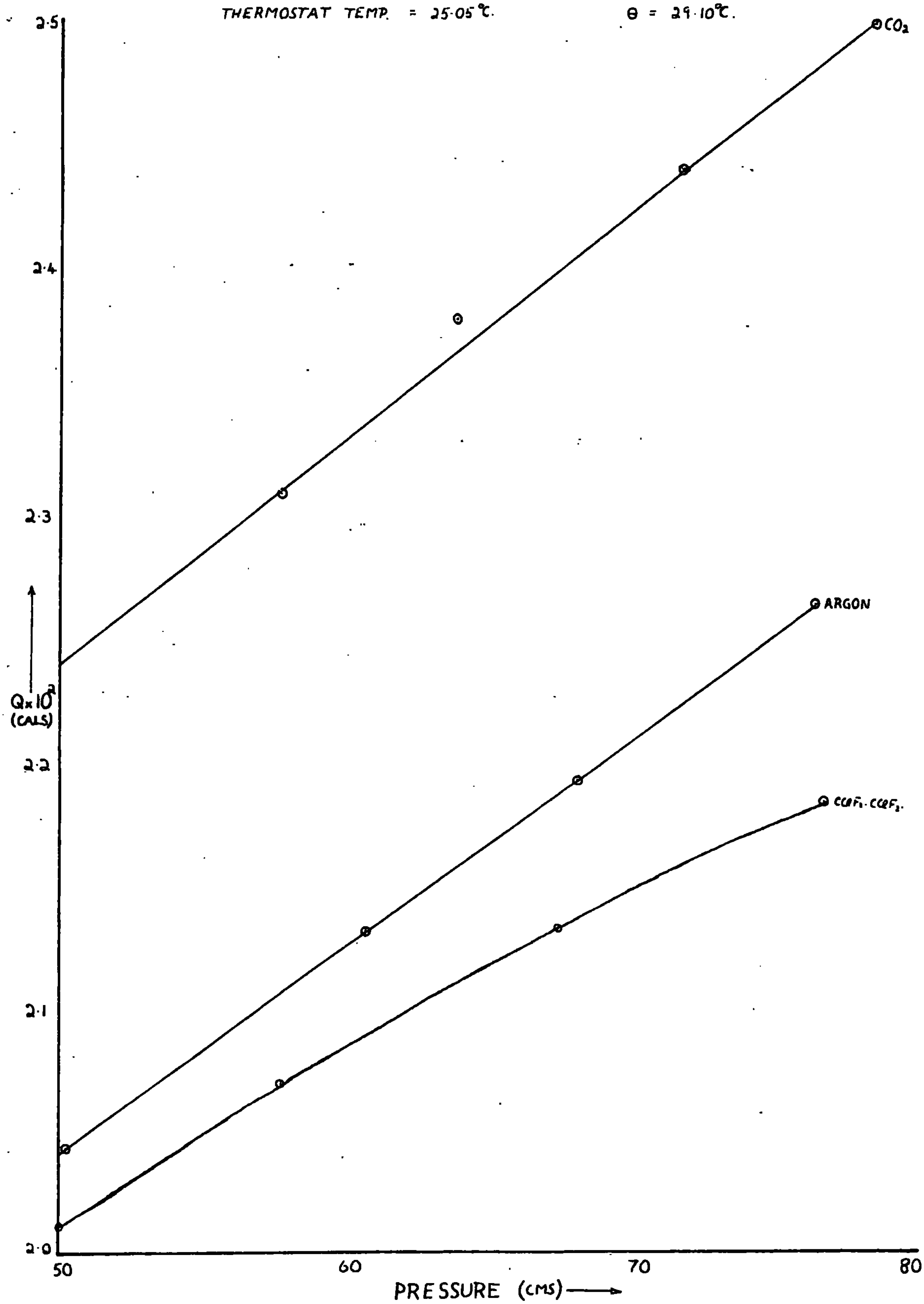


FIG. 19. Q AGAINST P CURVES FROM CELL I.

THERMOSTAT TEMP = 25·05°C   θ = 10·67°C

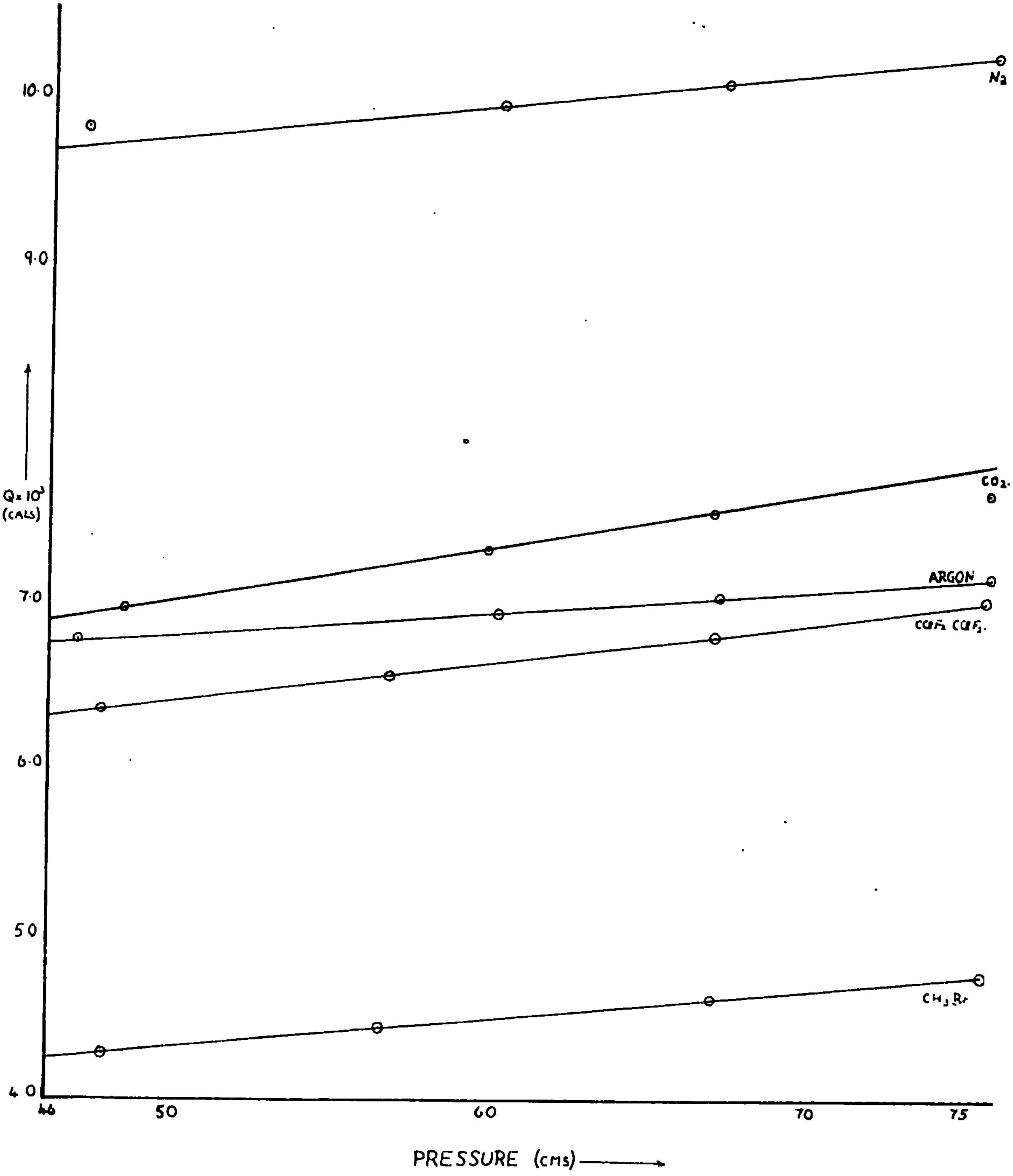


FIG. 20. Q AGAINST P CURVES FROM CELL II.

THERMOSTAT TEMP = 35·00°C θ = 17·00°C.

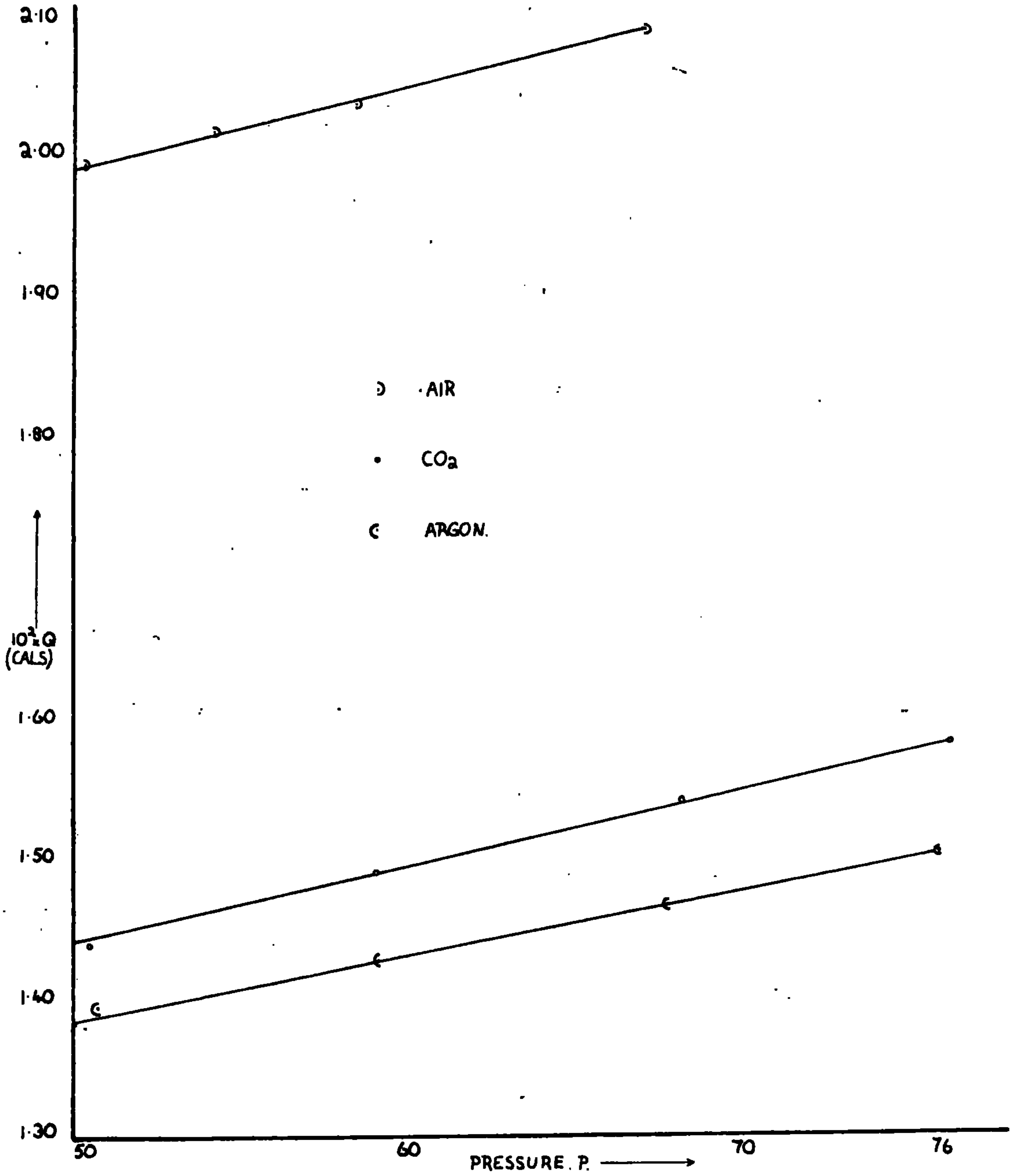
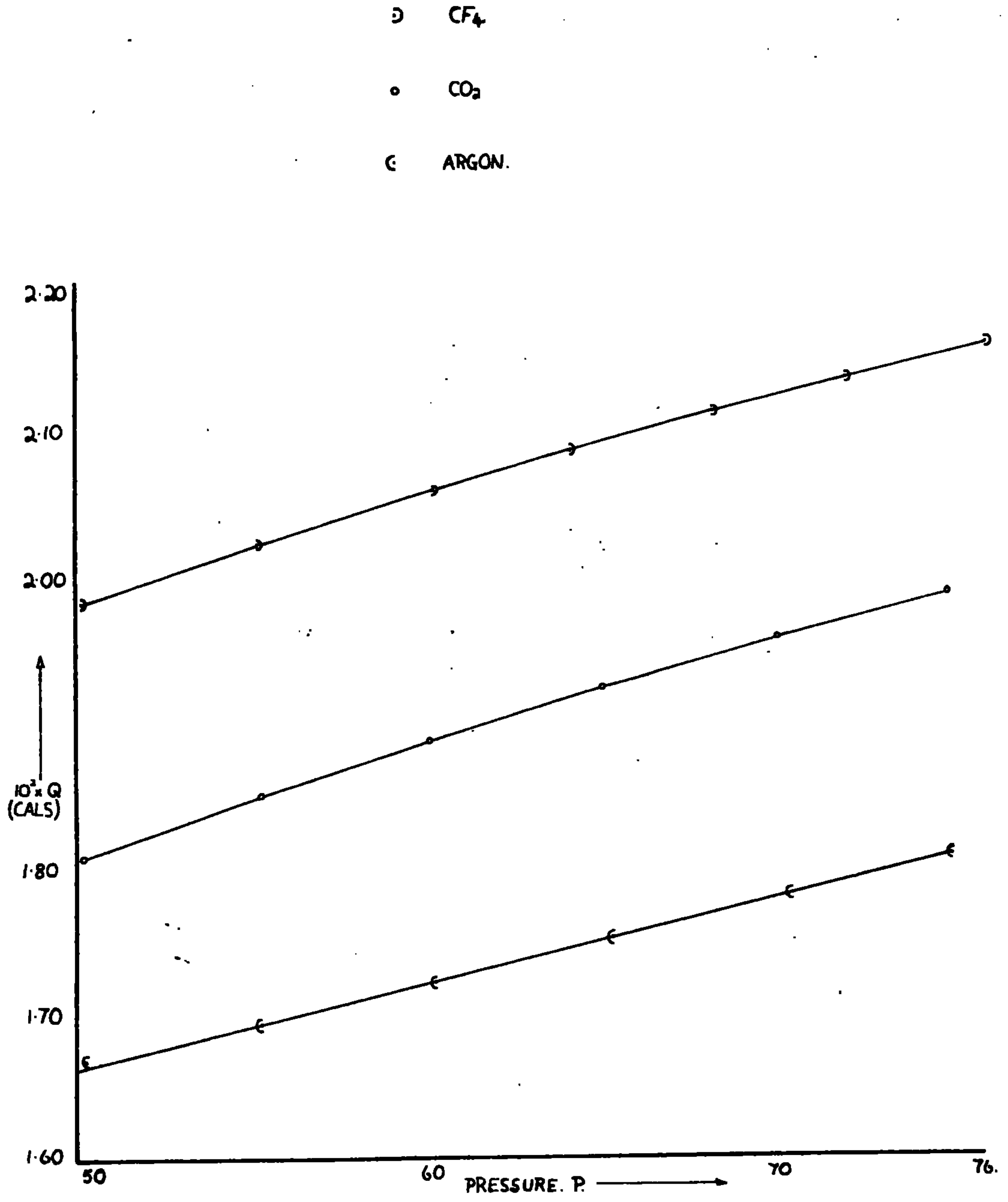


FIG. 21. Q AGAINST P CURVES FROM CELL III.

THERMOSTAT TEMP. = 35·00°C   θ = 20·00°C



APPENDIX II

APPARENT VARIATION OF Cp WITH PRESSURE

The Cp values obtained at various pressures for the materials used in this investigation are shown in Tables XVI, XVII, XVIII and XIX. With the exception of the values in Table XIX, all the values were obtained using ARGON as the reference gas. The values in Table XIX were obtained by comparison with CO_2. All the Cp values were calculated from measurements such that $p_o = p$, i.e. in equation (14), the term p_o/p is equal to unity and disappears. The calculated heat capacities apply at a temperature midway between the thermostat temperature and the temperature of the hot wire, i.e. thermostat temperature + $\Theta/2$°C. The apparent variation of Cp with pressure referred to earlier during the discussion of the results (Section IV.2) can easily be seen from these tables.

TABLE XVI

HEAT CAPACITIES IN CALS/°C/MOLE FROM CELL I

Thermostat temperature = 25.05°C. Θ = 10.67°C.

PRESSURE (CMS).	48.00	57.00	67.00	75.00
Cp (N_2).	7.10	7.02	6.97	6.93
Cp (CO_2).	8.71	9.71	11.01	11.47
Cp($CClF_2.CClF_2$).	27.40	29.07	31.10	31.85
Cp (CH_3Br).	12.50	13.46	14.54	14.92

TABLE XVII

HEAT CAPACITIES IN CALS/°C/MOLE FROM CELL I

Thermostat temperature = 25.05°C. Θ = 29.10°C.

PRESSURE (CMS).	51.31	55.04	59.64	-
Cp (AIR)	6.45	6.44	6.48	-
PRESSURE.	57.67	63.63	71.55	78.28
Cp (CO_2).	10.18	10.46	10.04	9.93
PRESSURE	49.98	57.57	67.32	76.54
Cp($CClF_2.CClF_2$).	30.45	29.33	27.30	24.93
PRESSURE	62.90	75.53	-	-
Cp (CH_3Br).	11.80	10.75	-	-

TABLE XVIII

HEAT CAPACITIES IN CALS/°C/MOLE FROM CELL II

Thermostat temperature = 35.00°C. Θ = 17.00°C.

PRESSURE (CMS)	50.0	59.0	67.0	76.0
Cp (AIR	6.91	6.70	6.57	6.36
Cp (CO_2).	9.43	9.79	9.90	9.66

TABLE XIX

HEAT CAPACITIES IN CALS/°C/MOLE FROM CELL III

Thermostat temperature = 35.00°C. θ = 20.00°C.

Reference gas ------- CO_2.

PRESSURE (CMS).	50.00	58.00	66.00	75.00
Cp (CF_4).	16.97	15.75	15.71	15.15

APPENDIX III

STANDARDISATION OF 'STANDARD' RESISTANCE R_2.

Two different 'standard resistances were used in this investigation and the procedure used to standardise these has been described earlier. (see Section V.2b). The voltage measurements made in these standardisations are set out in Table XX. The true standard resistance is denoted R_s, while the resistance being standardised is denoted R_2. The voltages across these resistances are denoted V_s and V_2 respectively.

TABLE XX

STANDARDISATION OF 'STANDARD' RESISTANCES

EXPERIMENTAL RESULTS

(a) Standard resistance $R_s = 1$ ohm. $R_1/R_2 \doteqdot R_2$

$10^2 \times V_s$ (VOLTS).	$10^2 \times V_2$ (VOLTS).	RATIO R_2/R_s.
0.00922	0.05622	6.0976
0.00922	0.05622	6.0976
0.01810	0.11053	6.1066
0.01808	0.11052	6.1128
0.01808	0.11049	6.1112
0.01808	0.11048	6.1106
0.09771	0.59727	6.1127
0.10540	0.64420	6.1120
0.20390	1.2440	6.1010
0.20350	1.2425	6.1057

Average ratio $R_2/R_s = R_2 = 6.1068$ ohms.

<u>TABLE XX</u>. (Continued).

(b) Standard resistance, R_s = 10 ohms. $R_2 = 10 \times \frac{R_2}{R_s}$

10 x V_s (VOLTS).	10 x V_2 (VOLTS).	RATIO R_2/R_s
0.19130	0.19357	1.0119
0.19130	0.19357	1.0119
0.19129	0.19356	1.0119
0.19128	0.19355	1.0119
0.19764	0.20000	1.0119
0.20325	0.20568	1.0119_5
0.20326	0.20569	1.0119_5
0.20327	0.20570	1.0119_5
0.20327	0.20570	1.0119_5
0.51420	0.52032	1.0019
0.83544	0.84538	1.0119
0.83532	0.84525	1.0119

Average ratio R_2/R_s = 1.0119 R_2 = 10.119 ohms.

APPENDIX IV

TEMPERATURE COEFFICIENT OF RESISTANCE OF THE CELL WIRES.

The method used to find the temperature coefficient of resistance of the cell wires has been described earlier (see Section V.2c). Some of the experimental results are set out in the tables below. These results are also expressed graphically in Figures 22,23 and 24, which show the variation of the ratio R_1/R_2 with temperature, where R_1 is the resistance of the cell wire and R_2 is a standard resistance whose value is constant and known (see Appendix III). For any given cell, the value of R_1/R_2 is characteristic of the temperature of the cell wire. Therefore, since R_2 is known, the value of R_1 can be found at any given temperature.

Some of the voltage measurements made using cell I are shown in Table XXI. V_1 is the voltage drop across the cell wire and V_2 is the voltage drop across the standard resistance R_2. The ratio V_1/V_2 is equal to the ratio R_1/R_2. Similar data readings are taken at several different temperatures to give the necessary data for the temperature against R_1/R_2 curves. The data for the three cells are set out in Table XXII below.

TABLE XXI

EXPERIMENTAL RESULTS FROM CELL I

Standard resistance, R_2 = 6.1068 ohms.

(a) Thermostat temperature = 53.90°C.

10^2x V_1 (VOLTS).	10^2x V_2 (VOLTS).	RATIO R_1/R_2.
0.07282	0.05519	1.3194
0.07280	0.05519	1.3191
0.07281	0.05519	1.3193
0.09384	0.07112	1.3195
0.09382	0.07112	1.3192

Average ratio R_1/R_2 = 1.3193

(b) Thermostat temperature = 56.66°C.

10^2x V_1 (VOLTS).	10^2x V_2 (VOLTS).	RATIO R_1/R_2.
0.09458	0.07110	1.3302
0.09458	0.07110	1.3302
0.09457	0.07110	1.3301
0.07381	0.05547	1.3306
0.07380	0.05548	1.3302

Average ratio R_1/R_2 = 1.3302

TABLE XXII

DATA FOR TEMPERATURE AGAINST R_1/R_2 CURVES.

CELL I. Standard resistance R_2 = 6.1068 ohms.

THERMOSTAT TEMPERATURE °C.	AVERAGE RATIO R_1/R_2.
30.45	1.2303
35.10	1.2475
47.99	1.2969
53.90	1.3193
56.66	1.3302

CELLS II AND III. Standard resistance R_2 = 10.119 ohms.

CELL II

THERMOSTAT TEMPERATURE °C.	AVERAGE RATIO R_1/R_2.
41.36	0.8334
45.69	0.8441
50.70	0.8570
56.16	0.8698
62.46	0.8861

CELL III

THERMOSTAT TEMPERATURE °C.	AVERAGE RATIO R_1/R_2.
40.19	0.9802
50.20	1.0091
60.01	1.0369
69.45	1.0636
79.97	1.0933
88.45	1.1180
99.81	1.1486

FIG.22. GRAPH OF RATIO R_1/R_2 AGAINST TEMP.°C. CELL I.

$R_a = 6{\cdot}1060\ \Omega$

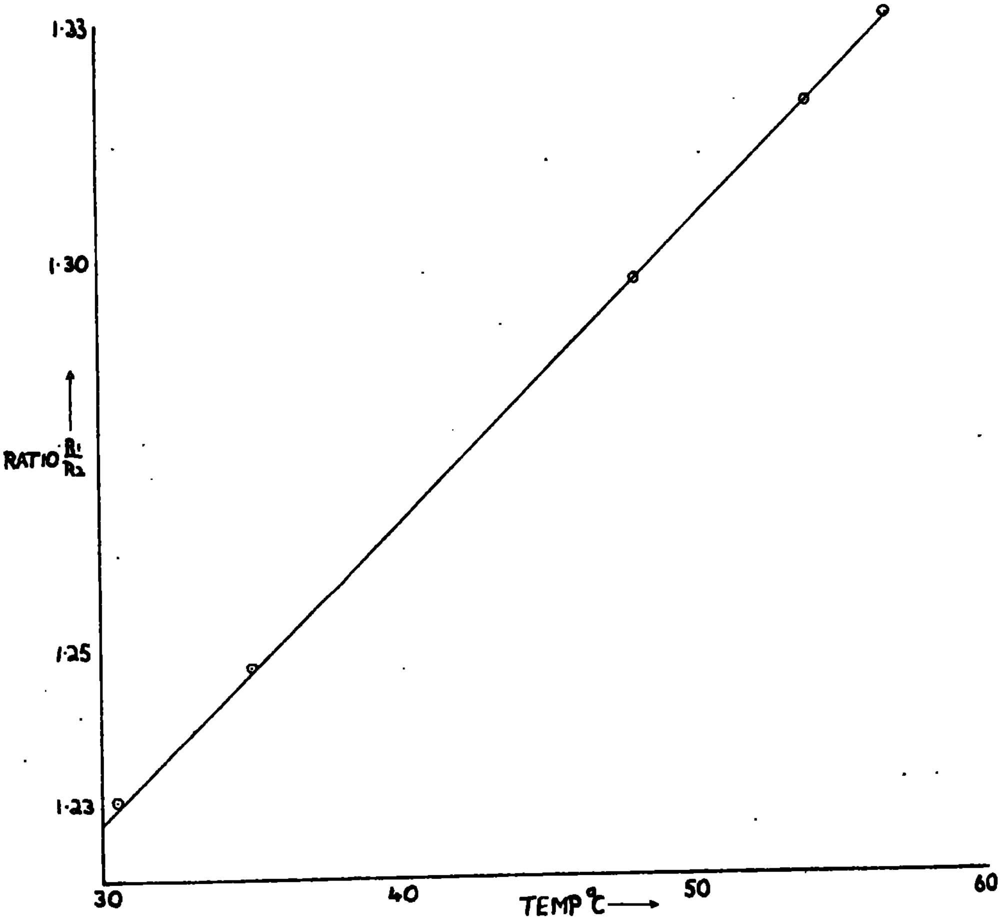


FIG. 23. GRAPH OF RATIO R_1/R_2 AGAINST TEMP °C. CELL II

$R_2 = 10{\cdot}119\ \Omega$

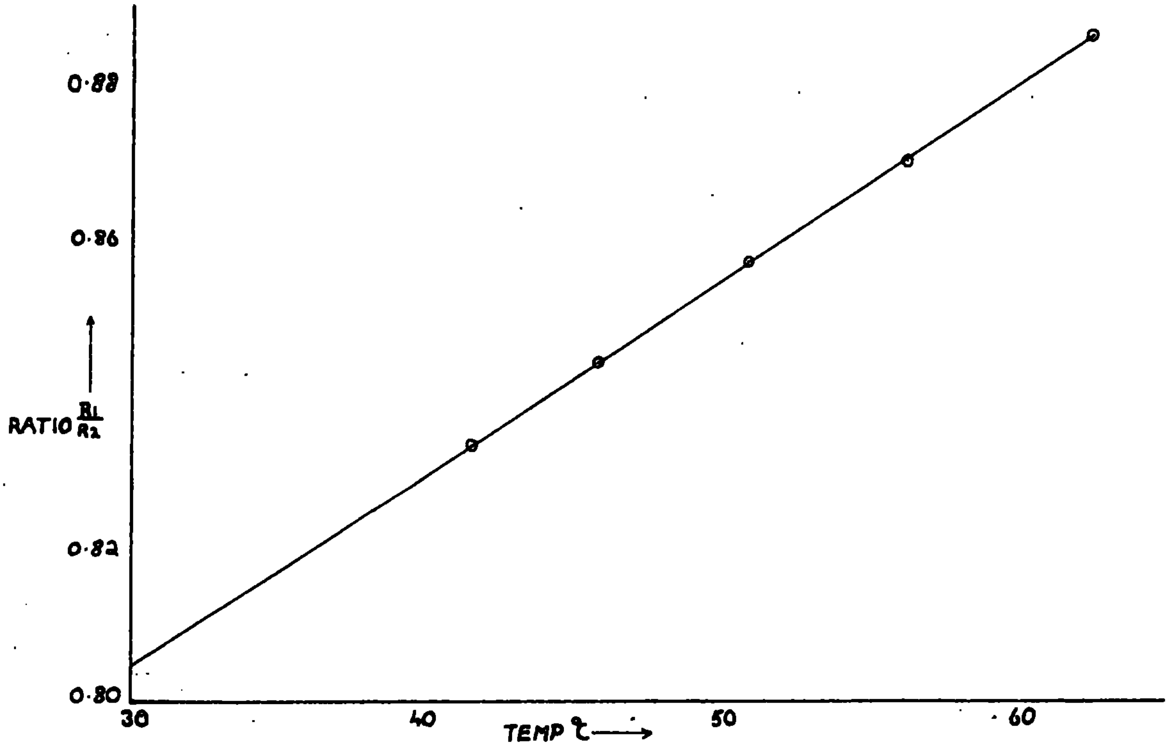
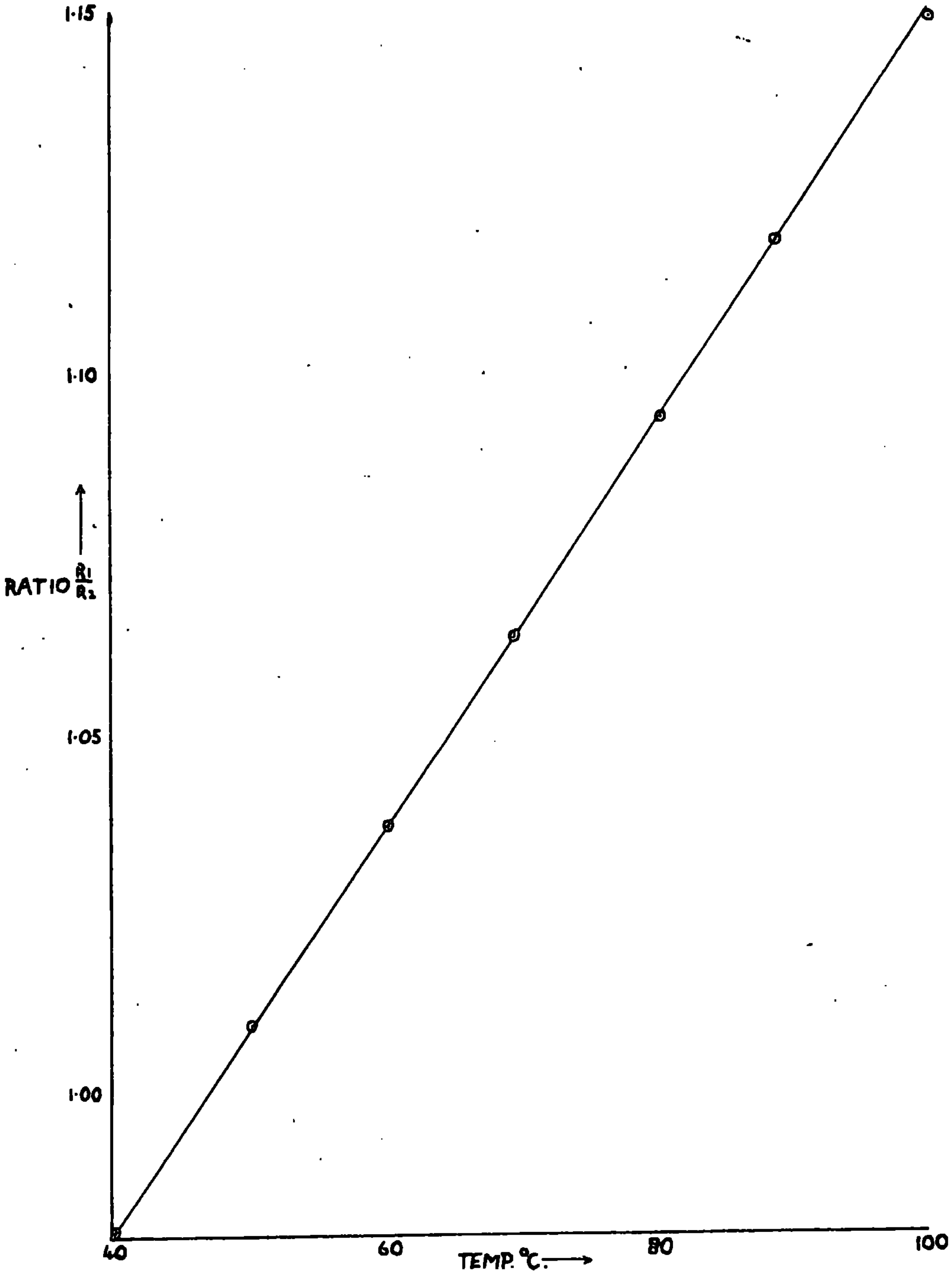


FIG. 24 GRAPH OF RATIO R_1/R_2 AGAINST TEMP °C, CELL III

$R_2 = 10{\cdot}119\,\Omega$.



APPENDIX V

THERMAL CONDUCTIVITIES FROM THE NATIONAL BUREAU OF STANDARDS CIRCULAR NUMBER 564

The references gases used in the determination of thermal conductivity in this investigation are ARGON, AIR and CO_2. The thermal conductivity values assumed for these gases are taken from the National Bureau of Standards Circular Number 564 (24). These values are the results of an analysis by the National Bureau of Standards of the experimental values obtained by many different workers. The sources of the experimental results are shown in references 20 (ARGON), 21 (AIR) and 22 (CO_2). To get the best possible expression for the variation of thermal conductivity with temperature, the experimental results are fitted to the empirical equation

$$\frac{\lambda}{\lambda_o} = \frac{1}{\lambda_o} \left(\frac{a. \sqrt{T}}{1 + \frac{6 \times 10^{-c/T}}{T}} \right)$$

where λ_o is the thermal conductivity at 0°C, λ is the thermal conductivity at temperature T, and a, b and c are constants for any gas or vapour. The values of λ_o, a, b and c for ARGON, AIR and CO_2 are shown in Table XXIII. These values of λ_o, a, b and c are determined from the analysis of the experimental results, and when they are known, the above equation can be used to express the variation of thermal conductivity with temperature.

The equation is expressed graphically for ARGON, AIR and CO_2 in Figures 4, 5 and 6.

TABLE XXIII.

DATA FROM THE NATIONAL BUREAU OF STANDARDS CIRCULAR NUMBER 564 FOR CALCULATING THERMAL CONDUCTIVITY VALUES FOR ARGON, AIR AND CO_2.

	ARGON.	AIR	CO_2.
$10^6 \times \lambda_o$.	39.05	57.70	34.77
$10^5 \times a$.	0.3790	0.6325	4.608
b.	179.59	245.40	6212.0
c.	10	12	10

APPENDIX VI.

PURITY OF THE GASES

ARGON

The ARGON was supplied in cylinders by the British Oxygen Co.Ltd., and its purity was better than 99.5%

CO_2.

Pure CO_2 was obtained by heating Analar sodium bicarbonate and freezing out the large quantities of water also produced.

AIR.

Atmospheric AIR was used after passage through strong alkali to remove CO_2 then through a 'Drikold' trap to remove moisture.

CH_3Br.

The CH_3Br vapour was passed through concentrated H_2SO_4 to remove ethylenic compounds which were the only suspected impurities.

CF_4.

This was purified by Dr. W.K.R. Musgrave using a gas-liquid chromatographic technique. It contained no detectable impurity.

$CCl_3.CF_3$.

The $CCl_3.CF_3$ was purified by fractional distillation.

APPENDIX VI.

PURITY OF THE GASES

ARGON

The ARGON was supplied in cylinders by the British Oxygen Co.Ltd., and its purity was better than 99.5%

CO_2.

Pure CO_2 was obtained by heating Analar sodium bicarbonate and freezing out the large quantities of water also produced.

AIR.

Atmospheric AIR was used after passage through strong alkali to remove CO_2 then through a 'Drikold' trap to remove moisture.

CH_3Br.

The CH_3Br vapour was passed through concentrated H_2SO_4 to remove ethylenic compounds which were the only suspected impurities.

CF_4.

This was purified by Dr. W.K.R. Musgrave using a gas-liquid chromatographic technique. It contained no detectable impurity.

$CCl_3.CF_3$.

The $CCl_3.CF_3$ was purified by fractional distillation.

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