MEASUREMENT OF THE THERMAL CONDUCTIVITY OF GASES

USING A PERIODIC LINE-SOURCE FLOW METHOD.

John Gordon O'Hair.

A thesis submitted to the University of Surrey (Physics Dept.) in 1974, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.
ACKNOWLEDGEMENTS

The research described in this thesis was performed on a collaborative basis between the University of Surrey and the British Gas Corporation. I would like to express my thanks to the British Gas Corporation for supporting research of this nature.

I would particularly like to express my appreciation of the guidance, encouragement and assistance given me by Dr. R.J. Huck and Mr. R.W. Whorlow of the University of Surrey and by Dr. A. Melvin, Dr. A.E. Humphreys and Dr. A. Mills of the British Gas Corporation.

Thanks are also due to relations and friends who have assisted me in various ways.
ABSTRACT

Reliable and accurate values of the thermal conductivity of gases and gas mixtures are much needed by engineers and theoreticians, this being particularly true for high temperature gases. However, such values are difficult to obtain because of the problems of eliminating, or accurately accounting for, heat transfer through the apparatus by mechanisms other than conduction through the gas. In some cases there are significantly large discrepancies between experimental values of thermal conductivity and values which have been calculated using theoretical equations in conjunction with experimental values of viscosity. Viscosity measurements are believed to be more reliable than thermal conductivity measurements, and the kinetic theory relating the two properties is not in doubt, so the reliability of methods of measuring thermal conductivity is questionable.

This thesis describes a technique for measuring thermal conductivity in which there are no corrections to be made for heat transfer by other mechanisms. The technique should, therefore, be free of the systematic errors which have proved most troublesome in many other methods. The technique involves the measurement of the temperature distribution downstream from a periodically varying line source of heat in a flowing gas. This information, along with knowledge of the velocity of the gas flow, enables the thermal diffusivity of the gas to be determined. The thermal conductivity can then be calculated if the density and specific heat of the gas at constant pressure are both known.

The results of using this technique to measure the thermal conductivity of nitrogen, carbon dioxide and nitrogen-carbon dioxide
mixtures are also given in the thesis. The results are compared with
the correlated results of many other workers but no systematic
discrepancies are apparent.
TABLE OF CONTENTS

CHAPTER I

INTRODUCTION 1

CHAPTER II

EXPERIMENTAL AND THEORETICAL METHODS OF DETERMINING THE THERMAL CONDUCTIVITY OF GASES AND GAS MIXTURES. 9

2.1 The cooling method. 10
2.2 The hot-wire method. 11
2.3 The parallel-plate and similar methods. 14
2.4 Other methods. 16
2.5 The line-source method. 19
2.6 Calculation of values of thermal conductivity from kinetic theory.
   a) Single monatomic gases. 25
   b) Single polyatomic gases. 29
   c) Gas mixtures (monatomic and polyatomic). 38

CHAPTER III

THEORY OF THE MEASUREMENT OF THERMAL CONDUCTIVITY USING A PERIODIC LINE-SOURCE OF HEAT. 46

3.1 The temperature distribution resulting from a periodic line source of heat in a flowing gas. 47
3.2 Theory for the measurement of the velocity of the gas. 53
3.3 Theory for the measurement of the thermal conductivity of the gas. 55
CHAPTER IV

THE CONSTRUCTION AND THE PERFORMANCE OF THE APPARATUS 61

4.1 Description of the apparatus.
   a) Mechanical and constructional details.  62
   b) Electronic equipment
      i) The measurement of the gas velocity.  70
      ii) The measurement of the thermal diffusivity of the
           gas: The measurement of the amplitude of the
           sinusoidal temperature variations of the gas.  77
   c) Apparatus required for ancillary measurements.
      i) Radiation correction to the thermocouple measurements 83
      ii) The correction for the heating effect of the source
           wire.  88
      iii) Apparatus used for the measurement of gas mixtures 89

4.2 The detector.
   a) The theory of the detector circuit.  92
   b) The effect of electrical heating of the detector wire.  99
   c) Experimental evidence of the satisfactory performance
      of the measuring system:  110

CHAPTER V

DIFFERENCES BETWEEN THE THEORETICAL AND THE
EXPERIMENTAL CONDITIONS.  116

5.1 The variations of the velocity and the temperature
   of the gas.
   a) Variations of the temperature of the gas.  117
5.1 b) Variations of the velocity of the gas.

   c) The effect of the variations of the velocity and
temperature of the gas.

5.2 Other differences between the theoretical and the
experimental conditions.

5.3 Evidence that the experimental measurements are consistent
with the theoretical equations.

CHAPTER VI

EXPERIMENTAL PROCEDURE AND THE RESULTS OF THE
MEASUREMENTS.

6.1 The experimental procedure.

6.2 The results of the measurements

   a) Nitrogen and carbon dioxide.

   b) Mixtures of nitrogen and carbon dioxide.

6.3 Discussion of results.

   6.4 Analysis of the errors in the measurements.

CHAPTER VII

CONCLUSIONS.

APPENDICES.

   I. The temperature distribution due to a periodic line source
      of heat in a moving gas.

   II. Evaluation of integrals of the form

I = \int_{-\infty}^{\infty} \left( x^2 + y^2 + z^2 \right)^{-\frac{1}{2}} \exp \left[ -(x^2 + y^2 + z^2)^{\frac{1}{2}} \right] dz

   III. Test of solution obtained in appendix I.

REFERENCES.
CHAPTER I

INTRODUCTION

The main object of this thesis is to describe a new technique for the measurement of the coefficient of thermal conductivity of a gas or gas mixture. Thermal conductivity is one of the most important properties of a gas and it has been the subject of much experimental and theoretical work. The kinetic theory of gases is now well advanced but, with present knowledge, it is necessary to make approximations to this theory before it can be used to calculate coefficients of thermal conductivity. Consequently, reliable experimental measurements of thermal conductivity are needed and improved measurement techniques are required to satisfy this need.

The basic process of heat conduction is quite simple. The molecules in the hotter regions of a gas possess, on average, more kinetic energy than those in the colder regions and consequently molecules moving from the hotter regions into the colder regions transport more heat energy than those moving in the reverse direction. This net transfer of heat to the colder regions is called 'conduction' of heat.

The direction of flow of heat at any point is the direction in which the temperature of the gas falls most rapidly. The maximum rate of change of temperature with position at any point is called 'the temperature gradient' and is denoted by 'grad T' where T is the local temperature of the gas. The rate at which heat is conducted through unit area of an infinitesimally small plane perpendicular to the direction of flow is proportional to the temperature gradient; the
constant of proportionality being the coefficient of thermal conductivity, or, briefly, the thermal conductivity, of the gas. This relation can be expressed mathematically in the form

\[ \frac{dQ}{dt} = -\lambda \nabla T \] \hspace{1cm} \text{(1.1)}

where \( dQ \) is the quantity of heat conducted per unit area, normal to the direction of heat flow, in time \( dt \) and \( \lambda \) is the thermal conductivity of the gas. The negative sign indicates that the direction of heat flow is down the temperature gradient.

To calculate the rate of heat conduction through any large, irregular surface of area \( A \), it is necessary to apply equation 1.1 to each infinitesimally small area \( dA \) on the surface, and then integrate over the complete surface. It is convenient to define a vector \( dA \) which has the magnitude of the area \( dA \) and which is perpendicular to the surface as shown in figure 1.1. It is clear, from equation 1.1, that the rate of heat conduction through the area \( dA \) is given by

\[ \frac{dQ}{dt} = -\lambda dA \cdot \nabla T. \] \hspace{1cm} \text{(1.2)}

![Figure 1.1](image)

Conduction of heat through an irregular surface.
Consequently, the rate of heat conduction through the complete surface is given by \( \frac{dQ}{dt} \) where

\[
\frac{dQ}{dt} = -\int_A \lambda \, dA \cdot \text{grad} T
\]

In this equation both \( \lambda \) and \( \text{grad} T \) are functions of the position of the area \( dA \) because, in general, the temperature over the surface is not constant. Furthermore, unless the gas has reached a steady state, both \( \lambda \) and \( \text{grad} T \) are also functions of time \( t \), so \( \frac{dQ}{dt} \) must, in general, be a function of time.

It is obvious, from the above equations, that the units of thermal conductivity are those of

\[
(\text{quantity of heat}) \ (\text{time})^{-1} \ (\text{length})^{-1} \ (\text{temperature})^{-1}
\]

The S.I. units of thermal conductivity are, therefore,

\[
(\text{Joules}) \ (\text{seconds})^{-1} \ (\text{metres})^{-1} \ (\text{degrees K})^{-1}
\]

or

\[
(\text{Watts}) \ (\text{metres})^{-1} \ (\text{degrees K})^{-1}
\]

However, values for the thermal conductivity of gases are most often quoted in units of

\[
(\text{calories}) \ (\text{seconds})^{-1} \ (\text{centimetres})^{-1} \ (\text{degrees C})^{-1}
\]

This unit can normally be equated, with sufficient accuracy, to

\[
418 \ (\text{Watts}) \ (\text{metres})^{-1} \ (\text{degrees K})^{-1}
\]

Another term which is often used in heat conduction problems is the thermal diffusivity \( K \). It is related to the thermal conductivity by the equation
\[ K = \frac{\lambda}{\rho c} \]

where \( \rho \) is the density of the gas and \( c \) is the specific heat, or heat capacity per unit mass, of the gas at constant pressure. The units of thermal diffusivity are, therefore,

\[ (\text{centimetres})^2 (\text{seconds})^{-1} \text{ or } (\text{metres})^2 (\text{seconds})^{-1}. \]

Accurate knowledge of the thermal conductivity of gases and gas mixtures is required by both engineers and theoreticians. An engineer, when designing equipment containing high temperature gases, needs to calculate the heat transfer within the equipment. To do this successfully he requires accurate knowledge of the thermal conductivity of the gases concerned but this knowledge is often not available because of the shortage of reliable experimental data. Such data is also required by the theoretician for it enables him to compare experimental values of thermal conductivity with those which have been obtained by making suitable approximations to the theory of heat conduction. This may help to establish the validity of a particular approximation which may result in a more reliable method of calculating the thermal conductivity of other gases for which little or no experimental data is available.

There already exists a well established method of calculating the thermal conductivity of monatomic gases \(^{(1)}\) but, because the theory of heat conduction can be applied much more easily to a monatomic gas than to a polyatomic gas, the establishment of a method of calculating the thermal conductivity of a polyatomic gas has proved to be much more difficult. The important difference between the theories
for monatomic and polyatomic gases arises from the fact that polyatomic molecules can transport both internal and translational energy whereas monatomic molecules, i.e. atoms, can transport translational energy only. The internal energy of a polyatomic molecule can be due to the molecule rotating about one or more of its axes, or it can be due to the atoms of the molecule vibrating relative to each other. A molecule may also have internal energy due to an electron being excited above its ground state but it is usually possible to ignore this effect because, for most gases, it only occurs at very high temperatures. A monatomic gas, if heated to a sufficiently high temperature, could have internal energy of this kind, in which case the monatomic theory would no longer be applicable.

The main problems in the theory for polyatomic gases are those of ascertaining the rate at which internal energy can diffuse through the gas and of ascertaining the ease with which internal energy is transferred from one molecule to another during a collision. These are difficult problems for a pure polyatomic gas but for a mixture of polyatomic gases, where energy transfer between unlike molecules can also occur, the problems are so complex that equations for calculating the thermal conductivity of a polyatomic mixture often rely, to some extent, upon empirical laws.

Most theories restrict their application to gases in which only binary collisions of molecules occur. Such theories predict that the thermal conductivity is independent of the pressure of the gas. This has been verified experimentally, though deviations from the theory have been observed at very low and very high pressures. At very low pressures the deviations become noticeable when the mean free path
of the molecules is of the same order of magnitude as the size of the apparatus. Measurements of 'thermal conductivity' under these conditions can have little significance. Deviations from the theory at high pressures are due to the gas becoming sufficiently dense that ternary collisions occur at a significant frequency. A ternary collision is a collision in which a molecule is appreciably affected by the force fields of two other molecules at the same time. Binary collisions become less and less likely as the pressure increases and it is found that, under these conditions, the thermal conductivity is pressure dependent. There are theories for dense gases (1), but such theories are very complicated. Consequently, it is important to have accurate experimental data available for the thermal conductivity of gases at high pressures as well as at high temperatures.

The apparatus described in this thesis was designed to give accurate values of thermal conductivity of gases at high temperatures, the working range of the apparatus being from $300^\circ K$ to approximately $1000^\circ K$. Most existing experimental methods suffer from problems associated with heat transfer by radiation, by convection and by conduction through the apparatus itself. A technique, known as the line-source method, which avoids these problems, has been developed by Westenberg and de Haas (2). It is an absolute technique which involves the measurement of the temperature distribution downstream from a line source of heat, a hot wire, placed in a gas flowing with uniform velocity. This method, which is described in more detail in section 2.5, can be improved, as will be shown in this thesis, if the steady line source of heat is replaced by a line source which varies periodically with time. This hitherto unused method can, therefore,
be best described as a 'periodic line-source of heat' method. This is the method described in this thesis.

The periodic line source results in a temperature distribution similar to that obtained from a steady line source except that, at any point downstream from the source, the temperature varies periodically. Furthermore, the amplitude of this temperature variation is a function of the frequency of the periodic heating current passing through the source wire as well as being a function of the velocity of the gas, the thermal diffusivity of the gas, and of position relative to the source of heat. Consequently, the measurement of this amplitude as a function of position and frequency, and the measurement of the velocity of the gas, enables the thermal diffusivity to be determined. The main improvements of this method over the steady line-source method are that frequency is available as an additional variable and that advantage can be taken of the fact that, in the presence of noise, small a.c. signals can be measured more accurately than equivalent d.c. signals.

The theoretical temperature distribution downstream from a periodic line source of heat is calculated in appendix I of this thesis, and the way in which this can be most conveniently used to determine the thermal conductivity by experiment is described in chapter III. The experimental apparatus required to achieve these measurements is described in chapter IV and the difference between the theoretical model and the experimental apparatus is discussed in chapter V. The results of the measurements of the thermal conductivity of nitrogen, carbon dioxide and mixtures of these two gases are given in chapter VI, where they are compared with the results of other workers and with results calculated from present theories. A brief description of these
theories is given in chapter II, along with a short account of many of the experimental methods which have been used in the past.
CHAPTER II

EXPERIMENTAL AND THEORETICAL METHODS OF DETERMINING THE THERMAL CONDUCTIVITY OF GASES AND GAS MIXTURES.

The collection of experimental data on the thermal conductivity of gases and gas mixtures was begun in earnest in the late nineteenth century and since then many different techniques have been used, the more important of which are described briefly in sections 2.1 to 2.4 of this thesis. In section 2.5 an account of the technique used by Westenberg and de Haas is given in some detail because it was from this technique that the periodic line-source method was developed.

In section 2.6 a short account is given of how kinetic theory has been developed to enable the thermal conductivity of gases and gas mixtures to be calculated. For the comparatively simple case of a pure monatomic gas the theory has been very successful but for pure polyatomic gases and for gas mixtures, particularly polyatomic gas mixtures, the theory is much more complex, often not fully rigorous, and hence not too reliable.

The experimental techniques and the different theories described in this chapter are described very briefly. For more detailed information the reader should consult the references cited in this chapter, those given by Tsederberg (3) or Westenberg (4), or those given in the data book of the Thermophysical Properties Research Centre (5).
2.1 The cooling method.

This method was one of the earliest methods used for measuring the thermal conductivity of gases. It is an unsteady-state method, i.e. a method in which changes of temperature within the gas are measured as a function of time. In order to achieve this the gas under investigation is maintained in the apparatus at the desired temperature and a heated thermometer, perhaps a thermocouple, is immersed in the gas. The rate at which the heated thermometer cools down is used to determine the thermal conductivity of the gas. However, factors other than the thermal conductivity of the gas are also involved. Heat is transferred from the thermometer to the gas by convection and it is also transferred from the thermometer to the walls of the apparatus by radiation and by conduction along the stem of the thermometer. Since these factors depend upon the geometry of the apparatus it is not practicable to obtain absolute measurements of thermal conductivity by this means, so only relative measurements can be made.

This method has been used by many workers, one of the more notable being Wassiljewa (6), but it is no longer regarded as a very satisfactory method. It is considered to be inferior to the hot-wire and the parallel-plate thermal conductivity cells which superseded it, because it gives only relative measurements of thermal conductivity and with rather poor accuracy, especially at high temperatures.
2.2 The hot-wire method.

This method, which has several variations, has been used by many workers. Unlike the cooling method, it is a steady-state method, i.e. it involves the measurement of a steady temperature gradient which is set up in the test gas. The apparatus consists, essentially, of an electrically heated wire placed along the axis of a cylinder which is filled with the gas under investigation. The cylinder is placed in a constant temperature enclosure, heated to the desired temperature, and the central wire is used as a thermometer as well as a heater. Ideally, heat flow from the wire is purely radial, the flow from unit length of the wire in unit time being given by $Q$ where

$$Q = \frac{2\pi \lambda (T_1 - T_2)}{\ln(r_2/r_1)}, \quad 2.2.1$$

$\lambda$ is the thermal conductivity of the gas

$T_1$ is the wire temperature,

$T_2$ is the cylinder temperature,

$r_1$ is the radius of the central wire,

and $r_2$ is the inner radius of the cylinder.

This heat loss is equated to the measured electrical heat input per unit length of the wire in unit time and measurement of $T_1, T_2, r_1$ and $r_2$ enables the thermal conductivity $\lambda$ to be calculated.

The main disadvantage of this method is that heat is conducted along the central wire to the rest of the apparatus, resulting in a non-isothermal temperature distribution along the wire and non-radial flow of heat in the cell. However, provided that the cell is sufficiently long, there will be a limited region in the centre where this effect is negligible and where equation 2.2.1 may still be applied.
This fact was utilised by Schliermacher (7) when he designed the 'potential lead cell' in which two fine wires are used to measure the heat input to the central region of the wire.

Goldschmidt (8) used an alternative approach to avoid the errors due to end losses. This technique, the 'compensating tube method', involves making measurements on two cells which are identical except for their length so that the end losses can be eliminated. A further variation, known as the 'thick hot-wire cell', was introduced by Kannuluik and his colleagues (9). In this technique the ends of the central wire are kept at the same temperature as the cylindrical cell and the non-isothermal temperature distribution is corrected for theoretically. This approach requires the knowledge of various properties of the wire itself.

Further corrections are necessary with all variations of the hot-wire cell. A correction must be made for the heat loss from the wire by radiation. If the emissivity of the wire is known, this can be done using Stefan's law, but it is more common to determine the required correction by repeating the experiment with the cell evacuated. It is therefore necessary to keep the surfaces highly polished so that the radiation characteristics are constant.

Heat transfer from the wire can also take place due to convection and it is very difficult to make corrections for this. However, its effect can be minimised by using a narrow bore tube for the cell, by making the temperature difference between the cylindrical cell and the hot wire as small as possible, and by keeping the density of the gas as low as possible. This means that extra care should be taken when using this method to measure the thermal conductivity of high pressure
Another important effect, that of temperature jump, must also be corrected for. Kinetic theory indicates that a temperature discontinuity must exist at an interface between a solid surface and a gas in which there is a temperature gradient. Since this is a pressure dependent effect, the required correction can be determined by repeating the measurements at different pressures. The temperature jump is smallest at high pressures.

There are other effects for which small corrections may be necessary. The wall effect, which accounts for a small temperature difference between the inside and outside surfaces of the conductivity cell, and the effect of non-axiality of the hot wire are two such effects.

One problem which this method has in common with most steady-state methods arises from the fact that the thermal conductivity is calculated from measurements of a temperature gradient set up between the cylinder (temperature $T_2$) and the wire (temperature $T_1$). Thus, the value of the thermal conductivity obtained from the measurements is an average value for the temperature range $T_2$ to $T_1$. In principle, this problem can be overcome by repeating the measurements with reduced temperature gradients and extrapolating to find a value for zero temperature gradient. Experimentally, however, it is usually found that the reduced accuracy of measurements made with small temperature gradients prevents satisfactory conclusions from being reached.
2.3 The parallel-plate and similar methods.

The parallel-plate cell consists of two horizontal, plane surfaces, maintained at different temperatures, between which the gas being studied is enclosed. The upper plate is heated to a higher temperature than the lower plate to reduce convection, and guard rings are required to eliminate heat losses from the edges of the cell. The thermal conductivity is then calculated from the simple relation which follows from equation 1.3, namely

\[ Q = \frac{\lambda A (T_1 - T_2)}{d} \]  

where \( Q \) is the heat transferred in unit time,
\( A \) is the cross-sectional area of the gas layer,
\( d \) is the thickness of the gas layer,
\( T_1 \) is the temperature of the hot, upper plate,
and \( T_2 \) is the temperature of the colder, lower plate.

A correction must be applied for the heat transferred by radiation and this is done experimentally by repeating the experiment with the cell evacuated, just as in the hot-wire method.

The basic idea of this method is very simple but great care must be given to the construction of the apparatus if reliable results are to be obtained. The surfaces of the two plates must be flat to within a few microns and they must be accurately parallel, the separation of the plates being usually less than 1 millimetre. These conditions are not easily maintained when the apparatus is heated to high temperatures and this has meant that the use of the parallel-plate cell has been confined mainly to low temperature measurements, usually in the studies of the thermal conductivity of high pressure gases. The
parallel-plate cell is more suitable than the hot-wire cell for such studies because the effect of convection is much less in the parallel-plate cell. Michels and his collaborators (10) have used this type of cell at pressures up to 2500 atmospheres.

Another cell, the concentric cylinder cell (11), combines the principles of the parallel-plate and hot-wire cells. This cell has two concentric cylinders which are mounted vertically and the gas is introduced into the small annular gap between the cylinders. If the thickness of the gap is small compared with the length of the cylinder then the heat flow will be radial and the relevant equation will be the same as for the hot-wire cell (equation 2.2.1). The inner cylinder, or emitter, is heated electrically as in the hot-wire method and end guards are needed to reduce end corrections. The radiation correction is found experimentally, as before, and this also accounts for the heat which is conducted along the supports that keep the emitter positioned centrally.

A further development from the concentric cylinder method is the concentric sphere (12). In theory, this has the advantage of being a case of perfectly radial flow with no end corrections though it is difficult to obtain this in practice because of the problem of accurately positioning and supporting the inner sphere. A more successful method, used by Leidenfrost (13), is the concentric sphero-cylinder method. This consists of two concentric, vertical cylinders with two concentric hemispherical end sections at each end. This is regarded as being the best form of the basic concentric cylinder method.

The methods described so far have all been based on fairly similar lines. Many other, less conventional approaches to the problem have been tried by different workers with varying degrees of success. Some of these methods are described in the following section.
2.4 Other methods.

A method known as the hot-wire thermal diffusion column method has been introduced by Blais and Mann (14). The apparatus itself is similar to a hot-wire cell but the principle of operation is different. The hot wire is heated to a temperature of one or two thousand degrees centigrade and the thermal conductivity of the gas is determined at the temperature of the wire. With such large temperature gradients convectional heat transfer cannot be avoided but it is small, or even negligible, compared with the large amount of heat conducted radially due to the very large temperature gradient. Other corrections which need to be taken into account are those due to the non-uniform distribution of temperature along the wire, temperature jump, radiation and wall effects.

Peterson and Bonilla (15) have developed a technique, the frequency response technique, in which a thin hot wire is heated by an alternating current rather than the direct current of the conventional hot-wire cell. This has the effect of generating the third harmonic of the fundamental heating frequency, the magnitude of which is a measure of the thermal conductivity of the gas. The advantages of the method over the conventional hot-wire cell are that the radiation correction is less, the orientation of the wire in the cell is not important, differential temperature measurements are not necessary and the cell need not be maintained at a constant temperature. However, because of the difficulty of accurately measuring the dimensions of the very fine wire, the method is only suitable for relative measurements of thermal conductivity.

A rather similar technique, the transient hot-wire method, has
been developed by Briggs and his collaborators (16). The basic cell design is that of the conventional hot-wire cell. The principle of the method is to observe the increase in temperature of the wire as a function of time from the instant at which the heating current is switched on. The temperature of the wire is determined by measuring its resistance and the rate of increase of the temperature is used to calculate the thermal conductivity of the gas. The experiment requires complex electrical equipment to measure the rapid changes of temperature and numerous corrections are necessary to obtain accurate results. This type of experiment has also been performed by Haarman (17) who explains in detail all the necessary corrections and precautions. The technique seems to offer a very accurate method of measurement of the thermal conductivity but it has not yet been performed at high temperatures and it requires very careful experimentation.

Eckert and Irvine (18) used a method by which they determined the thermal conductivity by measuring the Prandtl number Pr, given by

\[ Pr = \frac{c\nu}{\lambda} \]

though this requires knowledge of the viscosity \( \nu \) and the specific heat at constant pressure \( c \). The Prandtl number was determined by passing the test gas through a convergent nozzle and measuring the temperature of the gas at two particular positions in the stream, these being i) upstream of the nozzle, where the gas velocity was low, and ii) at the exit from the nozzle, where the gas velocity was greatest.

Carnevale and his co-workers (19) have used an ultrasonic pulse technique which can be used to determine the thermal conductivity of
gases at temperatures much higher than would be possible with any method described above. The method involves measurement of the velocity of sound through the test gas, which enables the temperature to be found, and the measurement of the absorption of the sound, which enables the transport properties to be determined. With this method, measurements can be made on gases at temperatures as high as 17,000°K.

Another method, which is used at very high temperatures, is the shock-tube method. This method has been used by many workers, among them Rolinski and Zakanycz (20) and Freidman and Fay (21). Measurements are made of the rate of heat transfer from the shock heated gas to the end wall of the shock tube. This rate of heat transfer is related to the thermal conductivity of the gas, though other factors are also involved. The temperature variation with time is monitored using thin film resistance thermometers, this being necessary because the short duration of the shock (<1μsec) necessitates the use of instrumentation capable of exceedingly rapid response.

A third method used for measurement at very high temperatures is the arc method (22) and (23). An electric arc, burning in the high temperature gas, enables the thermal conductivity to be found by equating the electrical energy supplied to a volume element in the gas to the heat lost from this volume element, this being due largely to the conduction of heat through the gas.

This completes the summary of many of the methods which have been used in the past to determine the thermal conductivity of a gas by experiment. One method, in particular, has not yet been described, the line-source method. This method, because of its relevance to this thesis, is given more detailed coverage in the next section.
2.5 The line-source method.

This method was developed by Westenberg and de Haas (2) and used by them to measure the thermal conductivity of various gases and gas mixtures up to temperatures of approximately 1200°K. It will be useful to consider the method in detail since the experiment described in this thesis is closely related to this technique. Indeed, the original intention was to use this technique, just as described by Westenberg and de Haas, but the problems which were encountered led to considerable modifications being made, resulting in the development of the periodic line-source method.

The basic idea of the line-source method is to measure the thermal wake resulting from a line source of heat placed in a uniform flow of heated gas. Knowledge of the shape of the thermal wake and the velocity of the gas enables the thermal conductivity, or more correctly, the thermal diffusivity, to be calculated from the theoretical relations. The required relations were first obtained by Wilson (24) and can be explained with reference to figure 2.5.1. The line source of heat is assumed to be of infinite length, perpendicular to the plane of the paper, and the gas is assumed to flow with a uniform velocity \( u \). The temperature at any point \( r \), where \( r = (x^2 + y^2)^{1/2} \), downstream from the source is given by \( T \), where

\[
T = T_0 + \Delta T \tag{2.5.1}
\]

and \( \Delta T = (q/\rho c) (4\pi \kappa ur)^{-\frac{3}{2}} \exp[(x-r)u/2\kappa], \)

\( T_0 \) being the temperature of the gas before passing over the wire, \( q \) being the heat transfer rate per unit length from the source to the gas and \( \rho \), \( c \), and \( \kappa \) being as defined in equation 1.4. This solution is
Figure 2.5.1

The temperature distribution resulting from a line source of heat in a flowing gas.
valid only for values of ur/2K≈1, a condition which is easily satisfied experimentally.

If the restriction y = 0 is imposed on equation 2.5.1, then r = x and ΔT takes the maximum value ΔT_{max} for that particular value of x. The expression for ΔT_{max} is

$$\Delta T_{max} = \frac{q}{\varepsilon c} \left(\frac{4\pi k u x}{x}\right)^{-\frac{1}{2}}.$$  \hspace{1cm} 2.5.2

This result alone could be used to determine the thermal conductivity, but it contains one quantity, q, which is very difficult to measure. Experimentally, the line source of heat is most conveniently a very fine platinum wire which is electrically heated. To determine the value of q, the heat transfer rate from the wire to the gas per unit length of the wire, it is necessary to know the power input to the wire and also the power lost by radiation from the wire, the latter being particularly difficult to determine at high temperatures.

Westenberg and de Haas avoided this problem by making a second measurement, at the same height x, where the temperature ΔT was observed to be one half of ΔT_{max}. This position, which is referred to as r_h, obviously satisfies the relation

$$\Delta T = \frac{1}{2} \Delta T_{max} = \frac{q}{\varepsilon c} \left(\frac{4\pi k u r_h}{x}\right)^{-\frac{1}{2}} \exp\left[\frac{(x - r_h)u}{2K}\right]$$

and combining this relation with equation 2.5.2 and rearranging, gives

$$\kappa = \frac{(r_h - x)u}{\ln(4x/r_h)}.$$  \hspace{1cm} 2.5.3

This equation can be used to calculate the thermal diffusivity of the gas. The required measurements are those of distance, gas velocity, and relative temperature. The fact that only relative temperature
measurements are required is a great advantage of the method because it is always difficult to make absolute temperature measurements at high temperatures.

The method used by Westenberg and de Haas to measure the gas velocity was that developed by Walker and Westenberg (25). This method, with minor modifications, is also used for the periodic line-source method. The equation which enables the velocity of the gas to be calculated can be derived from the theory of the periodic line-source. This shows that the equation given by Walker and Westenberg is not entirely satisfactory but that it can be corrected by the inclusion of an extra term which is usually quite small. The theoretical details of this method of velocity measurement are given in section 3.2 and the practical details are given in section 4.1 b) of this thesis.

The line-source method has many advantages over most of the techniques which have been described in the preceding sections. The influence of radiation and convection, other than the forced convection of the gas flowing past the wire upon which the technique relies, is negligible. Furthermore, it is not necessary to make any corrections for such things as temperature jump and end effects. However, the technique does have practical disadvantages. Two of the most troublesome practical problems which were encountered when measurements of thermal conductivity, by means of this technique, were attempted in the British Gas Corporation laboratories, are described below.

The first problem was that, due to the poor stability of the temperature wake, the measurement of the temperature distribution was very difficult. It was found that the maximum temperature $\Delta T_{\text{max}}$ could be measured satisfactorily, the fluctuations in temperature
being quite small because the temperature gradient at \( y = 0 \) must, obviously, be very small. However, the measurements at \( r = r_h \) were subject to large fluctuations in temperature because of the large temperature gradients at these points.

The second problem was associated with the measurement of the variable \( x \). Westenberg and de Haas used a method which was to make measurements in the \( x \) direction on a scale with an arbitrarily located origin and then to determine, at a later stage, the necessary correction term which had to be added or subtracted in order that the measurements of \( x \) should refer to the position relative to the source wire. There are two ways, apart from direct measurement with a traveling microscope, in which this correction term can be determined.

The first makes use of equation 2.5.2, from which it is clear that a plot of \( \Delta T_{\text{max}}^{-2} \) against \( x \) should give a straight line passing through the origin of the graph. By plotting this graph, the required correction term can be obtained by measuring the intercept on the \( x \) axis. The second method makes use of equation 2.5.3, from which it is clear that the value of \( (r_h - x)/\ln(4x/r_h) \) should be a constant when \( x \) and \( r_h \) are the only experimental variables. A search may easily be made to determine the correction for \( x \) which results in a constant value for this term. The second method was preferred by Westenberg and de Haas.

A problem arose when it was found that these two methods gave considerably different values for the correction term. This may well be due to variations in the velocity and thermal diffusivity of the gas, assumed in the theory to be constant, caused by the presence of the heated source wire. Of the two methods suggested above, the first
seems to offer the best method of finding the required correction term because any curvature of the graph, due to the variation $u$ and $K$, could be observed, and its effect estimated. The second method could not be used with any confidence because the ratio $(K/u)$ could vary slowly with $x$. Using this method to find the required correction term for $x$ may amount to minimising the experimental errors illegitimately by the appropriate selection of the correction term. Furthermore, the value obtained by this method, being slightly different from the true value, would cause the calculated value of the thermal diffusivity to be in error by a small amount.

These two problems, difficulty in the determination of $r^h$ and the uncertainty of the values of $x$, can be overcome, as will be shown in this thesis, by replacing the steady line source of heat by a source which varies periodically with time. With this improvement, it is no longer necessary to know absolute values of the variable $x$ which means that a scale with an arbitrarily located origin can be used and no correction term is needed. Furthermore, it is sufficient to make measurements at positions where $y = 0$ only. Thus, measurements are always made where the temperature gradient is small and where the signal is consequently more stable. In addition to overcoming these two problems, the periodic line-source method also has an advantage in that it involves measurement of a.c. signals. The accurate measurement of small a.c. signals in the presence of noise can be achieved quite easily whereas small d.c. signals are more difficult to deal with.

The periodic line-source method retains all the advantages of the steady line-source method and overcomes many of the disadvantages.
2.6 Calculation of values of thermal conductivity from kinetic theory.

a) Single monatomic gases.

The rigorous kinetic theory of dilute monatomic gases is now well established, though it is a very complicated theory. Enskog (26), Grad (27), Chapman and Cowling (28) and many other workers have made significant contributions to this theory, an excellent account of which is given by Hirschfelder, Curtiss and Bird (1). The theory has enabled the transport coefficients to be expressed in terms of a set of integrals $\Omega^{(1,s)}$, which are defined by equation 7.4-34 of reference (1). These integrals involve the dynamics of a molecular collision and it is necessary to know the intermolecular force law in order to evaluate them. Present knowledge of intermolecular forces is incomplete but, despite this, many model potential functions have been used to evaluate the $\Omega^{(1,s)}$ integrals, thereby enabling the transport coefficients to be calculated. One of the simplest models, the rigid sphere model, results in transport coefficients which, in some cases, agree quite well with experimental values. A more successful model function is the Lennard-Jones (6-12) potential. This potential has been used extensively, though it is not necessarily regarded as being the best known fit to the real potential. Other functions have been used, some of which have been mathematically quite complex, but the resulting values of the $\Omega^{(1,s)}$ integrals differ only slightly from values obtained using the Lennard-Jones (6-12) function, which has therefore remained popular because of its simplicity.

The form of the Lennard-Jones function is given by $\phi(r)$ where

$$\phi(r) = 4\varepsilon \left[ (\sigma/r)^{12} - (\sigma/r)^6 \right].$$

2.6.1
A sketch of the function is shown in figure 2.6.1. The two parameters σ and ε are characteristic of the molecule concerned, σ being the zero velocity collision diameter and ε being the depth of the potential well. The term \((σ/r)^{12}\) represents the short range, strongly repulsive forces between molecules and the term \((σ/r)^6\) represents the longer range, weakly attractive forces. The values of the \(\sigma^{1,6}\) integrals for the Lennard-Jones potential are readily available from tables (1). They are usually expressed as a function of the reduced temperature \(T^*\), where \(T^* = kT/\varepsilon\), k being the Boltzmann constant and T the temperature in degrees K. Furthermore, the values of the integrals are generally

![Figure 2.6.1](image)

**Figure 2.6.1**

The Lennard-Jones (6-12) potential.
quoted relative to the values calculated using the rigid sphere model, i.e. they are given as \( \Omega^{(1, s)} \) where

\[
\Omega^{(1, s)} = \left[ \Omega^{(1, s)} \right] / \left[ \Omega^{(1, s)} \right]_{\text{rig, sph.}}.
\]

Using the tabulated values of \( \Omega^{(1, s)} \) and suitable values of \( \sigma \) and \( \epsilon \), the transport coefficients can be calculated from the theoretical equations. These theoretical equations consist of a series of approximations to the exact coefficients but, for most purposes, the first approximation is sufficiently accurate.

The coefficient of thermal conductivity for a single monatomic gas is given, in the first approximation, by

\[
\lambda = \frac{3}{8} \frac{k}{M} \frac{\pi k T}{m} \frac{1}{\sigma^2 \Omega^{(2, 2)}}
\]

where \( m \) is the mass of the atom concerned. In practical units, this equation can be rewritten as

\[
\lambda = 1989.1 \times 10^{-7} \left( \frac{T}{M} \right)^{\frac{1}{2}} \sigma^2 \Omega^{(2, 2)}.
\]

where

- \( \lambda \) = the thermal conductivity in cal. cm.\(^{-1}\) sec.\(^{-1}\) °K\(^{-1}\)
- \( T \) = the temperature in degrees K
- \( M \) = the molecular weight
- \( \sigma \) = the collision diameter in Ångstrom units.

Likewise, the coefficient of viscosity of a single monatomic gas is given, in the first approximation, by

\[
\eta = \frac{5}{4} \frac{k}{M} \frac{\pi k T}{m} \frac{1}{\sigma^2 \Omega^{(2, 2)}}
\]

and, by combining this equation with equation 2.6.2, a simple expression for the ratio \((\lambda/\eta)\) can be obtained. This expression is
\[ \frac{\lambda}{\gamma} = \frac{15}{4} \left( \frac{k}{m} \right) = \frac{15}{4} \left( \frac{R}{M} \right) \]

where \( R \) is the gas constant. This relationship is independent of the force law provided that the basic kinetic theory assumptions are valid, i.e. only elastic collisions occur and only central forces exist.

The above equations give quite good agreement with experimental values for both the thermal conductivity and the viscosity of monatomic gases when the appropriate values of \( \sigma \) and \( \epsilon \) are used. The viscosity equation can also be used for polyatomic gases with reasonable success though, in the case of strongly polar gases, the Lennard-Jones (6-12) potential is obviously inadequate. The thermal conductivity equation, however, cannot be used for polyatomic gases because polyatomic gases have internal degrees of freedom in which energy can be transported, a fact which has been ignored in the theory of monatomic gases because monatomic gases have no internal degrees of freedom.
2.6 b) Single polyatomic gases.

In the previous section a brief description of the kinetic theory of monatomic gases was given and a relationship between the thermal conductivity and the viscosity of such gases was obtained. This relationship, given by equation 2.6.5, can be written in the more general form

\[ \lambda \frac{M}{\eta} = f C_v \] 2.6.6

where \( C_v \) is the heat capacity per mole, measured at constant volume, and \( f \) is a pure number. For a monatomic gas \( C_v = \frac{3}{2}R \) and \( f \) is almost exactly equal to \( \frac{5}{2} \). However, for polyatomic gases, the values of both \( \lambda \) and \( C_v \) are affected by the presence of internal degrees of freedom of the molecules and the value of \( f \) required to satisfy equation 2.6.6 is no longer equal to \( \frac{5}{2} \).

It was suggested by Eucken (29) that a more general form of equation 2.6.6 would be

\[ \lambda \frac{M}{\eta} = f(tr) C_v(tr) + f(int) C_v(int) \] 2.6.7

where the labels \( (tr) \) and \( (int) \) are used to refer to the contributions due to the translational degrees of freedom and the internal degrees of freedom respectively. The task then becomes that of finding expressions for \( f(tr) \) and \( f(int) \) which will satisfy equation 2.6.7 when applied to a polyatomic gas. The value of \( C_v(tr) \) can be put equal to \( \frac{3}{2}R \), as for a monatomic gas, and the value of \( C_v(int) \) can be found from experimental values of \( C_v \) and application of the equation

\[ C_v = C_v(tr) + C_v(int) \] 2.6.8
or

\[ C_v(\text{int}) = C_v - (3/2)R. \]  \hspace{1cm} 2.6.9

Eucken further suggested, though without any rigorous theoretical basis, that \( f(\text{tr}) \) be given the value of \((5/2)\), as for monatomic gases, and \( f(\text{int}) \) the value of unity. Introducing these values into equation 2.6.7 gives

\[ \lambda M/\n = f_{\text{Eucken}} C_v \]  \hspace{1cm} 2.6.10

where \( f_{\text{Eucken}} = 1 + 9R/4C_v \)

This expression was found to give reasonable agreement with experimental results at temperatures in the region of \(0^\circ C\) but at lower and higher temperatures the agreement was less good. Experiments suggested that \( f(\text{int}) \) should be temperature dependent and have a value ranging from 0.7 at \(80^\circ K\) to about 1.3 at \(380^\circ K\) or higher. It was later suggested (ref. (28) pp 238-240) that transport of internal energy was by a diffusive mechanism and that a better value for \( f(\text{int}) \) might be that obtained from the expression

\[ f(\text{int}) = \varrho D/\n \]  \hspace{1cm} 2.6.11

where \( D \) is the self diffusion coefficient and \( \varrho \) the density of the gas. The value of \( f(\text{int}) \) obtained from this expression is approximately 1.3 and is virtually independent of temperature. Consequently, it gives good agreement with experimental results at high temperatures but it is even worse than the simple Eucken expression at low temperatures.

It is only fairly recently, nearly 50 years after Eucken's suggestions, that rigorous theory has been applied to this problem.
Wang Chang and Uhlenbeck (30), along with de Boer (31) and Taxman (32),
developed a kinetic theory for polyatomic gases which takes inelastic
collisions into account. This theory involves very complex equations,
many of which, with present knowledge, can only be solved by making
suitable approximations. Mason and Monchick (33) applied this theory
to the problem in question. As a first approximation they ignored the
inelastic contributions and found that this led to a value of (5/2)
for $f(\text{tr})$ and a value of $(g D/\eta_1)$ for $f(\text{int})$. This provided theoretical
justification for the earlier assumptions. In order to obtain a better
approximation, Mason and Monchick went on to include the inelastic
collisions, though certain approximations were still necessary.

Before quoting the results of this second approximation, it is
necessary to define many of the terms which appear in the equations.
A collision number (or relaxation number) $Z_i$ is used as a measure of
the extent of the interaction between the energy modes. It is often
poorly defined, though Ganzi and Sandler (34) have given an exact
definition which indicates that, on average, $Z_i$ bimolecular collisions
are required for the difference between the energy in the $i$th mode
and its equilibrium value to decrease by a factor of $1/2.712$ i.e. by
a factor of $1/e$. A diffusion coefficient $D_i$ is used to represent the
diffusion of internal energy in the $i$th mode. Mason and Monchick have
pointed out that, in many cases, $D_i$ will be nearly equal to the
ordinary self-diffusion coefficient $D$, but that this will not be the
case if resonant collisions can occur, as in the case of polar gases.
They also defined an average diffusion coefficient, $D'(\text{int})$, such that

$$D'(\text{int}) = C_v(\text{int}) \left( Z_i C_i/D_i \right)^{-1}$$

2.6.12
where \( C_i \) is the heat capacity per mole, measured at constant volume, associated with the energy of the \( i \)th mode, it being further assumed that the internal energy modes are completely uncoupled such that

\[
C_v^{(\text{int})} = \sum_i C_i. \quad 2.6.13
\]

The ratio \( C_v^{(\text{int})}/Z \) is defined in a form similar to equation 2.6.12, resulting in the equation

\[
C_v^{(\text{int})}/Z = \sum_i (C_i/Z_i). \quad 2.6.14
\]

Using these definitions, the equations derived by Mason and Monchick can be written as

\[
f(tr) = \frac{5}{2} \left[ 1 - \frac{2}{\pi} \left( \frac{A}{B} \right) \left\{ C_v^{(\text{int})}/Z \right\} \left\{ C_v^{(tr)} \right\}^{-1} \right] \quad 2.6.15
\]

and

\[
f(int) = \left[ \frac{\varphi D'(int)/\eta}{\left[ 1 + \frac{2}{\pi} \left( \frac{A}{B} \right) \left\{ C_v^{(int)}/Z \right\} \left\{ C_v^{(int)} \right\}^{-1} \right] \right] \quad 2.6.16
\]

where

\[
A = \frac{5}{2} - \frac{\varphi D'(int)/\eta}{2.6.17}
\]

and

\[
B = 1 + \frac{2}{\pi} \left\{ C_v^{(int)}/Z \right\} \left[ \frac{(5/3)}{\varphi D'(int)/\eta} \right] \quad 2.6.18
\]

Mason and Monchick expressed their result in a slightly different form to that given above, their equations being a slightly less exact version of the above equations, obtained by setting \( B = 1 \), an approximation which is valid for large values of \( Z \). The form of the equations given above resembles that given by Monchick, Pereira and Mason (35) and by Sandler (36).

The above equations for \( f(tr) \) and \( f(int) \) can be substituted into equation 2.6.7 to give the equation
This is the general form of the equation which relates the thermal conductivity to the viscosity of polyatomic gases. However, it is usual to consider only two modes of internal energy, these being the rotational and the vibrational modes. Consequently, equation 2.6.14 can be written as

\[ \frac{C_y(\text{int})}{Z} = \frac{C_y(\text{rot})}{Z(\text{rot})} + \frac{C_y(\text{vib})}{Z(\text{vib})} \]  \hspace{1cm} (2.6.20)

and since, for most gases, \( Z(\text{vib}) \gg Z(\text{rot}) \), equation 2.6.20 can be adequately approximated by

\[ \frac{C_y(\text{int})}{Z} = \frac{C_y(\text{rot})}{Z(\text{rot})} \]  \hspace{1cm} (2.6.21)

Furthermore, from equations 2.6.12 and 2.6.13,

\[ D'(\text{int}) = C_y(\text{int}) \left[ \frac{C_y(\text{rot})}{D(\text{rot})} + \frac{C_y(\text{vib})}{D(\text{vib})} \right]^{-1} \]  \hspace{1cm} (2.6.22)

and

\[ C_y(\text{int}) = C_y(\text{rot}) + C_y(\text{vib}) \]  \hspace{1cm} (2.6.23)

As mentioned earlier, the values of \( D(\text{rot}) \) and \( D(\text{vib}) \) can often be approximately equated to the self-diffusion coefficient \( D \). This approximation may, in some cases, be rather poor but, because of the lack of knowledge of values of \( D(\text{rot}) \) and \( D(\text{vib}) \), there is often no better alternative. Sandler (36) has studied this problem and has proposed that a better approximation for \( D(\text{rot}) \) can be obtained by putting

\[ D(\text{rot}) = gD \]  \hspace{1cm} (2.6.24)

where

\[ g = 1 + 0.27/Z(\text{rot}) - 0.44/Z(\text{rot})^2 - 0.90/Z(\text{rot})^3 \]  \hspace{1cm} (2.6.25)
This equation was derived for a linear diatomic molecule so its validity for other types of molecule is doubtful. However, it does indicate that, for large values of \( Z(\text{rot}) \), the value of \( D(\text{rot}) \) is approximately equal to that of \( D \).

Upon substituting \( D(\text{rot}) = gD \) and \( D(\text{vib}) = D \) into equation 2.6.22, an expression for \( D'(\text{int}) \) is obtained which, together with equation 2.6.21, can be substituted into equation 2.6.19 to give

\[
\frac{\gamma M}{\pi R} = \left( \frac{15}{4} \right) + \left( \frac{gD}{\gamma} \right) \left\{ \frac{C_v(\text{int})}{R} \right\} g C_v(\text{int}) \left[ C_v(\text{rot}) + g C_v(\text{vib}) \right]^{-1}
\]

\[- \left( \frac{2}{\pi} \right) \left( A^2 / B \right) \left[ \frac{C_v(\text{rot})}{Z(\text{rot})} \right] R^{-1} \quad 2.6.26\]

where \( C_v(\text{tr}) \) has been put equal to \( (3/2) R \). The expressions for \( A \) and \( B \), given by equations 2.6.17 and 2.6.18, can now be written as

\[
A = \left( \frac{5}{2} \right) - \left( \frac{gD}{\gamma} \right) g C_v(\text{int}) \left[ C_v(\text{rot}) + g C_v(\text{vib}) \right]^{-1} \quad 2.6.27
\]

and

\[
B = 1 + \left( \frac{2}{\gamma} \right) \left\{ \frac{C_v(\text{rot})}{Z(\text{rot})} \right\} R^{-1} \left[ \left( \frac{5}{3} \right) + \left( \frac{gD}{\gamma} \right) R \left[ C_v(\text{rot}) + g C_v(\text{vib}) \right]^{-1} \right] \quad 2.6.28
\]

In order to calculate the thermal conductivity of a polyatomic gas using equation 2.6.26, several other properties of the gas need to be known. The viscosity \( \gamma \) can be obtained from results of experiment or, if the required value is not available, the simple theory for the viscosity of monatomic gases can be used (equation 2.6.4) since the influence of the internal degrees of freedom of the molecules upon the viscosity of the gas is small. The monatomic theory can only be used in this way for non-polar gases, though Monchick and Mason (37) have extended the monatomic theory to enable the viscosity of polar gases to be calculated.
The value of the self-diffusion coefficient appearing in equation 2.6.26 is also needed before the thermal conductivity can be calculated. However, accurate values of D are often difficult to obtain but, with the aid of equation 8.2-48 of reference (1), it is possible to replace the factor \((gD/\eta)\) by \((6/5)A^*\) where \(A^*\) is defined (equation 8.2-15) and tabulated in reference (1). It is clear, from this tabulation, that \(A^*\) is a very slowly varying function of temperature; for the Lennard-Jones (6-12) potential its value is approximately 1.1.

The remaining quantities which are needed for use in equation 2.6.26 are those of \(C_V\) (rot), \(C_V\) (vib) and \(Z\) (rot). The values of \(C_V\) (rot) and \(C_V\) (vib) can be calculated using the appropriate thermodynamic equations but it is often not necessary to do this because, in most cases, \(C_V\) (rot) is simply equal to \(\frac{1}{2} nR\) where \(n\) is the number of rotational degrees of freedom of the molecule. Knowing this, and using the fact that \(C_V\) (tr) = \((3/2)R\), the value of \(C_V\) (vib) can be determined from experimental values of \(C_V\) using equations 2.6.8 and 2.6.23. This leaves only the collision number \(Z\) (rot) to be determined. It is the most difficult factor in equation 2.6.26 to determine because most measurements of \(Z\) (rot) have been made at, or near, room temperature, and even then, with rather poor accuracy. Parker (38) has obtained, theoretically, a relation which gives the temperature dependence of \(Z\) (rot) for a homonuclear, diatomic molecule, the relation being

\[
Z(\text{rot}) = Z(\text{rot})^\infty \left[ 1 + \frac{1}{2} \frac{3/2}{(T^*)^{-1/2}} + \frac{\pi^2}{4} + \pi (T^*)^{-1} \right]^{-1} \tag{2.6.29}
\]

where \(Z(\text{rot})^\infty\) is the limiting value of \(Z(\text{rot})\) at very high temperatures.

The best method of assigning a value to \(Z(\text{rot})\) is to use Parker's formula, where applicable, with the most reliable experimental results.
available. Parker has suggested that, if suitable adjustments to the formula are made, it may be possible to use equation 2.6.29 for certain molecules which are not diatomic. He has proposed, for example, that carbon dioxide can be considered as being an elongated oxygen molecule and the scaling parameters can be adjusted accordingly to give a suitable value of $T^*$. 

Despite the problem of not being able to find an accurate value for $Z(\text{rot})$ it is still possible to use equation 2.6.26 to calculate reasonably accurate values of thermal conductivity because, except at very small values of $Z(\text{rot})$, $(\Lambda M/\eta R)$ is only a very slowly varying function of $Z(\text{rot})$. As an example of this, the thermal conductivity of nitrogen at 500 K would increase by just over 1% if $Z(\text{rot})$ was increased from 5 to 50. This serves to illustrate that it is not possible to calculate rotational relaxation numbers by measurement of thermal conductivity unless the measurements can be made with extremely high accuracy.

Though the Mason-Monchick theory often gives reasonably good predictions of the thermal conductivity of polyatomic gases there are other theories which can often be applied equally successfully. Saxena, Saksena and Gambhir (59) have developed such a theory, though it is only applicable to gases with one relaxation time and it is not as rigorous as the Mason-Monchick theory. Gambhir (40) however, has extended this theory to cover gases with more than one relaxation time and has obtained the expression

\[
\frac{\Lambda M}{\eta R} = \frac{15}{4} + (\varepsilon D/\gamma) \left[ C_\text{v}(\text{int})/R \right] - (3/2) \left( 5/2 - \varepsilon D/\gamma \right) \varepsilon \left[ \frac{C_1}{C_\text{v}(\text{tr})} + \frac{1}{C_1} \left[ 1 - \exp - \frac{C_\text{v}(\text{tr}) + C_1}{Z_1 C_\text{v}(\text{tr})} \right] \right] \]

2.6.30
By considering only the rotational and vibrational modes and using the fact that $Z(\text{vib})$ is very large, it is possible to rewrite equation 2.6.30 in the form

$$\frac{\lambda M}{\pi R} = \frac{15}{4} + \left(\frac{eD}{\eta}\right)\left[\frac{C_v(\text{int})}{R}\right] -$$

$$\left(\frac{3}{2}\right)\left(\frac{5}{2} - \frac{eD}{\eta}\right)\left[\frac{C_v(\text{rot})}{C_v(\text{tr}) + C_v(\text{rot})}\right]\left[1 - \exp\left(-\frac{C_v(\text{tr}) + C_v(\text{rot})}{Z(\text{rot}) C_v(\text{tr})}\right)\right]$$

$$\ldots \quad 2.6.31$$

This equation also gives quite close agreement with experimental results. However, the Mason-Monchick equation has an advantage over this equation in that its derivation is more rigorous. Furthermore, Sandler (36) has made a test of the various formulae available from which he was able to conclude that the Mason-Monchick formula appears to be the best. Sandler's test was carried out using model calculations rather than experimental results because the scatter of experimental results was found to be too large. Thus, for the purpose of this thesis, the Mason-Monchick equation is selected as being the most suitable equation for calculating the thermal conductivity of a pure polyatomic gas so equation 2.6.26 is used in chapter VI to make a comparison between the experimental results and theoretically predicted values.
2.6. c) Gas mixtures. (Monatomic and polyatomic).

The formulation of equations for calculating the thermal conductivity of gas mixtures has proved to be very difficult, particularly for polyatomic mixtures. For monatomic mixtures, where only translational energy is involved, the theory is much more successful though it is often necessary to use empirical laws to evaluate the force constants, $\varepsilon$ and $\sigma$, which are required to describe the interactions between pairs of unlike molecules. For polyatomic mixtures the theory is extremely complicated and it is normal practice to make suitable approximations to simplify the equations.

Hirschfelder, Curtiss and Bird (1) have given an equation for calculating the thermal conductivity of mixtures of monatomic gases. Their result is a first approximation to the thermal conductivity and is a rather formidable equation which involves the thermal diffusion constants of the gases concerned. These thermal diffusion terms make only a small contribution to the complete equation and, if they are ignored, the equation can be considerably simplified. Muckenfuss and Curtiss (41) have calculated the second approximation for the thermal conductivity of mixtures of monatomic gases and have found that this is exactly equal to the simplified form of the first approximation.

Their equation, for a mixture of $n$ components, is

$$\lambda(\text{mon}) = 4 \left| \begin{array}{cccc} L_{11} & L_{12} & \cdots & L_{1n} \\ L_{21} & L_{22} & \cdots & L_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ L_{n1} & L_{n2} & \cdots & L_{nn} \end{array} \right| x_1 \left| \begin{array}{cccc} L_{11} & L_{12} & \cdots & L_{1n} \\ L_{21} & L_{22} & \cdots & L_{2n} \\ \vdots & \vdots & \ddots & \vdots \\ L_{n1} & L_{n2} & \cdots & L_{nn} \end{array} \right|$$

$$\times x_2 \times \cdots \times x_n$$

2.6.32
where \( I_{ij} = (2x_i x_j M_i M_j) (55/4 - 3B_{ij}^* - 4A_{ij}^*) \div \)
\[ (M_i + M_j)^2 A_{ij}^* \lambda_{ij} \quad \text{for } i \neq j \] 2.6.33
and \( I_{ii} = -4x_i^2/\lambda_i \)
\[ \sum_{k \neq i} \frac{2x_i x_k (15 M_i^2/2 + 25M_k^2/4 - 3B_{ik}^* M_k^2 + 4A_{ik}^* M_k M_i)}{(M_i + M_k)^2 A_{ik}^* \lambda_{ik}} \] 2.6.34

In these equations, \( \lambda_{ij} \) can be obtained either theoretically, using a modified version of equation 2.6.2, namely
\[ \lambda_{ij} = (75k/64)[(m_i + m_j)\pi kT/2m_i m_j]^{1/2} [\pi \sigma_{ij}^2 \Omega_{ij}^{(2,2)*}]^{-1} \] 2.6.35
or by using experimental binary diffusion coefficients, if they are available, and the relation, given by equation 8.2-38 of reference (1),
\[ \lambda_{ij} = (25/8)(p/T)(D_{ij}/A_{ij}^*) \] 2.6.36

where \( D_{ij} \) is the binary diffusion coefficient and \( p \) the pressure of the gas.

In the above equations, \( x_i \) is the mole fraction of the \( i \)th component of the mixture and \( M_i \) is the molecular weight of the \( i \)th component. The terms \( A_{ij}^* \) and \( B_{ij}^* \) are the ratios of collision integrals and are defined by equations 8.2-15 and 8.2-16 of reference (1). The collision integrals themselves, such as \( \Omega_{ij}^{(2,2)*} \), are evaluated with the appropriate force constants \( \sigma \) and \( \varepsilon \) which describe the shape of the intermolecular potential for the two molecular species concerned.

The required values of the force constants can be obtained from measurements of diffusion in a binary gas mixture consisting of these two species or, if such measurements have not been made, a semi-empirical
combining rule is used. Such a combining rule relates the force constants for a collision between two unlike molecules to the individual force constants which are used for collisions between like molecules. The most commonly used combining rule, which has some theoretical justification, is

\[ \sigma_{ij} = \frac{1}{2}(\sigma_i + \sigma_j) \quad \text{and} \quad \varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{\frac{1}{2}}. \quad 2.6.37 \]

Tables of collision integrals, evaluated for many different potential functions, and values of \( \sigma \) and \( \varepsilon \) are quoted in appendix IA of reference (1). The use of these values and the application of the above equations enables the thermal conductivity of mixtures of monatomic gases to be calculated. The results of such calculations generally give reasonable agreement with experimental values.

The labour involved in calculating the values of the determinants in equation 2.6.32 can be quite tedious for multicomponent mixtures. However, for binary mixtures equation 2.6.32 can be reduced to

\[ \lambda(\text{mon}) = 4\left[ x_1 x_2 (L_{12} + L_{21}) - x_1^2 L_{22} - x_2^2 L_{11} \right] \div \]

\[ (L_{11} L_{22} - L_{12} L_{21}). \quad 2.6.38 \]

Furthermore, as will be obvious from equation 2.6.33, \( L_{12} = L_{21} \).

For polyatomic gases the above equations are not adequate because they do not consider the possibility of contributions to heat conduction arising from the internal energy of the molecules. Eucken's suggestion, discussed in section 2.6 b), of considering the translational and internal contributions to be quite separate, has been utilised by Hirschfelder (42). He suggested that the translational contribution should be calculated according to the theory for monatomic gases and
he derived an equation for calculating the contribution due to the internal degrees of freedom. The resulting equation for the thermal conductivity of a polyatomic gas mixture is known as the Hirschfelder-Eucken equation and can be written as

\[ \lambda = \lambda(\text{tr}) + \lambda(\text{int}) \]

where \( \lambda(\text{tr}) = \lambda(\text{mon}) \) as given by equation 2.6.32

and \( \lambda(\text{int}) = \sum_{i} \lambda_{i}(\text{int}) / \left[ 1 + \sum_{j} \frac{x_{i} D_{i}(\text{int})}{x_{j} D_{j}(\text{int})} \right] \).

This equation requires knowledge of the diffusion coefficients for internal energy but, since such information is generally unavailable, it is usual to put these coefficients equal to the ordinary diffusion coefficients. It is not easy to estimate the error caused by this approximation but it is likely to be small in many cases.

Monchick, Yun and Mason (43) have applied the rigorous kinetic theory of Wang Chang and Uhlenbeck (30) to this problem and obtained, to a first approximation, the above equations for \( \lambda(\text{tr}) \) and \( \lambda(\text{int}) \). This provided some justification of the Hirschfelder-Eucken equation, an equation which was derived using a less rigorous approach. Following this Monchick, Pereira and Mason (35) carried the rigorous approach to the second approximation and obtained a correction term \( \Delta \lambda \) which should be added to the Hirschfelder-Eucken equation. The term \( \Delta \lambda \) is mathematically extremely complicated and is not given here, but the reader is referred to equation 78 of reference (35) if he should wish to investigate further. The value of \( \Delta \lambda \) is usually very small and can be positive or negative. Because it is so small it is usually adequate to use the Hirschfelder-Eucken equation for comparison with experimental
There is a variety of ways in which the Hirschfelder-Eucken equation can be used, according to how the values for the pure components, $\lambda_{1}(tr)$ and $\lambda_{1}(int)$, are selected. Hirschfelder originally recommended that $\lambda_{1}(tr)$ should be calculated using equations which were derived for monatomic gases. Thus, if experimental values of the coefficient of viscosity are available, equation 2.6.5 should be used or, failing this, equation 2.6.2 should be used. Having calculated a value of $\lambda_{1}(tr)$, it has become common practice to select a value of $\lambda_{1}(int)$ such that

$$\lambda_{1}(int) + \lambda_{1}(tr) = \lambda_{1}(expt) \tag{2.6.41}$$

where $\lambda_{1}(expt)$ is the value of the thermal conductivity obtained by experiment.

This definition of $\lambda_{1}(int)$ ensures that the value of $\lambda$ which is calculated using equation 2.6.39 for the particular case of $x_{1} = 1$, is equal to the value observed by experiment. Indeed, this condition will be satisfied by any values of $\lambda_{1}(int)$ and $\lambda_{1}(tr)$ which satisfy equation 2.6.41. If an experimental value is not available, $\lambda_{1}(expt)$ can be given a value which has been calculated using one of the formulae given in section 2.6 b).

Maczek and Gray (44) have proposed alternative ways of assigning values to $\lambda_{1}(tr)$ and $\lambda_{1}(int)$. They argue that, since the theory for pure polyatomic gases indicates that the value of $f(tr)$ is decreased below the monatomic value of $5/2$ (see equation 2.6.15), it is reasonable to expect that $f(tr)$ should also be less than $5/2$ for mixtures of polyatomic gases. Consequently, for some gases, it may be preferable
to assume that $\lambda_i^{(\text{int})}$ retains the classical value given by

$$\lambda^{(\text{int})} M/\eta = \left[\varepsilon D^{(\text{int})}/\eta\right] C_v^{(\text{int})}$$  \hspace{1cm} 2.6.42

and then to calculate $\lambda_i^{(\text{tr})}$ using equation 2.6.41.

A third, and perhaps the most logical method suggested by Maczek and Gray was that $\lambda^{(\text{tr})}$ and $\lambda^{(\text{int})}$ should be assigned values according to the values of $f^{(\text{tr})}$ and $f^{(\text{int})}$ which are obtained from the Mason-Monchick theory. Equations 2.6.15 and 2.6.16 for $f^{(\text{tr})}$ and $f^{(\text{int})}$ can be written in the form

$$f^{(\text{tr})} = \left(\frac{5}{2}\right) \left[1 - \theta/C_v^{(\text{tr})}\right]$$  \hspace{1cm} 2.6.43

and

$$f^{(\text{int})} = \left[\varepsilon D'(\text{int})/\eta\right] \left[1 + \theta/C_v^{(\text{int})}\right]$$  \hspace{1cm} 2.6.44

where

$$\theta = \left(\frac{2}{\pi}\right) \left(\frac{A}{B}\right) \left[C_v^{(\text{int})}/Z\right].$$  \hspace{1cm} 2.6.45

Putting these expressions into equation 2.6.7 gives

$$
\lambda M/\eta = \left(\frac{5}{2}\right) C_v^{(\text{tr})} + \left[\varepsilon D'(\text{int})/\eta\right] C_v^{(\text{int})} - \\
\theta \left[\left(\frac{5}{2}\right) - \varepsilon D'(\text{int})/\eta\right].$$  \hspace{1cm} 2.6.46

This equation, with an experimental value for $\lambda$, can be used, in preference to equation 2.6.45, to calculate the value of $\theta$. Having done this, the value of $\theta$ can be used in equations 2.6.43 and 2.6.44 to give $f^{(\text{tr})}$ and $f^{(\text{int})}$ from which $\lambda^{(\text{tr})}$ and $\lambda^{(\text{int})}$ can be calculated.

This approach is used for each of the components of the mixture so that the values of $\lambda^{(\text{tr})}_i$ and $\lambda^{(\text{int})}_i$ can be assigned for all $i$ and can then be used in the Hirschfelder-Fucken equation.

This third method amounts to a compromise between the first two methods, though it is clear that such a compromise does have some
theoretical justification. It is unfortunate that the values of the thermal conductivity of a mixture which are obtained using the above formulae, vary very little with the choice of method of calculating $\lambda_i^{(tr)}$ and $\lambda_i^{(int)}$. Consequently, since experimental values of thermal conductivity are not very accurate, it is not possible to select any one of the three methods as being the best.

In addition to the theoretical formulae discussed above, there are several empirical formulae. The most successful of these was that suggested by Wassiljewa (6) as long ago as 1904. Her equation can be written as

$$
\lambda = \sum_i \left[ \frac{\lambda_i}{1 + \sum_j A_{ij} x_j / x_i} \right] \tag{2.6.47}
$$

where $x_i$ is the mole fraction of component $i$ and $A_{ij}$ is one of a set of adjustable parameters, known as the Wassiljewa coefficients. Tables of Wassiljewa coefficients have been compiled (5) and many empirical formulae for calculating $A_{ij}$ have been proposed. One of the most commonly used formulae is that due to Lindsay and Bromley (45), namely

$$
A_{ij} = \frac{1}{4} \left[ 1 + \left( \frac{\eta_i}{\eta_j} \left( \frac{M_i}{M_j} \right)^{\frac{3}{2}} \frac{T + S_i}{T + S_j} \right)^2 \frac{T + S_{ij}}{T + S_i} \right] \tag{2.6.48}
$$

where $S$ is the Sutherland constant and $S_{ij} = (S_i S_j)^{\frac{1}{2}}$.

Though the Wassiljewa equation is regarded as an empirical equation, it does have some theoretical justification. Brokaw (46) has shown that, for a mixture of monatomic gases, the Wassiljewa equation is equivalent to the first order approximation of the rigorous theory. This enables a theoretical expression for $A_{ij}$ to be obtained though it can only be used for monatomic mixtures. Furthermore, there is also a close resemblance between Wassiljewa's equation and
Hirschfelder's equation, equation 2.6.40. If $A_{ij} \text{ (int)}$ was equal to $D_{ii}/D_{ij}$, then Wassiljewa's equation would represent the diffusion of internal energy in a polyatomic gas mixture. It is clear, therefore, that the form of the Wassiljewa equation is such that one might expect it to be a successful empirical formula.

Wassiljewa's equation, and most other empirical equations, make no attempt to separate the translational and internal modes but, as pointed out by Wright and Gray (47), this does not necessarily imply a weakness in these formulae because there is some doubt about the validity of separating the two modes whenever polar gases are involved. Cowling (48) has suggested that the coefficients $A_{ij}$ can be regarded as being a measure of the ratio of the efficiencies with which molecules $j$ and molecules $i$ impede the transport of heat by molecules $i$. Cowling, Gray and Wright (49), using this idea, have shown, using theoretical arguments, that one is entitled to expect the Wassiljewa equation to give reasonably close agreement with experimental results.
CHAPTER III

THEORY OF THE MEASUREMENT OF THERMAL CONDUCTIVITY USING A PERIODIC LINE SOURCE OF HEAT.

The idea of measuring the temperature distribution downstream from a line source of heat in a flowing gas, and using this information to calculate the thermal conductivity of the gas, was first suggested by Wilson (24) in 1904. Wilson derived the theoretical relations which would be needed for such an experiment but no record of an attempt to put Wilson's idea into practice appears in the literature until 1962, when Westenberg and de Haas (2) reported their successful use of the method.

Upon attempting to repeat the experiments performed by Westenberg and de Haas, many practical problems were encountered. However, it was found that these problems, which have been described in section 2.5 of this thesis, could be overcome by using a periodically varying source rather than the steady source proposed by Wilson. As a consequence of making this change Wilson's equations were no longer applicable to the measurements so it became necessary to formulate a new set of theoretical relations.

The required equations are obtained in this chapter and consideration is given to the various ways in which they can be used to permit the thermal conductivity of a gas to be measured by experiment. It is necessary to know the velocity of the gas flow before the thermal conductivity can be calculated. The way in which this can be measured is also indicated in this chapter.
3.1 The temperature distribution resulting from a periodic line source of heat in a flowing gas.

The problem is to determine the temperature distribution, denoted by $T$, downstream from a line source of heat placed in a uniform gas flow of velocity $u$, given that the heat liberated from the source varies as a known function of time $t$. This function is taken to be of the form $(A + B \cos \omega t)$ where $\omega = 2\pi f$ and $f$ is a constant frequency. The terms $A$ and $B$ are constants which have the units appropriate to a measure of the rate of heat transfer to the gas from unit length of the source.

The solution to this problem is given in appendix I. The method used to obtain the solution closely follows the methods which have been used to solve similar problems, methods which are clearly and concisely described by Carslaw and Jaeger (50). Though Carslaw and Jaeger have solved many problems of this kind, the particular problem in question does not appear to have been solved by them, or by any other worker. Consequently, it was necessary to derive the required solution from the most basic equation given by Carslaw and Jaeger, an equation which represents the temperature distribution caused by a known amount of heat being instantaneously generated at a point in an infinite, stationary medium. This temperature distribution, which is given by the equation A.1 in appendix I, is a function of position, relative to the source of heat, and of time, measured from the instant when the heat was generated. Carslaw and Jaeger verify this general equation and indicate how it can be applied to individual problems.

To solve this particular problem the basic equation has to be extended to take into account the fact that the medium, in this case a gas, is moving past the source with a known velocity, $u$. Furthermore,
the instantaneous source must be replaced by a continuous source, a source from which heat is liberated at a rate which is a periodic function of time, and the resulting expression must be integrated with respect to time, thereby deriving an expression for the temperature distribution resulting from a periodic point source of heat in an infinite, flowing gas. The required solution, that for a periodic line source of heat in a moving gas, can then be obtained from the point source solution by simply integrating the expression with respect to the appropriate space variable.

The required solution, which is obtained in appendix I, can be written, using the notation of section 2.5, in the form

$$\Delta T = \left(\frac{A}{\varepsilon c}\right)\left(\frac{4\pi k u r}{c}\right)^{\frac{1}{2}} \Delta_1 \exp\left[\frac{(x - r) u}{2K}\right] +$$

$$\left(\frac{B}{\varepsilon c}\right)\left(\frac{4\pi k u r}{c}\right)^{\frac{1}{2}} R^{\frac{1}{2}} \Delta_2 \exp\left[\frac{(x - ur) u}{2K}\right] \sin\left(\omega t - \frac{ur}{2K} + \theta - \gamma\right)$$ 3.1.1

where

$$R = \left(1 + 16\kappa\omega^2 / \omega^2 / u^4\right)^{\frac{1}{2}}$$ 3.1.2

$$\alpha = \left[(R + 1)/2\right]^{\frac{1}{2}}$$ 3.1.3

$$\beta = \left[(R - 1)/2\right]^{\frac{1}{2}}$$ 3.1.4

$$\tan \theta = \beta / (R^{\frac{1}{2}} - \alpha)$$ 3.1.5

$$\Delta_1 = (1 - K/4ur)$$ 3.1.6

$$\Delta_2 = \left[1 + w^2 - 2w \cos(\omega t - \theta)\right]^{\frac{1}{2}}$$ 3.1.7

$$\tan \gamma = [w \sin(\omega t - \theta)] / [1 - w \cos(\omega t - \theta)]$$ 3.1.8

$$w = R^{\frac{1}{2}} (K/4ur)$$ 3.1.9

and

$$\tan \theta' = \beta (2\alpha - R^{\frac{1}{2}}) / (\alpha R^{\frac{1}{2}} - 1).$$ 3.1.10

This appears to be a very complicated equation but, fortunately, a
simpler form can be obtained which, though slightly less exact than equation 3.1.1, is quite adequate for the conditions likely to be encountered during the experiments. The theory in appendix I indicated that, for equation 3.1.1 to be a good approximation to the correct solution, it is necessary that \( ur/2K \gg 1 \). Assuming that \( r \gg 25K/u \), it is clear that both \( \Delta_1 \) and \( \Delta_2 \) can be taken as being equal to unity without introducing an error of more than 1%. It is also true that, whenever \( r \gg 25K/u \), \( Y \) is very much smaller than the terms with which it is associated, though this fact is not immediately obvious.

To demonstrate that \( Y \) can be ignored it is necessary to use approximate expressions for many of the terms which appear in equation 3.1.1. By assuming that \( (K^2\omega^2/u^4) \ll 1 \), \( R \) can be approximated by the expression

\[
R \simeq 1 + 8K^2\omega^2/u^4 \tag{3.1.11}
\]

and similarly

\[
\alpha \simeq 1 + 2K^2\omega^2/u^4 \tag{3.1.12}
\]

and \( \beta \simeq 2K\omega/u^2 \). \tag{3.1.13}

Using these expressions it is a simple matter to obtain the following approximate equations:

\[
\Theta \simeq \pi/2 - K\omega/u^2 \tag{3.1.14}
\]

\[
\Theta' \simeq \pi/2 - 3K\omega/u^2 \tag{3.1.15}
\]

and \( Y \simeq -(K^2\omega/2u^3r) \). \tag{3.1.16}

These approximate expressions are not adequate for general use but they do enable the relative magnitudes of the various terms to be estimated with ease. They can be used to estimate the relative magnitudes of the terms which appear in the expression

\[
\sin(\omega t - \beta ur/2K + \alpha - Y).
\]
Using the expressions for \( \phi \), \( \theta \) and \( \chi \) given above, this sinusoidal term becomes

\[
\sin \left[ (\omega t) - (\omega r/u) + (\pi/2 - \kappa w/u^2) + (\kappa^2 w/2ru^3) \right] \\
= \sin \left[ \omega t + \pi/2 - \kappa w/u^2 - (\omega r/u)(1 - \kappa^2/2u^2r^2) \right].
\]

If the same restriction is imposed upon \( r \) as was used earlier, i.e. \( r > 25K/u \), the value of \( (\kappa^2/2u^2r^2) \) is less than 0.001. From this it is obvious that \( \chi \) can be ignored without introducing an error of more than 0.1\%, and equation 3.1.1 can therefore be approximated by

\[
\Delta T = \frac{(A/\rho c)(4\pi ku r)^{-1/2}}{\exp[(x - r)u/2K]} + \\
\frac{B/\rho c)(4\pi ku r)^{-1}}{R^{-1/2}} \exp[(x - ar)u/2K] \sin(\omega t - \beta ur/2K + \theta). \tag{3.1.17}
\]

This equation has been shown to be within 1\% of the exact solution, provided that \( r > 25K/u \). If it should ever occur that \( r \) be less than \( 25K/u \), it may be possible, provided that \( r \) is not too small, to include \( \Delta_1 \) and \( \Delta_2 \) in the theory but still ignore \( \chi \), since the error involved in ignoring \( \chi \) is much less than that involved in ignoring both \( \Delta_1 \) and \( \Delta_2 \).

Equation 3.1.17 is used as a basis for the development of the theory of this chapter. Notice that the first part of the equation is identical, as one would expect, to equation 2.5.1, this being the steady temperature solution, and that the second part of the equation, the sinusoidal term, reduces to the steady temperature solution as the angular frequency \( \omega \) is reduced to zero.

The solution given above has been obtained for a line source of heat from which heat is liberated at the rate \( (A + B \cos \omega t) \) per unit length of the source. Such a source would be difficult to obtain in
practice. In the experiment, the line source consists of a very fine wire which is heated electrically by a combination of a d.c. voltage and an a.c. voltage applied across the wire. However, since the resistance of the wire will vary with its temperature, the power supplied to the wire, and hence the heat liberated from the wire, will be a complicated function of the applied voltage. Nevertheless, whatever the form of the equation for the heat liberated from the wire may be, it can be expressed as a Fourier expansion in the form

\[ A + B \cos \omega t + C \cos(2\omega t + \phi_2) + D \cos(3\omega t + \phi_3) + \ldots \]

and the solution for the temperature distribution downstream from the source will simply be that given by equation 3.1.17 with the addition of the appropriate higher frequency terms which can be obtained by suitable modification of equation 3.1.17.

The experimental arrangement is such that only the fundamental frequency is measured. Thus, for the purpose of the experiment, the only relevant part of the solution is the second term of equation 3.1.17 which, for convenience, can be written as

\[ \Delta T = br^{-\frac{1}{2}} \exp \left[ \left( x - \alpha r \right) u/2 \kappa \right] \sin \left( \omega t - \frac{\pi u}{2\kappa} + \theta \right) \]

where \( b = \frac{B}{\epsilon \mathbf{c}} \left( \frac{4\pi \kappa}{u} \right)^{\frac{1}{2}} R^{-\frac{1}{2}} \).

Note that \( b \) is a function of \( \omega \) since, by equation 3.1.2, \( R \) is a function of \( \omega \).

The derivation of equation 3.1.18 has involved a mathematical approximation which has been shown to be valid, to within 1%, provided that \( r > 25u/\kappa \). However, certain other approximations are also involved due to assumptions in the basic theory. The first of these is the
assumption that the thermal diffusivity $K$ is constant. In practice $K$ will vary slightly due to the variations of the temperature of the gas downstream from the source of heat, this effect being greatest very close to the wire where the temperature gradients are steepest. It has also been assumed that the velocity of the gas is constant but it will vary in the region where the measurements are made because of the disturbance of the gas flow caused by the presence of the source wire. This effect will also be greatest very close to the wire.

It would be very difficult to include the variable properties of $u$ and $K$ into the basic theory and consequently, throughout this chapter, it is assumed that both these factors are constant. In section 5.1 of this thesis an investigation is made into the consequences of making this assumption and it is found that the resulting error is small provided that the most appropriate values of the 'variables' $u$ and $K$ are chosen.

In the following sections, equation 3.1.18, being assumed to be sufficiently accurate for the purposes of this work, is used to show how the velocity and the thermal conductivity of the gas can be measured in an experiment. The thermal conductivity is determined from measurements of the amplitude of the sinusoidal temperature variations and the velocity of the gas is determined from measurements of the phase of these variations.
3.2 Theory for the measurement of the velocity of the gas.

The velocity of the gas is measured by observing the change in phase of the sinusoidal temperature variations of the gas between two points which are directly downstream from the source, i.e. two points where \( y = 0 \) and \( r = x \). If these two points are denoted by \( x_1 \) and \( x_2 \), and the phase difference between them by \( 2\pi/\nu \), it is clear, from equation 3.1.18, that

\[
(\beta u/2\kappa) (x_2 - x_1) = 2\pi/\nu. \tag{3.2.1}
\]

\( \beta \) is a rather complicated function of \( \kappa, \omega, \) and \( u \) but, using equations 3.1.2 and 3.1.4, it can be shown that

\[
\beta^2(\beta^2 + 1) = 4\kappa^2\omega^2/u^4. \tag{3.2.2}
\]

A suitable expression for \( u \), the velocity of the gas, can now be obtained by combining equations 3.2.1 and 3.2.2, eliminating \( \beta \). The resulting expression is

\[
u^2 = n^2 f^2(x_2 - x_1)^2 - 16\pi^2\kappa^2/n^2(x_2 - x_1)^2. \tag{3.2.3}
\]

It is convenient to substitute

\[
u_o = nf(x_2 - x_1) \tag{3.2.4}
\]

so that equation 3.2.3 can be rewritten as

\[
u = \nu_o (1 - 4\kappa^2\omega^2/\nu_o^4)^{1/2}. \tag{3.2.5}
\]

This result has also been obtained independently by Kielbasa (51), though his result was obtained by solving the one-dimensional differential equation of heat conduction which is not applicable to
this particular case. The same result can also be obtained, for the one-dimensional problem, from an equation given by Carslaw and Jaeger (50). It is interesting that the one-dimensional problem produces the same result as that obtained here, for the two-dimensional case.

To obtain the velocity of the gas from equation 3.2.5 it is necessary to know \( K \), the thermal diffusivity of the gas, but this, of course, is an unknown quantity. However, in section 3.3, an equation is obtained which gives a second relationship between \( K \) and \( u \) and other known factors. There will then be two simultaneous equations with two unknowns, \( u \) and \( K \), which can be solved to give both the velocity of the gas and the thermal diffusivity of the gas, the quantity that the experiment is designed to measure.

This method of measuring gas velocity was originated by Walker and Westenberg (25), though their theory did not take into account the conduction of heat through the gas. The equation they used to calculate the gas velocity is equivalent to equation 3.2.4, this being the expression for the gas velocity which results from setting \( K = 0 \) in equation 3.2.5 i.e. ignoring the effect of conduction. The error caused by using this less exact equation depends upon the conditions prevailing at the time, but it is likely to be small, though not negligible.

Westenberg and de Haas used the equation given by Walker and Westenberg to calculate the velocity of the gas flow in their experiments. It is apparent, therefore, that their values of thermal conductivity are in error by an unknown, though probably small, amount.
3.3 Theory for the measurement of the thermal conductivity of the gas.

The thermal conductivity, or more correctly, the thermal diffusivity of the gas is obtained by making measurements of the amplitude of the sinusoidal temperature variations of the gas at a series of different positions and frequencies. The electronic equipment used to measure this amplitude results in a voltage $V$, measured on a digital voltmeter, which is directly proportional to the amplitude in question. The constant of proportionality is found, in section 4.2 b), to be dependent upon the frequency of the signal detected so the relationship between the voltage $V$ and the amplitude of the sinusoidal temperature variations of the gas, $\Delta T_g$, should be written as

$$V = C(\omega) \Delta T_g$$  \hspace{1cm} 3.3.1

where $C(\omega)$ is given by equation 4.2.21, though, as will become clear, it is not necessary to know the form of $C(\omega)$. An expression for $\Delta T_g$ can be obtained directly from equation 3.1.18 and substituting this into equation 3.3.1 gives

$$V = C(\omega) b r^{-1/2} \exp\left[(x-\alpha r)/2k\right].$$  \hspace{1cm} 3.3.2

This equation contains two quantities, $C(\omega)$ and $b$, which are difficult to determine. However, by suitable choice of the method of performing the experiments, both these quantities can be eliminated leaving $K$ as the only unknown quantity after equation 3.2.5 has been used to eliminate $u$ from the equations. There are several ways in which the experiments can be performed to eliminate $C(\omega)$ and $b$; four such ways are described briefly below.
Method i). With this method, measurements are only made at positions where \( y = 0 \), and hence where \( r = x \). The amplitude of the sinusoidal variation is measured at the same position \( x \) but at two different frequencies, \( f_1 \) and \( f_2 \), where \( f_2 > f_1 \). Using the subscripts 1 and 2 to refer to measurements made at \( f_1 \) and \( f_2 \) and putting \( r = x \), equation 3.3.2 can be used to obtain an expression for the ratio \( (V_1/V_2) \). This expression can be written as

\[
\ln(V_1/V_2) = \ln[b_1 C(\omega_1)/b_2 C(\omega_2)] + x(\alpha_2 - \alpha_1)u/2K. \tag{3.3.3}
\]

By making repeated measurements of \( V_1 \) and \( V_2 \) at different values of \( x \) and then plotting a graph of \( \ln(V_1/V_2) \) against \( x \), the value of \( (\alpha_2 - \alpha_1)u/2K \) can be obtained by measuring the slope of the graph and the values of \( b \) and \( C(\omega) \) are eliminated since they are independent of \( x \). Denoting the slope of the graph by \( m \), the required equation is

\[
m = (\alpha_2 - \alpha_1)u/2K. \tag{3.3.4}
\]

This equation, in conjunction with equation 3.2.5, forms a pair of simultaneous equations with two unknowns, \( u \) and \( K \). The expression for \( u \), given by equation 3.2.5, can be substituted into equation 3.3.4 to give an expression for \( K \). However, because of the complicated dependence of \( \alpha_2 \) and \( \alpha_1 \) upon \( u \), it is not possible to obtain a simple expression for \( K \) and it becomes necessary to use a method of successive approximations to find the value of \( K \) which will satisfy the equation. A first approximation to \( K \) can be found by substituting the approximate expressions for \( \alpha_2 \) and \( \alpha_1 \), given by equation 3.1.12, into equation 3.3.4. This gives

\[
K = m u^2/\left(\omega_2^2 - \omega_1^2\right). \tag{3.3.5}
\]
from which an approximate value of $K$ can be calculated using the approximate value of $u$ given by equation 3.2.3. A series of trial values of $K$, starting with this approximate value, can then be substituted into equations 3.2.5 and 3.3.4 until a value is found which satisfies the equations. The thermal diffusivity of the gas is, therefore, determined and so also is the velocity of the gas.

This method, in addition to eliminating the unknown quantities $b$ and $C(\omega)$, also has the advantage that it does not require the knowledge of the absolute values of $x$, the position of the detector relative to the source. This is obvious from equation 3.3.3, which shows that the addition of the same constant to each value of $x$ would not cause the slope of the graph of $\ln(V_1/V_2)$ against $x$ to change. Consequently, it is only necessary to measure the distance that the detector is moved between successive positions of measurement.

Method ii). This method also involves making measurements of the amplitude of the sinusoidal temperature variations of the gas only at positions where $y = 0$. The method is similar to method i) in that relative measurements are made so that the unknown factors, $b$ and $C(\omega)$, can be eliminated. In this case, however, measurements are made at the same frequency at two different positions, $x_1$ and $x_2$. Using the subscripts 1 and 2 to refer to measurements made at $x_1$ and $x_2$ and using equation 3.3.2 with $r = x$, it is clear that

$$\ln(V_1/V_2) = \frac{1}{2} \ln(x_2/x_1) + (\alpha - 1)(x_2 - x_1)u/2K. \quad 3.3.6$$

The factor $(\alpha - 1)$ is a complicated function of frequency, determined by equations 3.1.2 and 3.1.3. $(\alpha - 1)$ is approximately proportional to the
square of the frequency, as can be seen from equation 3.1.12, but this approximation is not good enough for accurate determination of $k$. The best way to use equation 3.3.6 is to measure the ratio $(V_1/V_2)$ at the two positions $x_1$ and $x_2$ for a series of different frequencies and then to take a trial value of $k$ so that the value of the factor $(\alpha - 1)u/2k$ can be calculated for each of these frequencies using equations 3.1.2, 3.1.3 and 3.2.5. A plot of $\ln(V_1/V_2)$ against $(\alpha - 1)u/2k$ can then be made and, if the correct trial value of $k$ has been chosen, this will result in a graph of slope equal to $(x_2 - x_1)$. If this is not the case, a new trial value must be selected and the process repeated.

This method is more difficult than method i) in that more calculation is necessary to determine $k$. The slope of the graph, in each case, must be calculated using a formula which gives the best straight line for the given points i.e. the straight line for which the mean square deviation of the points from the line is a minimum. Unless computing facilities are available, this task can be very tedious. Having computed the slope, and the error associated with the slope, for a series of trial values of $k$, the value of $k$ which results in a slope equal to $(x_2 - x_1)$ can be selected and an error can be assigned to this value.

It is usually preferable to use method i) rather than method ii) because of the fact that the calculations are more simple, though, from the experimental point of view, there is little to choose between the two methods. Method ii), like method i), does not require absolute measurements of the variable $x$ since it is only necessary to know the value of $(x_2 - x_1)$.
Method iii). Maintaining the restriction that all measurements should be made at positions where \( y = 0 \), and hence where \( r = x \), equation 3.3.2 can be written in the form

\[
\ln(Vx^2) = \ln[bC(\omega)] + x(1 - \alpha)u/2K.
\]  

3.3.7

A plot of \( \ln(Vx^2) \) against \( x \) will give a straight line of slope \( (1 - \alpha)u/2K \) and both \( b \) and \( C(\omega) \) are again eliminated. The value of \( K \) can then be calculated from the measured slope of the graph by a procedure of successive approximations similar to that used for method i).

The main disadvantage of this method is that it requires the knowledge of absolute values of \( x \). If absolute values are not used in equation 3.3.7, a plot of \( \ln(Vx^2) \) against \( x \) will not be linear. In principle, this fact could be used to determine the necessary correction term required for measurements of \( x \) which have been made on a scale with an arbitrarily positioned origin. In practice, however, this is a very insensitive test for absolute values of \( x \) and it is therefore necessary to use a travelling microscope to find the required correction term or, better still, to use the method, described in section 2.5, of plotting \( \Delta T_{\text{max}}^{-2} \) against \( x \) whilst using a steady source of heat.

This method is considered to be inferior to the two methods described previously because it requires the knowledge of absolute values of \( x \). However, it does have one small advantage in that all measurements are made at one frequency, so fewer measurements are necessary in comparison to methods i) and ii).
Method iv). Finally, it is possible to use an approach which is identical to that used by Westenberg and de Haas (2), though the corresponding theoretical equation naturally includes an additional term, namely α. Following the procedure given in section 2.5, it is a simple matter to obtain the equation which is equivalent to equation 2.5.3. The resulting equation is

\[ \kappa = \alpha u \frac{r_h - x}{\ln(4x/r_h)} \]  

where \( r_h \) is as defined in section 2.5. One could, therefore, use the same method as used by Westenberg and de Haas though the final calculation of \( \kappa \) from the best value of the ratio \( (r_h - x)/\ln(4x/r_h) \) would again require a procedure of successive approximations similar to that described for method i).

This method is not recommended for use. It suffers from the same problems which are encountered in the steady line source method since it requires knowledge of absolute values of \( x \) and also requires that measurements be made at positions other than where \( y = 0 \). This means that an additional scale is required, upon which \( y \) can be measured, and it also means that measurements have to be made in regions where the signal is very unsteady. Furthermore, the problem of ascertaining the consequences of the variation of \( u \) and \( \kappa \) in the region of the measurements is considerably more difficult if measurements are not restricted to positions where \( y = 0 \).

Of the four methods described here, the first two are regarded as being the best, the first one being slightly preferable to the second.
CHAPTER IV

THE CONSTRUCTION AND THE PERFORMANCE OF THE APPARATUS.

The theory requires that a periodic line source of heat be placed in a uniform flow of gas, heated to the required temperature. The apparatus needed to achieve this is described in section 4.1 a) of this chapter. In order to determine the thermal conductivity of the gas, it is necessary to measure the phase and the amplitude of the sinusoidal temperature variations which are set up in the gas and the electronic equipment required to do this is described in section 4.1 b). In addition to these main measurements, the temperature of the gas must be measured and, for gas mixtures, the relative proportions of the different gases in the mixture must be determined. The measurement of the temperature involves making two corrections to a thermocouple measurement, corrections which must be determined experimentally. The apparatus needed to measure these correction terms is described in section 4.1 c), along with a description of the apparatus used for the measurement and control of gas mixtures.

The theory of section 3.3 assumed that electronic equipment used to measure the amplitude of the sinusoidally varying temperature resulted in a voltage \( V \), measured on a digital voltmeter, which was directly proportional to the amplitude in question. The theoretical arguments given in sections 4.2 a) and 4.2 b) show that this is the case and an expression for the constant of proportionality is derived. Experimental evidence is given in section 4.2 c) to support the theoretical findings.
4.1 Description of the apparatus.

a) Mechanical and constructional details.

The apparatus described in this section is essentially the same as that used by Westenberg and de Haas (2). The gas under investigation was passed through a vertical, stainless steel tube which had an internal diameter of 1.4 ins. (≈3.6 cm.) and was approximately 4 ft. long (≈120 cm.). The flow system for the gas, prior to its introduction into this tube, is described in section 4.1 c), where a description is also given of how mixtures of gases were obtained and measured. Two electric furnaces were used to heat the tube, and hence the gas, to the desired temperatures, the power supplied to each furnace being controlled by a variable transformer. The tube was packed with ceramic chips to improve the heat transfer to the gas, and the gas exit, which was flush with the top of the furnace, consisted of a series of nickel screens which were arranged as shown in figure 4.1.1. This design was intended to produce a uniform gas velocity across the exit, as required by the theory. An experimental investigation into the uniformity of the flow was carried out and is described in section 5.1.

The source wire, the line source of heat, was a platinum 10% rhodium wire which was positioned horizontally across the exit from the furnace, 3 or 4 mm. above the top screen. A very fine wire was used so as to produce the minimum possible disturbance to the gas flow and also to satisfy, as best as possible, the theoretical assumption that the source is a line source of infinitely small diameter. The finest wire used was nominally 0.1 thou. (2.5 microns) in diameter and this was used for gas temperatures up to approximately 500°C. At
Cross-section of apparatus used to produce a uniform flow of heated gas.
higher temperatures it was often necessary to use thicker wire, 0.3 thou. in diameter, because, except for the occasional exception, the finer wires tended to break too frequently for convenient use.

The source wire was mounted on thick copper support wires and was positioned across the exit from the furnace with the support wires well clear of the region of gas flow. This meant that the source wire was typically 5 or 6 cms, long. The tension in the wire could be adjusted by a screw mechanism which varied the separation of the copper support wires. This complete support system, shown in figure 4.1.2, was mounted on a micromanipulator and could be easily manoeuvred into the required position.

The use and manipulation of such fine wires was found to be very difficult at first but, after some practice, the renewing of a broken wire was not a lengthy task. The wires were obtained in the form of Wollaston wire, which consists of the required wire with a silver coating sufficient to increase the diameter of the wire to a more manageable size, approximately 1 thou. To replace a broken wire, this Wollaston wire, cut to the required length, was soft soldered to the copper support wires and was dipped into hot, dilute nitric acid (about \(10\% \text{HNO}_3\)) to a depth which left the copper support wires and approximately \(\frac{1}{2}\) cm. of the Wollaston wire clear of the acid. The silver coating was dissolved away in a few seconds, leaving the required length of platinum 10\% rhodium wire supported by the two short sections of undissolved Wollaston wire. The wire was then carefully tensioned until the two stronger, undissolved sections became slightly bent from their original positions. Because of the springiness of the stronger wire, this slight bending was sufficient to maintain the
Figure 4.1.2.

The apparatus used for supporting the source wire.
tension in the source wire when it expanded upon being heated.

The detector wire was also a platinum 10% rhodium wire which was used, in effect, as a resistance thermometer. It was approximately 0.5 to 1.0 cms. long and it was necessary to use 0.3 thou. diameter wire, even at the lower temperatures, because the detector wire was more difficult to support and tension than the source wire. Two stainless steel capillary tubes, which were cemented into a twin bore ceramic tube, were used to support the detector wire, as shown in figure 4.1.3.

The detector wire was manufactured by threading the Wollaston wire down through one capillary and up through the other and then, using the hot nitric acid, as before, the silver jacket was dissolved away from a short length of the wire between the two capillaries. The Wollaston wire was carefully pulled up through the capillaries until the detector wire was located centrally and adequately tensioned. The friction between the Wollaston wire and the capillaries was sufficient to prevent movement of the wire and the tension in the detector wire could be easily maintained. The two loose ends of the Wollaston wire were soft soldered to two copper wires, held in a terminal block, from which connections were made to the rest of the apparatus. This complete arrangement was mounted on a micromanipulator, capable of moving in three perpendicular directions, so that the temperature distribution downstream from the source could be conveniently investigated.

The source and detector wires were positioned as shown in figure 4.1.4. The wires were adjusted to be parallel to each other in both the vertical and the horizontal planes. This ensured that the total length of the detector wire was at the same temperature, i.e. the
Figure 4.1.3.
The apparatus used for supporting the detector wire.
Figure 4.1.4:

The positioning of the source and detector wires at the furnace exit.
detector wire was positioned along an isotherm in the gas. This could be done quite successfully with the naked eye, though the visibility of the wires could be improved, if necessary, by temporarily inserting black paper behind the wires and using an adjustable light source. The movement of the detector wire in the vertical direction was measured using a dial gauge which was firmly fixed to the framework of the apparatus. This dial gauge, which was graduated in divisions of 0.001 mm., enabled the movement of the detector wire to be measured very accurately.

The description given here, of the construction of the source and detector wires, has referred to the use of platinum 10% rhodium wires. Initial efforts were directed at making pure platinum wires but it was found that platinum 10% rhodium wires, being much stronger than pure platinum wires, lasted much longer. The only disadvantage of using platinum 10% rhodium is that the temperature coefficient of resistance is approximately half that of platinum which means, as will be shown in section 4.2 a), that the sensitivity of the detector is halved. Despite this fact, it was considered preferable to use the platinum 10% rhodium wire. It may well be, however, that other wires, pure rhodium perhaps, would be even better but there is only a limited range of wires available from manufacturers in the form of Wollaston wire.
4.1 b) Electronic equipment.

Special electronic equipment is needed to measure both the phase and the amplitude of the sinusoidal temperature variations in the gas. These measurements are required in order to determine the velocity of the gas, as indicated in section 3.2, and the thermal diffusivity of the gas by one of the methods described in section 3.3. The amplitude and phase are both determined by measurement of the changes of the voltage across a simple Wheatstone bridge network, one arm of which is the detector wire, due to changes in the temperature of the gas. The performance of the detector circuit is described in section 4.2 but, for practical purposes, it is sufficient to use the fact that a change in temperature of the gas will produce a change in the measured voltage which is directly proportional to the change in temperature. The additional electronic equipment required to measure the changes in the phase of the sinusoidal temperature variations, is described below and this is followed by a description of the equipment which is needed to measure the amplitude of these variations.

1) The measurement of the gas velocity (phase measurements).

The apparatus that was used for measuring the velocity of the gas is shown schematically in figure 4.1.5. The source wire was heated by means of a d.c. power supply and an oscillator (oscillator A). The capacitor C was required to prevent direct current from passing through the oscillator and was chosen to have a sufficiently large value (1000μF) that its impedance to signals of the order of 50 Hz. was small compared to the resistance of the source wire and of $R_s$. The
Figure 4.1.5

Apparatus for the measurement of the gas velocity.
resistor $R_s$ was required to supply a path for the direct current from the power supply. The values of $R_s$ which were used in the experiment are shown in the table below, along with a typical example of the voltage across the source wire. The values of $R_s$ were chosen purely on the grounds that they enabled the required voltages to be obtained across the source wire, though $R_s$ should not be chosen so small that it dissipates too much a.c. power or so large that it dissipates too much d.c. power. None of the values shown in the table need to be measured during the experiments; the table is included here only to show the values normally used.

<table>
<thead>
<tr>
<th>Wire diameter</th>
<th>Wire resistance</th>
<th>Resistance of $R_s$</th>
<th>Voltage across wire</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 thou.</td>
<td>2 kΩ</td>
<td>900 Ω</td>
<td>$45 + 15 \cos wt$ volts</td>
</tr>
<tr>
<td>0.3 thou.</td>
<td>200 Ω</td>
<td>220 Ω</td>
<td>$15 + 5 \cos wt$ volts</td>
</tr>
</tbody>
</table>

The frequency of oscillator A, used for heating the source wire, was controlled by a second oscillator, oscillator B. The output of oscillator B was connected to the synchronising input of oscillator A via a four-stage binary frequency divider, shown in figure 4.1.6. By this means, the two oscillators could be phase-locked with the frequency of oscillator B being 2, 4, 8 or 16 times that of oscillator A. The relative phase of the two oscillators could be changed, by a small amount, by adjusting the dial which, under normal operation, would control the frequency of oscillator A.

The most common arrangement used during the experiments, was to set oscillator B at 500 Hz, divide this by 8, and thus drive oscillator A at 62.5 Hz. The tuned amplifier was also set to 62.5 Hz so that unwanted signals and low frequency noise were filtered out before the
Figure 4.1.6

Four-stage binary frequency divider.
signal, suitably amplified, was connected to the x plates of an oscilloscope. The y plates of the oscilloscope were connected to oscillator B so that a Lissajous figure, with an 8 to 1 ratio, could be obtained on the oscilloscope. With this arrangement, any change of the position of the detector caused a phase change in the detector circuit, resulting in a corresponding change in the shape of the Lissajous figure.

Using the theory of section 3.2 and the apparatus described above, it was a simple matter to measure the velocity of the thermal signals from which the velocity of the gas could be calculated using equation 3.2.5. A phase change of 1 cycle of the higher frequency signal (500 Hz), equivalent to a phase change of $\frac{1}{8}$ of a cycle of the lower frequency signal (62.5 Hz), could be measured very accurately using the Lissajous figure patterns and the distance moved by the detector could be measured accurately using the dial gauge. Use of equation 3.2.3 with $n$, in this example, being 8 and $f$ being 62.5 Hz, enabled the velocity of the thermal signal to be calculated. It should be noted that the measurement results in an average value for the velocity between the two positions of measurement, $x_1$ and $x_2$, and that this distance can be made large or small, as required, by suitable selection of the parameters $n$ and $f$.

This procedure for measuring the velocity of the gas is essentially the same as that used by Westenberg and de Haas (2) and originated by Walker and Westenberg (25). The only differences are that a correction term is included in the theory and the detector wire is operated parallel to the source wire rather than at right angles to it.
Walker and Westenberg (25), when they developed this method of
gas velocity measurement, reached certain conclusions about the limita-
tions of the method which may require modification in the light of
the fact that the theory which they used was not exact. Consider the
value of the ratio \( \frac{u_0}{u} \) which, using equation 3.2.5, can be plotted
as a function of \( u_0 \) for given values of \( K \) and \( \omega \). By taking
\( K = 0.2 \)
cms\(^2\)/sec, a value suitable for nitrogen at room temperature, and by
taking the frequency to be 100 Hz, the frequency used by Walker and
Westenberg, the graph shown in figure 4.1.7 is obtained.

\[
\begin{align*}
\text{Figure 4.1.7} \\
\text{The dependence of } \frac{u_0}{u} \text{ upon } u_0. \\
\end{align*}
\]

This graph is almost identical to figure 5 of Walker and
Westenberg's paper, a graph which they obtained by comparing their
measured velocity, equivalent to \( u_0 \) of this thesis, with the true
velocity which they determined from measurements of the mass flow
rate. Walker and Westenberg were of the opinion that the increase of
the ratio \( \frac{u_0}{u} \) at low values of \( u_0 \) was due to the effects of buoyancy
or free convection, and they concluded that the method was not satis-
factory for measurements of gas velocity below 40 cms./sec. However,
in view of the close similarity between the theoretical curve given here and the experimental curve given by Walker and Westenberg, it seems certain that the effects of buoyancy are very much less than Walker and Westenberg believed. Consequently, it is clear that this method of measuring gas velocities can be used at velocities less than 40 cms./sec. provided that equation 3.2.5 is used rather than the less exact equation, equivalent to equation 3.2.3. It is difficult to estimate the lowest gas velocity that can be accurately measured using this method but it is probably below 20 cms./sec.

The fact that the measurements of the gas velocity were made with the detector wire parallel to the source wire, rather than at right angles as recommended by Walker and Westenberg, requires further explanation. The source wire, fine though it is, has an appreciable effect upon the velocity of the gas downstream of the wire so, in addition to the thermal wake behind the heated source wire, there is also a velocity wake. If the two wires are parallel, the distributions of the velocity and the temperature of the gas along the length of the wire are both constant, so the periodic variations of temperature that are measured by the detector circuit are less distorted than would be the case if the two wires were perpendicular. Furthermore, it is shown in section 5.1, that the value of $u$, the velocity of the gas, required for calculating the thermal diffusivity of the gas is the value of $u$ in the region where the measurements are made, not the free-stream value of $u$. Consequently, the required value of $u$ can be conveniently and accurately measured by operating with the detector wire parallel to the source wire. If, as may be the case for other applications of the two wire anemometer, it is required to determine the velocity of
the gas when undisturbed by the presence of the source wire, then a correction must be applied to the measurements made as described.

ii) The measurement of the thermal diffusivity of the gas: The measurement of the amplitude of the sinusoidal temperature variations of the gas.

The apparatus required for the measurement of the amplitude of the sinusoidal temperature variations of the gas is shown in figure 4.1.8. The arrangement is conveniently very similar to that used for measuring the velocity of the gas. The only changes necessary were:

i) The tuned amplifier was replaced by a wide-band amplifier, though a low-pass and a high-pass filter were included in the amplifier circuit so that the band-width could be restricted to a convenient range of frequencies, approximately 30 to 100 Hz in this particular case. The output from the wide-band amplifier was connected to the signal channel of a phase sensitive detector, hereafter referred to as a p.s.d.

ii) The synchronising input to oscillator A was disconnected so that the frequency of oscillator A was controlled only by the setting on the dial of the instrument itself. In addition to heating the source wire, the signal from oscillator A was connected, via a reference unit, to the reference channel of the p.s.d. The output from the p.s.d. was displayed on a d.c. digital voltmeter.

It is useful, at this stage, to give a brief description of the
Figure 4.1.8

Apparatus for the measurement of the thermal diffusivity of the gas.
performance of a p.s.d. The d.c. output voltage of a p.s.d. is directly proportional to the amplitude of the a.c. input signal provided that the frequency of the input signal is the same as that of the reference signal. Signals which do not have the same frequency as the reference signal do not contribute to the d.c. voltage so they are effectively filtered out. The output voltage $V_{out}$ is also dependent upon the phase angle $\psi$ between the input signal and the reference signal, $V_{out}$ being given by the relation

$$V_{out} = cV_{in} \cos \psi$$  \hspace{1cm} 4.1.1

where $V_{in}$ is the amplitude of the input signal and $c$ is a constant of the instrument. Consequently, in order to make consistent measurements of $V_{in}$, it is necessary to keep $\cos \psi$ constant, and preferably equal to unity. This can be easily achieved with the reference unit with which it is possible to adjust the phase of the two signals. Thus, if all measurements are made with $\cos \psi = 1$, then

$$V_{out} = cV_{in}.$$  \hspace{1cm} 4.1.2

The value of using a p.s.d. is that it can enormously reduce noise and other unwanted signals and it is more practical than conventional filters. The effective band-width of the p.s.d. could be set as narrow as 0.03 Hz, a figure which could not be equalled with a conventional filter because of the problem of frequency instability. The p.s.d. overcomes the problem of frequency instability by deriving both the input signal and the reference signal from the same source. Furthermore, if the operating frequency is changed, there is no retuning to be done, as would be the case with conventional filters.
The only signals which are not enormously attenuated using a p.s.d. are those whose frequency is an odd multiple of the frequency of the reference signal. Such signals are present in the experiment due to the method of producing the variations of the temperature of the gas. The voltage across the source wire is a combination of a d.c. voltage and a sinusoidal voltage. Consequently, if the resistance of the source wire is assumed to be constant, the power supplied to the wire is proportional to the square of the voltage across it. The temperature of the gas is proportional to the power supplied to the wire and is therefore of the form

\[ T_g = T_0 + T_1 \cos \omega t + T_2 \cos 2\omega t. \]

However, it is not valid to assume that the resistance of the wire is constant, it will vary as the temperature of the wire varies. This effect introduces higher harmonic terms into the expression for the temperature of the gas, resulting in the expression

\[ T_g = T_0 + T_1 \cos \omega t + T_2 \cos 2\omega t + T_3 \cos 3\omega t + \ldots \]

though the amplitudes \( T_1 \) and \( T_2 \) will be much greater than \( T_3, T_4 \) etc.

For each of the terms in the above expression there will be a corresponding signal at the input to the p.s.d., though the output will depend only on the magnitude of the terms which have a frequency of \( \omega, 3\omega, 5\omega, \) etc. However, \( T_3 \) is much less than \( T_1 \) and, furthermore, the signals due to these higher harmonics are attenuated by the filters in the wide-band amplifier. Consequently, the output voltage of the p.s.d. is a measure of the signal arising from the term \( T_1 \cos \omega t \) only, the signals arising from the other terms being negligibly small.
Having dealt with the performance of the p.s.d., there remains only the performance of the detector wire and the Wheatstone bridge network to be considered. A detailed investigation into the performance of this part of the apparatus was made and is described in section 4.2 where it is shown that the output voltage of the p.s.d. is proportional to the amplitude of the sinusoidal variations of the temperature of the gas. The voltage $V$ measured on the digital voltmeter is, therefore, a measure of the amplitude in question, and relative measurements can be made with ease.

The only other measurements which were necessary during the course of the experiments were those of gas temperature and mixture content. The apparatus required for making these measurements is described in the following section.
Having completed the main measurements, from which the thermal conductivity of the gas is later calculated, it is naturally important to determine the temperature of the gas to which the result of the calculations should be assigned. Essentially, this means measuring the temperature of the gas with a thermocouple but two corrections to this measurement are necessary. The thermocouple reading obtained for this measurement needs a correction because the thermocouple takes up a temperature slightly less than that of the gas due to radiation of heat to the surrounding walls. A second correction is required to take into account the fact that the temperature of the gas in the region of the experimental measurements is slightly greater than the temperature of the main gas stream because of the heating effect of the source wire. These two corrections are best made experimentally, and the apparatus used to achieve this is described in this section.

The only other ancillary equipment used during the experiment is that which is needed to measure the flow rate of the individual gases which make up the gas mixture. Measurement of the flow rates of the individual gases must be made before an experimental measurement is begun so that the flow rates can be adjusted, if necessary, to produce the required mixture. Once the required flow rates have been obtained, they must be monitored during the measurements so that any change can be detected and suitable action taken. The apparatus required for this is also described in this section.
1) Radiation correction to the thermocouple measurements.

The thermocouple used for measuring the gas temperature was manufactured from 5 thou. (0.125 mm) diameter platinum and platinum-13% rhodium wires. The hot junction was made by butt-welding the wires together in a very fine oxygenated flame, this being done with the minimum possible distortion to the wire so that the radiation from the thermocouple was uniform through the junction. The thermocouple wire was held in a length of twin bore quartz tube, there being a loop of wire, about 4 or 5 cms long with the hot junction approximately in the middle, protruding from the end of the quartz tube. The cold junction of the thermocouple simply consisted of a terminal block which was used to connect the platinum and platinum-13% rhodium wires to copper wires which led off to a digital voltmeter upon which the thermoelectric e.m.f. was measured. The cold junction was totally immersed in an ice bath.

The problem of determining the correction which must be applied to measurements of gas temperatures made with a thermocouple is very difficult. There are many experimental ways of tackling the problem and there is also the possibility of calculating the required correction theoretically. The experimental method described here was regarded as the best method available and was found to give correction terms which agreed reasonably well with values calculated using theoretical arguments. The experimental values were considered to be more reliable than the theoretical values because of the difficulty of constructing a mathematical model to accurately represent the experimental conditions.

The basic principle of the experimental method used is to heat
the thermocouple wire electrically, so that its temperature is the same as that of the gas, and then to measure this temperature by measuring the e.m.f. of the thermocouple. Unfortunately, it is not possible to do this directly because the voltage which is applied to the wire to produce the electrical heating makes the measurement of the small thermo-electric e.m.f. impracticable. The method used to overcome this problem was to switch off the heating current and then, a very short time later, to switch the thermo-electric e.m.f., suitably amplified, onto a storage oscilloscope where it could be monitored as a function of time. The oscilloscope was triggered at the instant the heating current was switched off and the thermocouple, as it cooled down to the steady level normally measured, caused a display, similar to that sketched in figure 4.1.9, to be left on the screen of the oscilloscope. By extrapolating the cooling curve back to

![Diagram](image)

**Figure 4.1.9**

The measurement of the radiation correction to the gas temperature measurement.
the trigger point, the difference in millivolts, later converted into
degrees, between the temperature of the thermocouple at the instant
when the heating current was switched off and the temperature at which
it finally settled was a direct measure of the radiation correction.

The most difficult feature of this method was that of finding
how much heating current was required to raise the temperature of the
thermocouple to the temperature of the gas. An experimental approach,
involving the use of a second thermocouple, was used to do this. The
second thermocouple - a chromel-alumel thermocouple was chosen because
of its greater sensitivity - was used to measure the gas temperature
at a point as close as possible downstream of the junction of the
Pt v Pt-13%-Rh thermocouple. The heating current passing through the
Pt v Pt-13%-Rh thermocouple was adjusted until the temperature of the
gas, as measured by the chromel-alumel thermocouple, was the same
whether the Pt v Pt-13%-Rh thermocouple was present or not. Under such
conditions it is clear that the temperature of the Pt v Pt-13%-Rh
thermocouple must be at the same temperature of the gas, it would,
otherwise, have a heating or cooling effect upon the gas passing
over it.

Several experimental points require further explanation.
Figure 4.1.10 gives a schematic representation of the apparatus
that was used. The a.c. power was obtained from a mains connected
variable transformer, an a.c. source being preferred to a d.c. source
because, if a d.c. current had been used, heating or cooling of the
junction, depending upon the direction of the current, would have
occurred by means of the Seebeck effect. This effect, which is
additional to the 'i^2R' heating, is not desirable because it makes
Figure 4.1.10

Apparatus used for determining the radiation correction.
the process of finding the desired heating current a more difficult task due to the junction being at a different temperature to the rest of the wire. Furthermore, the heating current was not passed through the cold junction because this would heat the junction above 0°C and thereby lead to an incorrect estimate of the radiation correction. A final point is that, when the heating current was passed through the thermocouple, the d.c. amplifier was eliminated from the circuit, as shown in figure 4.1.10, so that it was not overloaded.

The magnitude of the corrections which were measured by this method were naturally dependent upon the conditions prevailing in the experiment, though a theoretical study indicated that the correction term should not be strongly dependent upon the velocity of the gas. The three examples given below indicate typical values of the radiation correction measured in nitrogen with a 5 thou diameter thermocouple, the gas velocities being as indicated.

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>velocity cms/sec.</th>
<th>radiation correction</th>
</tr>
</thead>
<tbody>
<tr>
<td>498</td>
<td>55</td>
<td>$2 \pm 1$ °K</td>
</tr>
<tr>
<td>688</td>
<td>76</td>
<td>$11 \pm 2$ °K</td>
</tr>
<tr>
<td>870</td>
<td>96</td>
<td>$22 \pm 2$ °K</td>
</tr>
</tbody>
</table>
ii) The correction for the heating effect of the source wire.

This is a simple correction which was determined during the course of the experiment, there being no additional apparatus needed. The procedure adopted was to use the detector wire as a resistance thermometer to measure the increase in temperature of the gas, due to the heating effect of the source wire, in the region where the main measurements were made. The resistance of the detector wire was measured with the heating current to the source wire switched off and again with the heating current switched on. The increase in resistance, being proportional to the increase in the temperature, was used to determine the required correction. The constant of proportionality, needed for this purpose, was found by experiment, the resistance of the wire being measured in gas flows at a series of different temperatures. This calibration procedure had to be repeated every time a broken detector wire was replaced by a new one.

The increase in the temperature of the gas was measured, by this means, at the two extremities of the region of the main measurements, and the average value was taken as being the required correction. This correction, which was usually close to 10°C, in conjunction with the radiation correction, enabled the required value of the gas temperature to be obtained from the measurement given by the thermocouple.
iii) Apparatus used for the measurement of gas mixtures.

The components of the gas mixture under investigation, i.e. nitrogen and carbon dioxide, were monitored and controlled by a series of manometers and valves, arranged as shown in figure 4.1.11. The gases were obtained from commercial high pressure cylinders and reducing valves were used to give a working pressure of 30 p.s.i. When using carbon dioxide, it was necessary to heat the gas, prior to its passage through the reducing valve, so that it did not freeze upon expansion.

Mixtures of nitrogen and carbon dioxide, of stipulated proportions, were obtained by repeated adjustment and measurement of the flow rates of the individual gases until the required flow rate of each was obtained. The flow rate of nitrogen was controlled by the valves V1(a) and V2(a) and was monitored using the manometers M1(a) and M2(a). The restriction shown in figure 4.1.11 consisted of a length of glass capillary tube, of which various lengths and bore sizes were available. A suitable restriction was selected so that, with the flow rate being used, there was a large pressure drop over the length of the capillary. This pressure drop was measured on the mercury manometer M1(a) and the pressure at the exit from the capillary was measured using the dibutyl phthalate manometer M2(a). The pressure at this point was usually about 150 cms. of 'phthalate so, for convenience, a double U-tube, as shown in the diagram, was used.

The nitrogen, having passed through the controlling valves, could be directed to a wet meter so that the flow rate could be measured. A wet meter consists of a number of vanes, forming a 'paddle-wheel', which is caused to rotate by the gas entering the
Figure 4.1.11.

Apparatus used for the measurement of gas mixtures.
meter. The speed of rotation, measured with a stop-watch, is a measure of the flow rate of the gas, though a correction is needed to take into account the fact that the gas becomes saturated with water vapour as it passes through the meter. A valve V3 was attached at the outlet from the wet meter so that the pressure in the meter, which was measured on another phthalate manometer M3, could be adjusted as required.

The flow rate of carbon dioxide was controlled and measured in exactly the same way as that described above for nitrogen. When measuring the flow rate with the wet meter, the pressure in the manometer M3 was adjusted, by means of the valve V3, to be the same as during the measurement of the flow rate of nitrogen. This enabled relative flow rates of the two gases to be obtained without the necessity for making the corrections for the water vapour content.

When the required flow rates of the individual gases had been obtained, and the corresponding readings of the manometers M1(a), M2(a), M1(b) and M2(b) noted, the necessary alterations to the flow system were made to allow the gases to flow through the furnace. The control valves were then readjusted so that the four manometer readings returned to the values noted after the flow rate measurements. Under these conditions the flow rate of each gas was the same as when measured with the wet meter, so the relative proportions of nitrogen and carbon dioxide in the mixture were known. The pressures on the manometers were checked frequently during the measurements of the thermal diffusivity to ensure that the flow rates had not changed.
4.2 The detector.

a) The theory of the detector circuit.

The detector circuit, which is a simple Wheatstone bridge network, is shown in figure 4.2.1. In this diagram, \( R \) represents the resistance of the detector wire and \( R_1, R_2 \) and \( R_3 \) represent the total resistance in each of the other three arms of the bridge. The driving voltage is represented by \( E \) and the out-of-balance voltage by \( V_1 \). The 10\( \Omega \) resistor is a standard resistor which enables direct measurements of the value of \( R \) to be made, when required, by comparing the voltage drop across \( R \) with that across the 10\( \Omega \) resistor. When not in use, this 10\( \Omega \) resistor is eliminated from the circuit by closing the switch \( S_2 \) and, since this direct method of measurement is not normally used during the course of the experiment, the calculations in this chapter are made with the assumption that \( S_2 \) is closed.

The main purpose of the Wheatstone bridge network is to enable any change in the resistance \( R \) to be measured by measuring the change in the voltage \( V_1 \). The resistance of the detector wire depends upon its temperature and this, in turn, depends upon the temperature of the gas in which it is placed and upon the heating effect of the current passing through it. Thus, the voltage \( V_1 \) can be used as a measure of the temperature of the gas in which the detector wire is placed. For the purpose of this experiment, it is important to establish a relationship between a change, \( \Delta T_g \), in the temperature of the gas and the corresponding change, \( \Delta V_1 \), in the out-of-balance voltage. In this section the relationship between \( \Delta V_1 \) and a change \( \Delta T_w \) in the temperature of the detector wire is calculated and in section 4.2 b)
Figure 4.2.1

The detector circuit.
the relationship between $\Delta T_g$ and $\Delta T_w$ is calculated.

The first step towards finding the relationship between $\Delta V_1$ and $\Delta T_w$ is to assume that the resistance $R$ of the detector wire varies with its temperature $T_w$ according to the relation

$$ R = R_0(1 + \alpha T_w) $$

where $R_0$ is the resistance of the wire at $0^\circ C$ and $\alpha$ is the temperature coefficient of resistance of the wire which, for platinum 10% rhodium, is $0.0017 \, ^\circ C^{-1}$. Differentiating this expression with respect to $T_w$ gives

$$ \frac{dR}{dT_w} = R_0 \alpha. $$

It can be shown that the current $i_A$ passing through the amplifier, the impedance of which is $R_A$, is given, approximately, by

$$ i_A = \left(\frac{E}{R_3 R_A}\right) \left(\frac{R_3 - R_1 R_2}{R_1 + R}\right). $$

the approximation being very good provided that $R_3 \gg R_2$ and $R_A \gg R_2$.

From this equation it follows that

$$ \frac{dV_1}{dR} = R_A \frac{di_A}{dR} = \frac{R_1 E}{(R_1 + R)^2}. $$

Combining equations 4.2.2 and 4.2.4 gives

$$ \frac{dV_1}{dT_w} = R_1 R_0 \frac{E \alpha}{(R_1 + R)^2} $$

or

$$ \Delta V_1 = S \Delta T_w. $$

where $S$, the sensitivity of the network, is given by

$$ S = \frac{R_1 R_0 E \alpha}{(R_1 + R)^2}. $$

It would obviously be convenient if $S$ were constant throughout
a particular experiment but equation 4.2.6 indicates that it will vary because $R$ will change as the detector wire is moved around in the gas. However, it can be shown that, for the particular values of $R$ and $R_1$ normally used, the change $\Delta R$ in the value of $R$ has a very small affect upon the sensitivity of the network. A typical value of $\Delta R$ can be obtained with the aid of equation 4.2.2, which indicates that

$$\Delta R = R_0 \Delta T_w.$$ 

$R_0$ is generally in the region of 30Ω and $\Delta T_w$ is unlikely to be greater than 10°C. Consequently, $\Delta R$ is normally 0.5Ω or less. In contrast to this, it can be seen from figure 4.2.1, that the value of $R_1$, which consists of a fixed resistor (1.2kΩ) and a variable resistor (0-5kΩ), can never be less than 1.2kΩ. Therefore, the value of $(R_1 + R)$ must be greater than 1.2kΩ and it cannot change by more than 0.5Ω as the detector wire is moved around in the gas, so the sensitivity $S$ can be regarded as constant during a particular experiment without introducing an error of more than 0.1%.

The required relationship between $\Delta V_1$ and $\Delta T_w$ has now been obtained, viz. equation 4.2.5, and it has been established that $S$ is effectively constant. A more simple, though slightly less exact, expression for $S$ can be obtained by using the fact that, since $R_A > R_1$, the current $i$ passing through the detector is given, to a close approximation, by

$$i = \frac{E}{(R_1 + R)} \quad 4.2.7$$

Also, the ratio $R_1/(R_1 + R)$ can be approximated by unity, so the expression for $S$ can be written as
Thus, since $\alpha_w$ is fixed by the choice of the material, the requirements for maximum sensitivity are that the detector wire should be long and fine i.e. $R_o$ should be large, and there should be a large current passing through the wire. There are, of course, limits to which these values can be taken. The factors which govern the final choice will become clear later.

Consider, now, the case where the temperature of the detector wire varies sinusoidally with time. Taking the temperature to be of the form

$$T_w = T'_w + \Delta T_w \cos \omega t,$$

then the voltage $V_1$ will be given by an equation of the form

$$V_1 = V'_1 + \Delta V_1 \cos \omega t,$$

where $\Delta V_1$ and $\Delta T_w$ are related by equation 4.2.5 and where $V'_1$ is determined by the balance conditions of the bridge. In the experiment, the temperature $T'_w$ is of the form given above, and the voltage $V_1$ is fed to an a.c. amplifier which eliminates the d.c. component and amplifies the sinusoidal component. The amplified signal is measured using a phase sensitive detector and a digital voltmeter, as described in section 4.1 b)(ii). The digital voltmeter measures a voltage $V$ which is directly proportional to the amplitude of the sinusoidal signal at the input to the a.c. amplifier, i.e. $V$ is directly proportional to $\Delta V_1$. The constant of proportionality may be frequency dependent so the relationship between $V$ and $\Delta V_1$ should be written as
\[ V = G(\omega) \Delta V_1. \]  

Combining this equation with equation 4.2.5 gives

\[ V = G(\omega) S \Delta T_w. \]

This equation shows that, at a particular frequency, the voltage, \( V \), measured on the digital voltmeter is directly proportional to the amplitude of the sinusoidal variation of the temperature of the detector wire.

At this stage it will be useful to mention certain details which are important from an experimental point of view. The values of the two resistances, \( R_3 \) and \( R_4 \), do not affect the sensitivity of the network, as can be seen from equation 4.2.6, and it would appear that any value could be selected for use. However, values for \( R_3 \) and \( R_4 \) should be selected by considering the following requirements: Firstly, it is desirable that the bridge be approximately balanced which means that, since \( R_1 \) is much larger than \( R \), \( R_3 \) needs to be much larger than \( R_2 \). It must be remembered that, since the d.c. signal is eliminated by the a.c. amplifier, it is not necessary that the bridge be perfectly balanced but it is preferable that it be nearly balanced so that large d.c. signals are not fed to the a.c. amplifier. The second, and more important, requirement is that the network as a whole should present a suitable impedance to the a.c. amplifier so that a high signal-to-noise ratio is obtained. Now, since \( R_1 \gg R \) and \( R_3 \gg R_2 \), the effective impedance is approximately equal to \( (R_2 + R) \). Furthermore, \( R \) is very small, so \( R_2 \) effectively determines the noise figure for the system. Having selected a suitable value for \( R_2 \), \( R_3 \) must be selected so as to approximately balance the bridge.
In practice, $R_2$ was chosen to be a fixed resistor (6.8kΩ) in series with a variable resistor (0-5kΩ) and $R_3$ was chosen to be a fixed resistor only (680kΩ). The two variable resistors were included in the circuit so that adjustments could be made whenever necessary. The variable resistor which was part of the resistor $R_1$ was found to be particularly useful because it enabled the sensitivity of the network to be adjusted. These resistors were never adjusted during the course of an experiment.

One last point of experimental importance should be mentioned. The driving voltage, 18 volts, for the bridge network was obtained from batteries because, if a mains operated power supply had been used, there would have been a danger of unwanted, 50 Hz signals affecting the measurements.

In this section, a relationship between the voltage $V$, measured on a digital voltmeter, and the amplitude $\Delta T_w$ of the sinusoidal temperature variations of the detector wire has been obtained, a relationship expressed by equation 4.2.10. The next task is to find the relationship between the temperature variations of the detector wire and the temperature variations of the gas. If the current through the detector wire was very small and resulted in a negligible amount of heating, the temperature of the wire would be equal to the temperature of the gas. However, because of the requirement that the current $i$ be large, to give greater sensitivity, it is not possible to ignore the effect of heating. The following section takes this effect into account and calculates the relationship between the temperature of the wire and the temperature of the gas.
4.2 b) The effect of electrical heating of the detector wire.

In this section, an equation is obtained which relates the temperature variations of the detector wire to the temperature variations of the gas in which the detector wire is placed. The temperature of the detector wire will be greater than that of the gas due to the heating effect of the current passing through the wire. For the sake of simplicity, it is assumed that all the heat produced in the detector wire is transferred to the gas by forced convection. The error caused by this assumption should be very small provided that the current through the detector is sufficiently small that radiation from the wire and conduction to the support wires are both negligible.

Consider a detector wire, length \( L \), which is at a temperature \( T_w \) and which is placed in a flowing gas, the temperature of which is \( T_g \). The resistance \( R \) of the wire is assumed to vary with its temperature according to equation 4.2.1 and it is assumed to carry a current \( i \) given by equation 4.2.7 which, as shown in section 4.2 a), is effectively constant. The electrical heat transfer to the wire in time \( \delta t \) is, therefore,

\[
i^2 R_0 (1 + \alpha \frac{T_w}{T_w}) \delta t
\]

and the heat lost by forced convection in time \( \delta t \) is

\[
iH(T_w - T_g) \delta t
\]

where \( H \) is the heat transfer coefficient per unit length of wire, the units of \( H \) being (watts \( \text{cms}^{-1} \circ \text{C}^{-1} \)).

These two expressions enable the increase in the temperature of
the wire, \( \delta T_w \), in the time \( \delta t \), to be written as

\[
\delta T_w = \left[ i^2 R_o (1 + \alpha_T) \delta t - \mathcal{L} H (T_w - T_g) \delta t \right] / Q
\]

where \( Q \) is the amount of heat required to raise the temperature of

the wire by 1°C. The above equation can be written in differential

form and it can then be used to calculate an expression for \( T_w \) if

an expression for \( T_g \) is assumed. The appropriate differential equation is

\[
(dT_w/dt) = i^2 R_o (1 + \alpha_T)/Q - \mathcal{L} H (T_w - T_g)/Q. \tag{4.2.11}\]

If the gas temperature is taken to be of the form

\[
T_g = T_g' + \Delta T_g \cos \omega t \tag{4.2.12}
\]

then equation 4.2.11 can be written as

\[
(dT_w/dt) = L + M \cos \omega t - T_w / \gamma \tag{4.2.13}
\]

where

\[
L = i^2 R_o / Q + \mathcal{L} H T_g' / Q \tag{4.2.14}
\]

\[
M = \mathcal{L} H \Delta T_g / Q \tag{4.2.15}
\]

and

\[
\gamma^{-1} = \mathcal{L} H / Q - i^2 R_o \alpha / Q. \tag{4.2.16}
\]

The solution to equation 4.2.13 is

\[
T_w = L \gamma + M (\gamma^{-2} + \omega^2)^{-\frac{1}{2}} \sin(\omega t + \theta) + c \exp(-t/\gamma) \tag{4.2.17}
\]

where \( \tan \theta = 1/\omega \gamma \) and \( c \) is a constant.

In the steady state, i.e. as \( t \to \infty \), the last term in the above equation

becomes zero.
If, as in equation 4.2.10, $\Delta T_w$ is used to denote the amplitude of the sinusoidal temperature variations of the wire, then it follows from equations 4.2.15 and 4.2.17, that the required relationship between $\Delta T_w$ and $\Delta T_g$ is

$$\Delta T_w = (LH/\omega g)^2 (\omega^2 + \omega^2)^{-\frac{1}{2}}$$  

4.2.18

It is possible, when $\omega^2 \gg \omega$, for $\Delta T_w$ to be greater than $\Delta T_g$ because, under these conditions,

$$(LH/\omega g)(\omega^2 + \omega^2)^{-\frac{1}{2}} \omega (LH/\omega g)(\omega)$$

$$= (LH/\omega g)/(LH/\omega g - l^2 R_\omega \omega g/Q)$$

which is greater than one. However, as will soon be shown, values of $\omega g$ are more than ten times greater than values of $(l^2 R_\omega \omega g)$ in the experimental arrangement used, so the gain for such a case would only be small. Furthermore, in order that $\omega^2 \gg \omega$, the frequency of the sinusoidal signals would have to be less than 10 Hz.

The relationship between the voltage, $V$, measured by the digital voltmeter and the amplitude, $\Delta T_g$, of the sinusoidal temperature variations of the gas, can be obtained by combining equations 4.2.10 and 4.2.18. This results in the expression

$$V = G(\omega)S(LH/Q)(\omega^2 + \omega^2)^{-\frac{1}{2}} \Delta T_g.$$  

4.2.19

or

$$V = C(\omega) \Delta T_g.$$  

4.2.20

where $C(\omega) = G(\omega)S(LH/Q)(\omega^2 + \omega^2)^{-\frac{1}{2}}$.  

4.2.21

Equation 4.2.20 is the same as equation 3.3.1. However, equation 3.3.1 was an assumed expression and the function $C(\omega)$ was unknown. The
validity of equation 3.3.1 has, therefore, been verified and the form of the function \( C(\omega) \) has been calculated.

It will be of great assistance to put some typical values into equation 4.2.19. This should give a clear idea of how the detector will perform during the experiment. The typical values to be used are

\[
I = 15 \text{ mA.} \quad R_0 = 40.6 \Omega \quad L = 1.1 \text{ cms.}
\]

\[
\alpha = 0.0017 \text{ } ^{\circ}\text{C}^{-1} \quad \text{and} \quad d = 7.5 \times 10^{-4} \text{ cms.}
\]

where \( d \) represents the diameter of the detector wire. The values of \( H \) and \( Q \) are also needed. The value of \( Q \) can be easily calculated from the properties of platinum 10% rhodium and from the dimensions of the wire. The value calculated by this means is \( 1.5 \times 10^{-6} \) joules. However, the value of \( H \) is a little more difficult to determine. It can be calculated using theoretical, or empirical, relations of other workers, or it can be estimated by performing a simple experiment.

The theoretical approach involves calculating the Nusselt number, denoted by \( \text{Nu} \), for forced convection from the wire. The value of \( H \) can then be calculated using the equation

\[
H = \pi \lambda \text{Nu},
\]

though this method requires the knowledge of the thermal conductivity, \( \lambda \), of the gas. Dennis, Hudson and Smith (52) have studied many formulae which have been suggested for calculating Nusselt numbers. The Collis and Williams (53) equation, equation 19 of reference (52), was selected as being a suitable equation for calculating the Nusselt number, and the resulting values of \( H \) which, as expected, are dependent upon the velocity and temperature of the gas concerned, are shown graphically.
in figure 4.2.2. These calculations, which were made for nitrogen only, required the knowledge of the density, viscosity and thermal conductivity of the gas, values of which were taken from tables of the National Bureau of Standards (54).

The method of estimating $H$ by experiment involves measuring the resistance of the detector wire as a function of the current passing through it, the detector wire being maintained in a gas flow of known, and constant, temperature. It is clear from equation 4.2.11 that, in the steady state i.e. $(dT_w/dt) = 0$, and with $T_g$ constant,

$$i^2 R_o (1 + \alpha_w T_w) = \frac{\mathcal{L} H}{R} (T_w - T_g)$$

and using equation 4.2.1 to eliminate $T_w$, and then rearranging, gives

$$i^2 = \frac{\mathcal{L} H}{R_o \alpha_w} - \frac{\mathcal{L} H}{R_o} \left( T_g + \frac{1}{\alpha_w} \right) / R.$$ 

Thus, if $i^2$ is plotted against $R^{-1}$, the value of $H$ can be calculated from the slope and the intercept of the graph.

This simple experiment was carried out in nitrogen at a temperature of 24°C, the gas velocity being 28 cms./sec. The graph so obtained is shown in figure 4.2.3. The slope was found to be 0.38 watts and the intercept $9.1 \times 10^{-3}$ amps. Both of these values result in a value of approximately $5.6 \times 10^{-4}$ joules cms$^{-1}$ sec$^{-1}$ °C$^{-1}$. The agreement between this result and the value which would be obtained, for these conditions, from figure 4.2.2, i.e. $3.8 \times 10^{-4}$ joules cms$^{-1}$ sec$^{-1}$ °C$^{-1}$, is not particularly good but, in view of the simplicity of the method and the various ways in which the Nusselt number can be calculated, the agreement is satisfactory for the purposes of this work.

Taking $H$ to have a value of $4.7 \times 10^{-4}$ watts cms$^{-1}$ °C$^{-1}$, the mean
The dependence of $H$ upon the gas velocity and temperature.
slope = -0.38 watts.
intercept = 9.1 \times 10^{-3} \text{amps}^2.

Figure 4.2.3

Determination of \( R \) by experiment.
of the theoretical and experimental values given above, the values of \( L, M \) and \( \tau^{-1} \) as given by equations 4.2.14, 4.2.15 and 4.2.16, can be calculated. The resulting values are

\[
L = (27i^2 + 345T_g') \degree C \sec^{-1} \quad 4.2.22
\]

\[
M = (345\Delta T_g) \degree C \sec^{-1} \quad 4.2.23
\]

\[
\tau^{-1} = (345 - 0.046i^2) \sec^{-1} \quad 4.2.24
\]

where the current \( i \) is expressed in milliamps.

Putting \( i = 15 \) in the above equations and then substituting the resulting values into equation 4.2.17 gives

\[
T_w = (18.1 + 1.03T_g') + \Delta T_g \left[ 0.94 + (\omega/345)^2 \right]^{-\frac{1}{2}} \sin(\omega t + \phi) + c \exp(-335 t) \quad 4.2.25
\]

where \( \tan \phi = (335/\omega) \).

This shows that, when \( T_g' \) is 24 \degree C, the temperature of the wire, under static conditions, is approximately 19 \degree C above the temperature of the gas for the particular conditions used in the above calculations. This compares well with a value of 22 \degree C which was estimated by determining the resistance of the wire from measurements of the voltage across the wire and the current passing through it.

The second term in equation 4.2.25 shows how the amplitude of the temperature variation of the wire is related to the amplitude of the temperature variation of the gas. Figure 4.2.4 shows how the value of the function \( [0.94 + (\omega/345)^2]^{-\frac{1}{2}} \) varies with frequency and it shows that, for frequencies less than 90 Hz, the amplitude of the variations
Figure 4.2.4

The dependence of the sensitivity of the detector upon the frequency f.
in the wire is greater than half the amplitude of the variations of the gas temperature. Consequently, it is clear that there is no appreciable loss in sensitivity due to the influence of this term unless measurements are made at frequencies greater than 100 or 200 Hz.

The third term in equation 4.2.25 is zero in the steady state, i.e. when $t \rightarrow \infty$. This term indicates the speed of response of the wire to a change in the steady conditions of the gas. The value of $\gamma$, which is $1/335$ seconds or 3.0 millisecs., can be regarded as the characteristic response time of the wire. Equation 4.2.24 indicates that $\gamma$ increases as the current $i$ is increased though, with the very small currents normally used, this effect is small. It would appear, from equation 4.2.24, that $\gamma$ could become very large and could even be negative if the current was increased beyond 87 mA. However, as can be seen from the first term of equation 4.2.17, the temperature of the wire would be infinitely large when $\gamma^{-1}$ was zero so the wire would burn out before this point was reached. Furthermore, because radiation from the wire would be very important, the theory would no longer be applicable.

The above calculations apply to the particular case of nitrogen at $24^\circ$C flowing at a velocity of 28 cms/sec but the factors involved in the equations do not change very rapidly with changing conditions. Consequently, equations 4.2.22, 4.2.23 and 4.2.24, whilst only applying to the particular conditions stated, would not be vastly different in different conditions.

To summarise, the results obtained in this section have shown that the amplitude of the sinusoidal temperature variations of the detector wire is proportional to the amplitude of the sinusoidal
temperature variations of the gas (equation 4.2.18). The constant of proportionality is quite strongly dependent upon the value of \( \omega \) but, for currents of 15 mA or less, it depends very little upon the value of \( i \). This fact, along with the fact that the theory is exact for very small currents, i.e. for \( i \to 0 \), suggests that a current of 15 mA is sufficiently small for the theory given here to be adequate.

It has also been shown that the voltage \( V \), measured at the output of the p.s.d., is related to the amplitude of the sinusoidal temperature variations of the gas by equation 4.2.19. This equation is strongly dependent upon \( i \) through the dependence of the sensitivity \( S \) upon \( i \), \( S \) being given by equation 4.2.6 or, less exactly, by equation 4.2.8. This indicates that \( i \) should be as large as possible. The value used, 15 mA, was sufficiently large to give an adequate signal, enabling \( V \) to be measured accurately, and sufficiently small that the measuring apparatus performed in a manner consistent with the theory. It is probable that an even larger current could have been used if necessary, but this was not considered to be the case.

Experimental evidence of the satisfactory performance of the measuring equipment is given in the following section.
4.2 c) Experimental evidence of the satisfactory performance of the measuring system.

Various simple tests were made to check that the measuring system performed in a manner consistent with the theory of sections 4.2 a) and 4.2 b). It was assumed, in section 4.2 a), that the voltage V measured on a digital voltmeter was proportional to the amplitude of the sinusoidal signal at the input of the a.c. amplifier. This would certainly be true if the a.c. amplifier and the p.s.d. performed perfectly, but it is as well to verify that this is the case.

To do this, a slightly modified form of the Wheatstone bridge circuit was used. The modified circuit, shown in figure 4.2.5, included a chain of ten resistors, each nominally 100Ω, and the tapping point P for the signal to the a.c. amplifier could be moved anywhere along this chain. The detector wire was placed in the gas, in the wake of the periodic line source, where a large and steady signal could be detected, and the detector wire was kept in this position throughout the test. The input to the a.c. amplifier was varied by moving the tapping point along the chain of resistors and the output voltage V, measured on the digital voltmeter, was noted for each of the different tapping points.

An expression for the amplitude, ΔV₁, of the sinusoidal signal applied to the a.c. amplifier can be obtained by means of a similar calculation to that given in section 4.2 a). The required expression is

\[ ΔV₁ = R₀ \alpha \left( R + R₁ + R₂ + R₃ \right)^{-1} (V₂ + V₃) ΔT_w \]

4.2.26

where V₂ and V₃ represent the voltages across R₂ and R₃ respectively. The only factor which varies in the above equation, as the tapping point is changed, is the voltage (V₂ + V₃). Consequently, the amplitude of the
Figure 4.2.5.

Wheatstone bridge arrangement used to test the performance of the a.c. amplifier and the p.s.d.
A sinusoidal signal applied to the a.c. amplifier is proportional to the voltage \((V^2 + V_3^2)\) so, to check that the voltage \(V\) is proportional to the input to the a.c. amplifier, it is sufficient to check that the voltage \(V\) is proportional to the voltage \((V^2 + V_3^2)\).

The results of four such tests, each carried out at a different frequency, are shown in figure 4.2.6. The slopes of the four lines are different because a different value of \(\Delta T_w\) was used in each case. The tests verify that the voltage \(V\) is proportional to the input to the a.c. amplifier. The deviation of the points from the best straight line was worst for the measurements made at 106.3 Hz but, even for this case, the mean percentage deviation was only 0.3% and the deviation of the worst point was only 0.7% of the voltage measured. These deviations are probably due to random errors in the measurements rather than to systematic errors arising from non-linear behaviour of the equipment.

Having established that the voltage \(V\) is proportional to the input signal to the a.c. amplifier, it must now be established that this input signal is proportional to \(\Delta T_g\), the amplitude of the temperature variations of the gas. This amounts to verifying equation 4.2.19 and, unfortunately, is rather difficult to do. There is no way, other than that proposed here, of measuring \(\Delta T_g\) and it cannot be varied by a known amount without assuming that the theory of chapter III is correct. Furthermore, the angular frequency \(\omega\) cannot be changed without causing a corresponding change in \(\Delta T_g\). The only variable in equation 4.2.19 which can be conveniently changed, is the current \(i\) which appears in equation 4.2.19 through the dependence of \(S\) and \(\gamma\) upon \(i\). If the heating effect of the current had been ignored in the theory, \(S\) would have been the only term appearing in equation 4.2.19 which depended
Figure 4.2.6

Results of the test to check the linearity of the a.c. amplifier and the p.s.d.
upon the current $i$. The equation for $S$, equation 4.2.6, can be written in the form

$$ S = R_0 \alpha_w \left[ \frac{iR_1}{(R_1 + R)} \right] = R_0 \alpha_w \left( \frac{iV_1}{E} \right) \quad 4.2.27 $$

where $V_1$ is the voltage across $R_1$.

Consequently, if the detector wire is placed in the gas stream where a large and steady value of $\Delta T$ exists, the voltage $V$ should vary with the current $i$ through the dependence of $S$ upon $i$ as given above. Figure 4.2.7 shows the results of measurements of $V$ as a function of $i$. Instead of plotting the value of $i$ along the x-axis the value of $(iV_1/E)$ has been plotted because the ratio $(V_1/E)$ which appears in equation 4.2.27, is slightly dependent upon the current. It is clear, from figure 4.2.7, that $V$ is proportional to $(iV_1/E)$ for currents up to 15 mA. Additional measurements showed that the dependence was linear for currents up to 30 mA.

This test has not directly verified equation 4.2.19. However, in the case of an extremely small current the theory should be exact and this test has shown that as the current is increased from zero, the measured voltage $V$ increases by a proportional amount. Consequently, the test indicates the the values of $V$ which are used in the experiments are suitable measures of the amplitude of the sinusoidal temperature variations in the gas.
Figure 4.2.7.

Verification that the sensitivity is proportional to the current.
CHAPTER V

DIFFERENCES BETWEEN THE THEORETICAL AND EXPERIMENTAL CONDITIONS.

The ideal conditions, assumed in the theory, cannot be obtained in practice. Consequently, the results of the measurements of thermal conductivity may be slightly in error. To investigate this possibility, and estimate the magnitude of the errors involved, the deviations from the ideal conditions were either measured or determined theoretically.

For the purposes of the theory of chapter III, both the thermal diffusivity $K$, and the velocity $u$, of the gas were assumed to be constant. However, this is not the case in the experiment. Since $K$ is a temperature dependent factor, it was established, as a result of the measurements of the velocity and temperature of the gas which are described in section 5.1, that both $K$ and $u$ vary in the region where the measurements of thermal diffusivity are made. The consequences of having ignored these variations in the theory are discussed in section 5.1, though certain approximations were necessary to simplify the task of estimating the magnitude of the resulting errors.

Other deviations from the theory also occur, though they are less serious than those mentioned above. It is assumed that both the line source of heat and the detector wire are of infinitely small diameter and that the detector wire is parallel to the source wire and perpendicular to the direction of flow of the gas. The consequences of the two wires being slightly out of alignment are considered in section 5.2.

The ultimate test of the satisfactory performance of the apparatus is to check that the measurements made during an experiment are consistent with the theory of chapter III. The results of such a test are described in section 5.3.
5.1 The variations of the velocity and the temperature of the gas.

The variations of the velocity and temperature of the gas are caused by a combination of three effects. In the first place, the passage of the gas through the furnace causes large variations of velocity and temperature to develop in the gas. The magnitude of these variations is reduced considerably as the gas passes through the series of nickel screens at the furnace exit, but it is impossible to obtain a perfectly uniform flow. Secondly, since the heated gas flows through stationary, room temperature air, there is a boundary layer between the gas and the air in which there are large velocity and temperature gradients. In the initial stages of the flow, i.e. close to the nickel screens, this boundary layer is very thin and the velocity and temperature of the gas near the centre of the stream is unaffected by its presence. However, in the later stages of the flow, the boundary layer becomes gradually thicker and the velocity and temperature gradients extend into the central regions of the gas stream. Finally, the heated source wire produces a temperature wake and a velocity wake, both of which extend into the region where the measurements of thermal diffusivity are made.

Experimental and theoretical investigations into the magnitude of the variations of the temperature and velocity of the gas were made. The results of this work are given in this section and the consequences of having ignored these variations in the theory are considered. The variations in the direction of flow of the gas are more important than those in other directions because the detector wire measures an average temperature over the length of the wire.
a) Variations of the temperature of the gas.

The variations of the temperature of the gas were more easily
determined than the variations of the velocity. The temperature
distribution across the full width of the gas stream was measured
using a thermocouple and the temperature distribution downstream from
the line source of heat was measured using the detector wire as a
resistance thermometer.

The random variations of temperature caused by the first of the
three effects mentioned earlier were found to be very small, less than
1°C, and, since the detector wire measures an average temperature over
the length of the wire, these variations were regarded as insignificant.
The second effect was studied by making measurements of the temperature
distribution at a series of different distances downstream from the
furnace exit. An example of such a measurement is shown in figure 5.1.1.
This shows that, even at a distance of 10 mm. from the screens, the
variation in temperature along the length of a detector wire which is
less than 12 mm. long is, in this case, less than 4°C, i.e. less than
1% of the difference between the gas temperature and the room temper­
ature. Experimental measurements are usually made at distances less
than 10mm. from the screen where the variations will clearly be less
than 1%. Measurements at other gas temperatures gave similar results.

The variations caused by the third effect, the heating effect
of the source wire, were found to be much greater, and much more
important, than those caused by either of the first two effects.
Rather than make a detailed series of measurements of the temperature
distribution downstream from the source wire, the appropriate theor­
etical equation, equation 2.5.1, could have been used. However, a more
Figure 5.1.1

The variation of the gas temperature across the furnace exit.
convenient approach was used which involved combining the theoretical equation with experimental measurements. The temperature of the gas in the region of the measurements, i.e. positions where \( y = 0 \), is all that is required so equation 2.5.2 can be used in preference to equation 2.5.1. Equation 2.5.2 can be written in the form

\[
\Delta T = (\text{constant}) \left( x \right)^{\frac{1}{2}} \tag{5.1.1}
\]

and one measurement of \( \Delta T \), at a known position \( x \), is sufficient to determine the value of the constant. This enables a simple expression for the temperature variation of the gas downstream from the source wire to be obtained.

The value of the constant in equation 5.1.1 varies according to the conditions but values were usually between 5 \( {^\circ}C \text{ cm}^2 \) and 10 \( {^\circ}C \text{ cm}^2 \). Consider, as an example, a value of 7 \( {^\circ}C \text{ cm}^2 \). This shows that \( \Delta T = 16^\circ C \) when \( x = 0.2 \text{ cm} \) and \( \Delta T = 10^\circ C \) when \( x = 0.5 \text{ cm} \). The change of 6\(^\circ^{\circ} C\) over a distance of 3 mm clearly indicates that the effect of electrical heating is more important than the other effects.

b) Variations of the velocity of the gas.

The variations of the velocity of the gas are likely to cause more error than the variations of the temperature because, as can be seen from equation 3.3.5, the relevant equations depend, approximately, upon the cube of the velocity. It is unfortunate that the variations of the velocity are also the more difficult to determine.

Measurements of the velocity of the gas were made using a commercial constant-temperature, hot-wire anemometer, manufactured by
DISA (Dansk Industri Syndikat A/S). This instrument is very useful for making rapid measurements of gas velocities though its use is limited to gases which are at a uniform temperature. Consequently, it could only be used to make measurements in room temperature gas flows since, as has been shown in the previous section, temperature variations exist in the gas when it is heated. This limitation also means that the instrument cannot be used to measure the velocity distribution downstream from the heated line source so measurements had to be made with the source wire unheated.

The variations of the velocity of the gas within the gas stream were measured by slowly traversing the DISA hot wire probe across the stream at different heights above the furnace exit, the top nickel screen. The probe was traversed at a constant speed using a synchronous motor and the output from the DISA instruments was recorded on a chart recorder. The DISA equipment was then calibrated, using gas flows of known velocity, so that the signal recorded on the chart recorder could be used as a measure of the velocity of the gas at the position of the probe.

The results of these measurements showed that the presence of the boundary layer had little or no effect upon the velocity of the gas near the centre of the stream for the first few centimetres of the flow. The traces obtained on the chart for two traverses near the centre of the gas stream are shown in figure 5.1.2. The measurements which were made at a distance of 1.5 mm. above the screens indicate that rapid and regular changes of the velocity of the gas were present. It is clear, from the spacing of these variations, that they were caused by the gas flowing through the individual holes of the screen,
The variation of the gas velocity across the furnace exit.

**Figure 5.1.2**

- Continuous line. 1.5 mm. above screen.
- Broken line. 2.5 mm. above screen.

**Velocity (cms/sec)**

Distance in mm. from centre.
which had a mesh of 40 holes per inch (15.75 holes per cm.). The measurements made at a distance of 2.5 mm. above the screens showed that these regular variations were no longer present but that a certain amount of random variation remained. Further measurements at greater distances downstream from the furnace exit showed little change in the velocity distribution, indicating that velocity gradients in the direction of flow were very small.

In an effort to express the uniformity of flow of the gas by a measurable quantity, the average velocity in the central region of the flow was calculated using the measurements represented by the broken line of figure 5.1.2 and the mean deviation from this average value was calculated. The average velocity was approximately 39.7 cm/sec and the mean deviation was approximately 0.4 cm/sec, 1% of the average velocity. This figure can be used as a measure of the uniformity of the flow.

It is difficult to know whether or not this flow is sufficiently uniform for the theory of chapter III to be applicable. However, as a result of measurements of the velocity distribution downstream from the source wire, it was obvious that the insertion of the source wire into the gas stream caused variations in the gas velocity which were considerably greater than those shown in figure 5.1.2. Consequently, the uniformity of the flow was considered to be adequate for the experiment though the effect of the velocity wake downstream from the source upon the measurements of thermal diffusivity obviously requires investigation.

The required measurements of the gas velocity downstream from the line source of heat were made using the DISA hot wire anemometer,
though these measurements could only be made with the heating current switched off because of the sensitivity of the DISA instrument to changes in temperature. The velocity distribution will not be greatly different when the heating current is switched on though it is bound to be slightly different due to small changes in the density and the viscosity of the gas.

The results of four such measurements are shown in figure 5.1.3. It is clear that, very close to the wire, there are large velocity gradients but that, at distances greater than 2 or 3 mm. from the wire, the velocity distribution changes quite slowly with increasing distance.

Measurements were also made, again using a DISA anemometer, of the minimum velocity i.e. the velocity directly downstream of the wire, for a series of different distances from the wire. These measurements were then repeated, at the same positions, with the wire removed from the gas so that the effect of the presence of the wire could be determined. The results of these measurements are shown in figure 5.1.4. This figure shows that the presence of the wire causes a reduction in the gas velocity of several percent but that the velocity downstream of the wire changes quite slowly with increasing distance. For distances greater than 3 mm. the rate of change of the velocity is less than 3% per mm.

The measurements described in this section have shown that the velocity of the gas in the region where the measurements of thermal conductivity are made is not constant and equal to the free-stream gas velocity, as was assumed in the theory. This is due mainly to the presence of the source wire. The effect of the presence of the heated source wire therefore requires further investigation.
Figure 5.1.3

The velocity distribution in the gas stream at various distances downstream of the source wire.
Figure 5.1.4

Determination of the effect of the presence of the source wire on the velocity of the gas.
5.1 c) The effect of the variations of the velocity and temperature of the gas.

The theory of chapter III was calculated using the assumption that both the velocity $u$ and the thermal diffusivity $K$ of the gas were constant. However, as has been shown in the previous sections, variations of velocity and of temperature, and therefore of thermal diffusivity, exist in the gas, due largely to the presence of the heated source wire. It is therefore necessary to study the consequences of having made this erroneous assumption.

A quantitative analysis of this problem would be exceedingly difficult. It would require detailed knowledge of the variations of $u$ and $K$ for all conditions encountered during a series of experiments. However, a fairly simple analysis can show that a practical experiment, i.e. an experiment in which $u$ and $K$ vary, can be virtually identical, over a limited region, to an ideal experiment, in which $u$ and $K$ are constant, provided that suitable values of $u$ and $K$ are chosen for the ideal experiment. It is shown, as a result of the arguments given below, that the required values of $u$ and $K$ for this ideal experiment are the average values of these variables over the region in which the measurements are made in a practical experiment.

An expression for the amplitude of the sinusoidal temperature variations of the gas in an ideal experiment can be obtained from equation 5.1.18. The required expression is

$$\Delta T_s = b r^{-\frac{1}{2}} \exp[(x - \alpha r)u/2K] \quad 5.1.2$$

The approximate expression for $\alpha$, that given by equation 3.1.12, is adequate for this work and, since all measurements during an
experiment were made at positions where \( y = 0 \), it is also convenient to put \( r = x \) in equation 5.1.2, which then becomes

\[
\Delta T_g = b x^{-\frac{1}{2}} \exp(-\kappa w^2 x/u^3)
\]  

This equation could be used to plot \( \Delta T_g \) as a function of \( x \), given suitable values of the variables, but the shape of the resulting curve can be more conveniently studied using the equation

\[
(d/dx)(\Delta T_g) = -\Delta T_g (\frac{1}{2} x^{-1} + \kappa w^2 / u^3)
\]

which follows directly from equation 5.1.3.

The above equation, having been derived from equations in which \( u \) and \( \kappa \) were assumed to be constant, is only exact for an ideal experiment, but it can be used to give an indication of how \( \Delta T_g \) depends upon \( x \) in a practical experiment. This can be done by introducing the dependence of \( (\kappa/u^3) \) upon \( x \) into the equation. For convenience, the value of \( (\kappa/u^3) \) in an ideal experiment can be denoted by \( (\kappa/u^3)_I \), and in a practical experiment it can be denoted by \( (\kappa/u^3)_x \) to indicate that it is a function of \( x \). The average value of \( (\kappa/u^3)_x \) in a particular interval \( x = x_1 \) to \( x = x_2 \) is denoted by \( (\kappa/u^3)_{x_{1-2}} \). The results of the measurements described in the previous two sections indicate that \( (\kappa/u^3)_x \) is a slowly decreasing function of \( x \), \( \kappa \) being a decreasing function of \( x \) and \( u \) being an increasing function of \( x \).

Consider the dependence of \( \Delta T_g \) upon \( x \), as determined by equation 5.1.4, in the region \( x = x_1 \) to \( x = x_2 \) for both an ideal and a practical experiment. Clearly the two cases can only be similar if \( (\kappa/u^3)_I \) has a value close to that of \( (\kappa/u^3)_x \). Since \( (\kappa/u^3)_x \) is only
a slowly varying function of $x$, a convenient value for $(\kappa/u^3)_1$ is $(\kappa/u^3)_{1-2}$. Using this value for $(\kappa/u^3)_1$ ensures that the values of $(d/dx)(\Delta T_g)$ for the ideal and practical cases are identical at a point somewhere near the middle of the region concerned. Furthermore, by introducing typical values of the variables into equation 5.1.4, it can be shown that the values of $(d/dx)(\Delta T_g)$ for the two cases differ, at the worst positions i.e. at the extreme ends of the region, by no more than 2%. Consequently, it is apparent that $(\kappa/u^3)_{1-2}$ is a suitable value for $(\kappa/u^3)_1$. Therefore, each practical experiment should be regarded as an ideal experiment with a value of $(\kappa/u^3)$ equal to the average value of $(\kappa/u^3)$ for the interval where the measurements are made.

The average value of $(\kappa/u^3)$ in any interval is not easy to determine exactly. However, the average value of $\kappa$, which can be denoted by $\bar{\kappa}$, and the average value of $u$, denoted by $\bar{u}$, can both be determined quite easily so that the ratio $(\bar{\kappa}/\bar{u}^3)$ can be found. This ratio can be used as an alternative to the average value of $(\kappa/u^3)$, the difference between the two being negligibly small.
5.2 Other differences between the theoretical and experimental conditions.

There are other differences between the theoretical and the experimental conditions but their effect is probably much less than the effect of the variations of \( u \) and \( K \) which were discussed in the previous section. Both the line source of heat and the detector wire were assumed, in the theory, to be of infinitely small diameter. They were also assumed to perfectly aligned, being parallel to each other and being perpendicular to the direction of flow of the gas. In view of the very small diameters of the wires used for the source and the detector it is apparent that the effect of misalignment is more serious than the effect of the finite size of the wires. The misalignment of the wires causes the detector wire to measure an average temperature over a small range of temperatures due to the detector not being situated along an isothermal. Consequently, the greater the temperature gradient at the point of measurement the greater will be the effect of misalignment.

The effect of misalignment can easily be estimated. Equation 3.3.2 shows the dependence of \( V \) upon \( r \) and equation 3.3.3 was obtained from equation 3.3.2 by assuming that \( r \) was equal to \( x \) i.e. \( y = 0 \). If the wires are not parallel it is equivalent to assuming that \( y \) is not equal to zero. If \( r \) is not put equal to \( x \) in equation 3.3.2 the effect upon equation 3.3.3 is that the last term becomes \( r(\alpha_2 - \alpha_1)u/2K \) and it then becomes necessary to plot \( \ln(V_1/V_2) \) as a function of \( r \) instead of \( x \). For the small values of \( y \) anticipated, \( r \) can be approximated by

\[
r = x \left( 1 + \frac{1}{2} \frac{y^2}{x^2} \right)
\]

Inserting likely values for \( y \) and \( x \) indicates that \( r \) can be approximated
by x without introducing an error of more than \( \frac{1}{3} \% \).

The only other difference between the theoretical and experimental conditions has already been considered in 4.2 b), which deals with the effect of the electrical heating of the detector wire. The theory given in that section assumed that the effect of radiation from the detector wire was insignificant compared with the heat transferred from the wire by forced convection. A theoretical study of the problem has shown the assumption to be valid to within 1\% but the fact that the measurements made with the detector are differential temperature measurements of the order of 1°C means that the effect of radiation from the detector on the differential measurements will be considerably less than 1\%. 
Evidence that the experimental measurements are consistent with the theoretical equations.

Equation 3.3.7 was chosen as the most suitable equation to use to enable the compatibility of the theory and the experimental measurements to be established. Tests were carried out by making measurements of $V$ as a function of $x$ and then the value of $\ln(V^2x)$ was plotted against $x$. The slope of the graph was then compared with the theoretically predicted slope i.e. $(1-\alpha)u/k$.

These tests required the knowledge of the absolute value of the variable $x$, which were normally measured on a scale with an arbitrarily located origin. The value of the constant needed to convert these measurements to absolute measurements was determined using the method described in section 2.5 i.e. the method of plotting $\Delta T_{\text{max}}^{-2}$ against $x$ whilst using a steady line source of heat.

Figures 5.3.1 and 5.3.2 show examples of the measurements that were obtained in these tests. Only one of the variables $u$, $f$ and $K$ which appear in equation 3.3.7 were changed from one test to the next so that it could be established that the dependence of $V$ upon these variables was as predicted theoretically. The table below shows the values of the variables that were used and the theoretical and experimental values of the slopes are shown also.

<table>
<thead>
<tr>
<th>frequency $f$ Hz</th>
<th>velocity $u$ cms/sec</th>
<th>diffusivity $\text{cm}^2$/sec</th>
<th>experimental slope</th>
<th>theoretical slope</th>
</tr>
</thead>
<tbody>
<tr>
<td>31.58</td>
<td>30.82</td>
<td>0.240</td>
<td>0.640</td>
<td>0.637</td>
</tr>
<tr>
<td>85.26</td>
<td>30.82</td>
<td>0.240</td>
<td>4.243</td>
<td>4.324</td>
</tr>
<tr>
<td>106.4</td>
<td>30.82</td>
<td>0.240</td>
<td>6.58</td>
<td>6.47</td>
</tr>
<tr>
<td>64.07</td>
<td>30.82</td>
<td>0.240</td>
<td>2.447</td>
<td>2.527</td>
</tr>
<tr>
<td>64.07</td>
<td>25.30</td>
<td>0.240</td>
<td>4.340</td>
<td>4.342</td>
</tr>
<tr>
<td>64.07</td>
<td>34.69</td>
<td>0.240</td>
<td>1.825</td>
<td>1.806</td>
</tr>
</tbody>
</table>
Check that $\log_e (v^2 x)$ is proportional to $x$. 

$u = 30.82$ cm/sec
$\kappa = 0.240$ cm$^2$/sec
Check that $\log_e(V^2x)$ is proportional to $x$. 

$u = 34.69 \text{ cms/sec}$

$u = 25.30 \text{ cms/sec}$

$f = 64.07 \text{ Hz}$

$\kappa = 0.240 \text{ cm}^2/\text{sec}$.
The agreement between the theoretical and experimental values for the slopes indicates that equation 3.3.7 is the correct expression for the dependence of $V$ upon the variables involved. The test has not verified that the term in equation 3.3.7 which involves the terms $b$ and $C(\omega)$ is correct. This would be very difficult to do because of the complicated way these two terms depend upon the many variables involved. In view of this, and bearing in mind that it is not necessary to know the values of these terms to measure the thermal diffusivity, it was considered to be unnecessary to verify that they were correct.

The points plotted in figures 5.3.1 and 5.3.2 may be slightly in error if an incorrect correction term was used for the measurements of $x$ on the arbitrarily located scale. It was because of this problem that this method of measuring the thermal diffusivity was considered to be inferior to methods i) and ii) of section 3.3. Despite this possibility, it is clear that the experimental and theoretical values of the slope are sufficiently close to each other to indicate that the experimental measurements are consistent with the theory.

The effect of using an erroneous value of the correction term for the measurements of $x$ is to cause the plot of $\log_e (V^2 x)$ against $x$ to be slightly curved. There is a certain amount of evidence of this having occurred in figures 5.3.1 and 5.3.2.
CHAPTER VI

EXPERIMENTAL PROCEDURE AND THE RESULTS OF THE MEASUREMENTS.

The procedure followed when making measurements of thermal conductivity is described in section 6.1 of this chapter. The method of making many of the measurements has already been described in earlier chapters, so it is only necessary to give a few additional details in this section.

The results of the measurements are given in section 6.2. The results for nitrogen and carbon dioxide are given first and they are compared with the correlated results of the many experimental values available. They are also compared with values obtained from a theoretical equation which involves the viscosity of the gas, a property for which accurate values are available. The results for mixtures of nitrogen and carbon dioxide follow. They too, are compared with other experimental values, though there are fewer such values available, and with values obtained from a theoretical relation.

The results are discussed in section 6.3 of this chapter and the errors associated with the measurements are considered in section 6.4.
6.1 The experimental procedure.

The procedure which was used for making measurements of the thermal diffusivity of a gas at a particular temperature can be described in three separate stages. In the first place, a certain amount of preparatory work was necessary to obtain the required working conditions. The second stage involved the measurements of the phase and amplitude of the sinusoidally varying temperature, from which the thermal diffusivity was later calculated, and the third stage involved the making of all the ancillary measurements.

a) The preparatory work.

Having decided at what temperature the measurements were to be made, the first task was to select a flow rate of gas which would result in the gas, when heated to the required temperature, having a flow velocity, at the furnace exit, in the range 30–50 cms/sec. When making measurements on pure gases, it was a simple matter to adjust the flow rate as required but, for gas mixtures, the selection of the necessary flow rates was more difficult. The procedure for setting the flow rates has been described in section 4.1 c) and it is clearly not a simple matter to make adjustments to the original settings. Fortunately, because of the wide range of suitable flow velocities, a satisfactory flow rate for the room temperature mixture could be selected using knowledge gained from previous runs.

When the required flow rate of gas, or gas mixture, had been obtained, the power supplied to the furnaces was set to an amount which would heat the gas to the selected temperature. Because of the
large thermal capacity of the furnaces it was necessary to allow the apparatus to run for several hours in order to obtain a steady gas temperature. As the temperature of the gas approached a steady value several pre-measurement tests were made. The tension and alignment of the source and detector wires were checked and corrected whenever necessary. The measuring equipment was then tested, the gain of the amplifier and the sensitivity of the detector circuit being adjusted so that convenient signals could be measured by the p.s.d. for all frequencies and positions to be used during the experiment. Finally, to avoid having to change the high pressure gas cylinders in the middle of the measurements, a full cylinder was switched into use at this stage, if it was considered to be necessary.

b) The measurement of the phase and the amplitude of the sinusoidal variations of the temperature.

The procedure for making the required measurements of the phase and the amplitude of the temperature variations of the gas has been described in section 4.1b). A few additional experimental details are given here.

The measurements of the phase i.e. the gas velocity measurements, were made both before and after the measurements of the amplitude. This enabled any change in the flow rate to be detected. Furthermore, the temperature of the gas was monitored, using a chromel-alumel thermocouple, throughout these measurements so that any change in the gas temperature could also be detected.

Accurate measurements of the gas velocity are essential to the
success of the experiments. Consequently, many phase measurements were made in the region of interest, each over a slightly different interval, so that accurate knowledge of the gas velocity was obtained.

Four methods of extracting the value of the thermal diffusivity from the measurements of the amplitude of the temperature variations were described in section 3.3. Of these, only the first two were used in practice, and the first method was used more often than the second. The first method requires that \( \ln\left(\frac{V_1}{V_2}\right) \) be measured, and plotted, as a function of \( x \) (see equation 3.3.3) so that the slope of the graph may be determined and the thermal diffusivity calculated using equation 3.3.4. Two sample plots of \( \ln\left(\frac{V_1}{V_2}\right) \) against \( x \) are shown in figure 6.1.1. In practice, it was not necessary to draw these graphs because the slope, and the error in the slope, could be calculated using a 'least squares fit' analysis.

When the amplitude measurements had been completed and the gas velocity had been remeasured, the necessary ancillary measurements were made.

c) The ancillary measurements.

First of all, the gas temperature was measured, using a platinum/platinum-13% rhodium thermocouple, and the required radiation correction was determined as described in section 4.1 c). The correction for the heating effect of the source wire, also described in section 4.1 c), was then measured. The two frequencies, \( f_1 \) and \( f_2 \), at which the measurements \( V_1 \) and \( V_2 \) were made were measured using a timer counter because the dial on the oscillator
\[ \ln(V_1/V_2) \]

slope = 0.6809 ± 0.0125 (1.9%)
temperature = 479 °K
gas velocity = 42.8 cms/sec
frequencies \( f_1 = 64.06 \) Hz
\( f_2 = 85.35 \) Hz

slope = 0.6205 ± 0.0063 (1.0%)
temperature = 310 °K
gas velocity = 35.3 cms/sec.
frequencies \( f_1 = 64.08 \) Hz
\( f_2 = 85.29 \) Hz

Figure 6.1.1.
was found to be inaccurate. When measurements of gas mixtures were
being made the flow rates of the individual components were remeasured
using the method described in section 4.1 c) so that any change in
the mixture content could be determined. Finally, the atmospheric
pressure was measured so that all the measurements could be corrected
to a standard pressure of 760 mm of mercury, the thermal diffusivity
being inversely proportional to the pressure through the dependence
of the density upon pressure.

This completed all the measurements which were needed to enable
the thermal diffusivity of the gas to be calculated. When method i) of
section 3.3 was being used the necessary calculations were made using a
programmable desk calculator but when method ii) was being used, the
calculations were performed on a computer.
6.2 The results of the measurements.

a) Nitrogen and carbon dioxide.

The results of the measurements of the thermal diffusivity of nitrogen and carbon dioxide are given in tables 6.2.1 and 6.2.2 and they are plotted in figures 6.2.1 and 6.2.2. The short dashed lines in these two figures indicate values of thermal diffusivity which were calculated from values of thermal conductivity taken from the data book of the Thermophysical Properties Research Centre (5), hereafter referred to as the T.P.R.C. data book, and values of density and specific heat taken from tables published by the National Bureau of Standards (54). These were regarded as the most reliable values available.

Figures 6.2.3 and 6.2.4 indicate the percentage departure of the experimental values from the values calculated from the T.P.R.C. data. The percentage departure was calculated using the relation

\[
\text{Percentage departure} = \frac{\text{experimental value} - \text{T.P.R.C. value}}{\text{T.P.R.C. value}} \times 100
\]

The T.P.R.C. values are believed to be correct to within 5% and the errors in the experimental values are indicated in the figures. The agreement can be seen to be reasonable, apart from the occasional stray point, though there is a tendency for the experimental values to be greater than the T.P.R.C. values, particularly for the results of the nitrogen measurements, which did not agree with the T.P.R.C. values as well as did the results for carbon dioxide.

The long dashed lines in figures 6.2.1 and 6.2.2 indicate values of thermal diffusivity which were calculated from theoretical values.
Table 6.2.1.
Results for nitrogen.

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>Thermal Diffusivity cm²/sec.</th>
<th>Thermal Conductivity cal/cm/sec/°C 10⁻⁵</th>
<th>Thermal Conductivity mW cm⁻¹ °K⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>304</td>
<td>0.205</td>
<td>5.73</td>
<td>0.240</td>
</tr>
<tr>
<td>307</td>
<td>0.240</td>
<td>6.64</td>
<td>0.278</td>
</tr>
<tr>
<td>310</td>
<td>0.234</td>
<td>6.40</td>
<td>0.268</td>
</tr>
<tr>
<td>310</td>
<td>0.244</td>
<td>6.68</td>
<td>0.280</td>
</tr>
<tr>
<td>310</td>
<td>0.226</td>
<td>6.19</td>
<td>0.259</td>
</tr>
<tr>
<td>368</td>
<td>0.308</td>
<td>7.12</td>
<td>0.298</td>
</tr>
<tr>
<td>374</td>
<td>0.317</td>
<td>7.22</td>
<td>0.302</td>
</tr>
<tr>
<td>452</td>
<td>0.469</td>
<td>8.89</td>
<td>0.371</td>
</tr>
<tr>
<td>453</td>
<td>0.457</td>
<td>8.65</td>
<td>0.361</td>
</tr>
<tr>
<td>478</td>
<td>0.489</td>
<td>8.79</td>
<td>0.367</td>
</tr>
<tr>
<td>556</td>
<td>0.653</td>
<td>10.20</td>
<td>0.426</td>
</tr>
<tr>
<td>539</td>
<td>0.657</td>
<td>10.22</td>
<td>0.427</td>
</tr>
<tr>
<td>652</td>
<td>0.840</td>
<td>11.42</td>
<td>0.478</td>
</tr>
<tr>
<td>677</td>
<td>0.858</td>
<td>11.29</td>
<td>0.471</td>
</tr>
<tr>
<td>680</td>
<td>0.883</td>
<td>11.57</td>
<td>0.484</td>
</tr>
<tr>
<td>688</td>
<td>0.936</td>
<td>12.14</td>
<td>0.507</td>
</tr>
<tr>
<td>739</td>
<td>1.05</td>
<td>12.8</td>
<td>0.535</td>
</tr>
<tr>
<td>741</td>
<td>1.06</td>
<td>12.9</td>
<td>0.539</td>
</tr>
<tr>
<td>743</td>
<td>1.16</td>
<td>14.1</td>
<td>0.589</td>
</tr>
<tr>
<td>792</td>
<td>1.14</td>
<td>13.2</td>
<td>0.552</td>
</tr>
<tr>
<td>826</td>
<td>1.18</td>
<td>13.2</td>
<td>0.552</td>
</tr>
<tr>
<td>907</td>
<td>1.24</td>
<td>12.8</td>
<td>0.535</td>
</tr>
<tr>
<td>309</td>
<td>0.109</td>
<td>3.91</td>
<td>0.163</td>
</tr>
<tr>
<td>472</td>
<td>0.277</td>
<td>7.50</td>
<td>0.314</td>
</tr>
<tr>
<td>509</td>
<td>0.307</td>
<td>7.91</td>
<td>0.331</td>
</tr>
<tr>
<td>563</td>
<td>0.388</td>
<td>9.34</td>
<td>0.391</td>
</tr>
<tr>
<td>640</td>
<td>0.473</td>
<td>10.40</td>
<td>0.435</td>
</tr>
<tr>
<td>697</td>
<td>0.583</td>
<td>12.06</td>
<td>0.505</td>
</tr>
<tr>
<td>757</td>
<td>0.634</td>
<td>12.36</td>
<td>0.517</td>
</tr>
<tr>
<td>824</td>
<td>0.740</td>
<td>13.58</td>
<td>0.568</td>
</tr>
</tbody>
</table>

Table 6.2.2.
Results for carbon dioxide.
Figure 6.2.1

Thermal Diffusivity
$K$ (cm$^2$/sec)

Results for nitrogen

- Periodic line-source values
- Theoretical values
- T.P.R.C. values

Temperature °K.

5%
Results for carbon dioxide

Thermal Diffusivity
K (cm²/sec)

Figure 6.2.2.

- Periodic line-source values
- Theoretical values
- T.P.R.C. values

X 15%
Figure 6.2.3. Departure plot for nitrogen results.

- Error bars have been omitted for clarity.
- They are typically ±6%.

Mean values:

- \( \bar{d} = +1\% \)
- \( |d| = 14\% \)

\[ \downarrow -9.5 \]
Figure 6.2.4.

Departure plot for carbon dioxide results.
of thermal conductivity. A simplified version of equation 2.6.26 was used to calculate the theoretical values of thermal conductivity, the simplification being that Z(rot) was taken to be so large that the last term in the equation could be ignored. The values of the other variables in equation 2.6.26 were obtained from the N.B.S. tables (54) with the exception of the factor (\(gD/\eta\)), which was put equal to \((6/5)A^*\) (see page 35) and \(A^*\) was obtained from the tables in reference (1). Equation 2.6.9 was used to find \(C_v^*(\text{int})\), and \(g\) was taken to be unity.

In principle, the value of the last term in equation 2.6.26 can be found by comparing the values of thermal diffusivity obtained from this equation with the experimental values, and the appropriate value for Z(rot) can then be determined. However, as can be seen from figures 6.2.1 and 6.2.2, the difference between the theoretical curve and the experimental values is small, and the errors very large in comparison, so that it is quite impossible to attempt to evaluate Z(rot) from the measurements.

It is also apparent, particularly for carbon dioxide at the higher temperatures, that the experimental values of thermal diffusivity can be greater than the theoretical values indicated by the long dashed lines in the figures. This implies that the last term of equation 2.6.26 should be added to, not subtracted from, the other two terms. However, since none of the factors in the last term can be negative, this is theoretically impossible. This discrepancy between theory and experiment is quite common. It is likely that the fault lies either in the assumptions about \(D'(\text{int})\) being closely approximated by \(D\) (see equation 2.6.22) or in the evaluation of \(D\) itself. In either case,
the fault cannot be easily corrected.

b) Mixtures of nitrogen and carbon dioxide.

Three sets of measurements were made on mixtures of nitrogen and carbon dioxide, the relative proportions of the gases in the mixtures being $75\% N_2 - 25\% CO_2$, $50\% N_2 - 50\% CO_2$ and $25\% N_2 - 75\% CO_2$. However, because of the method used to obtain the mixtures, it was not always possible to achieve the desired mixture exactly, though the discrepancy was usually small. The results of the measurements of the thermal diffusivity of these mixtures are given in tables 6.2.3, 6.2.4 and 6.2.5 and the exact mixture ratio is given for each measurement. These tabulated values are also plotted in figures 6.2.5, 6.2.6 and 6.2.7.

There is very little experimental data on the thermal conductivity of mixtures of nitrogen and carbon dioxide with which the results of this work can be compared. Westenberg and de Haas (2), Keyes (55), Rothman and Bromley (56) and Vines (57) have all made measurements on these gases and the long dashed curve in figures 6.2.5, 6.2.6 and 6.2.7 represents the best fit to the results of these workers.

The theoretical equations for the thermal conductivity of gas mixtures were discussed in section 2.6 c). The experimental values of thermal diffusivity given in tables 6.2.3, 6.2.4 and 6.2.5 were compared with values obtained using the Hirschfelder - Eucken equation, equation 2.6.39. The necessary equations needed to enable equation 2.6.39 to be evaluated are all given in the theory in
Table 6.2.3.
Results for 75%\textsubscript{N\textsubscript{2}} - 25%\textsubscript{CO\textsubscript{2}} mixture.

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>Percent CO\textsubscript{2}</th>
<th>Thermal Diffusivity \textsubscript{cm\textsuperscript{2}/sec.}</th>
<th>Thermal Conductivity \textsubscript{mW cm\textsuperscript{-1} °K\textsuperscript{-1}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>512</td>
<td>25.1</td>
<td>0.522</td>
<td>0.416</td>
</tr>
<tr>
<td>512</td>
<td>25.1</td>
<td>0.475</td>
<td>0.379</td>
</tr>
<tr>
<td>518</td>
<td>24.3</td>
<td>0.485</td>
<td>0.383</td>
</tr>
<tr>
<td>518</td>
<td>24.3</td>
<td>0.492</td>
<td>0.389</td>
</tr>
<tr>
<td>554</td>
<td>24.9</td>
<td>0.552</td>
<td>0.415</td>
</tr>
<tr>
<td>594</td>
<td>24.9</td>
<td>0.592</td>
<td>0.417</td>
</tr>
<tr>
<td>629</td>
<td>24.9</td>
<td>0.682</td>
<td>0.459</td>
</tr>
<tr>
<td>678</td>
<td>24.8</td>
<td>0.803</td>
<td>0.503</td>
</tr>
<tr>
<td>686</td>
<td>24.9</td>
<td>0.783</td>
<td>0.491</td>
</tr>
<tr>
<td>686</td>
<td>24.9</td>
<td>0.785</td>
<td>0.492</td>
</tr>
<tr>
<td>728</td>
<td>25.0</td>
<td>0.855</td>
<td>0.511</td>
</tr>
<tr>
<td>743</td>
<td>24.9</td>
<td>0.957</td>
<td>0.563</td>
</tr>
<tr>
<td>761</td>
<td>25.0</td>
<td>1.10</td>
<td>0.635</td>
</tr>
<tr>
<td>811</td>
<td>24.9</td>
<td>1.10</td>
<td>0.604</td>
</tr>
<tr>
<td>814</td>
<td>25.0</td>
<td>1.19</td>
<td>0.652</td>
</tr>
</tbody>
</table>
Table 6.2.4.
Results for 50% N\textsubscript{2} - 50% CO\textsubscript{2} mixture

<table>
<thead>
<tr>
<th>Temperature °K</th>
<th>Percent CO\textsubscript{2}</th>
<th>Thermal Diffusivity (\text{cm}^2/\text{sec.})</th>
<th>Thermal Conductivity (\text{mW cm}^{-1}\ \text{°K}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>458</td>
<td>49.9</td>
<td>0.327</td>
<td>0.317</td>
</tr>
<tr>
<td>486</td>
<td>51.1</td>
<td>0.375</td>
<td>0.347</td>
</tr>
<tr>
<td>537</td>
<td>50.3</td>
<td>0.435</td>
<td>0.373</td>
</tr>
<tr>
<td>582</td>
<td>50.0</td>
<td>0.506</td>
<td>0.410</td>
</tr>
<tr>
<td>628</td>
<td>49.8</td>
<td>0.595</td>
<td>0.452</td>
</tr>
<tr>
<td>695</td>
<td>50.0</td>
<td>0.695</td>
<td>0.489</td>
</tr>
<tr>
<td>701</td>
<td>50.0</td>
<td>0.715</td>
<td>0.499</td>
</tr>
<tr>
<td>767</td>
<td>50.2</td>
<td>0.883</td>
<td>0.576</td>
</tr>
<tr>
<td>810</td>
<td>49.8</td>
<td>0.955</td>
<td>0.597</td>
</tr>
<tr>
<td>856</td>
<td>49.8</td>
<td>1.055</td>
<td>0.646</td>
</tr>
<tr>
<td>501</td>
<td>74.9</td>
<td>0.337</td>
<td>0.336</td>
</tr>
<tr>
<td>556</td>
<td>75.1</td>
<td>0.423</td>
<td>0.392</td>
</tr>
<tr>
<td>605</td>
<td>74.5</td>
<td>0.488</td>
<td>0.424</td>
</tr>
<tr>
<td>664</td>
<td>75.0</td>
<td>0.621</td>
<td>0.504</td>
</tr>
<tr>
<td>718</td>
<td>75.6</td>
<td>0.625</td>
<td>0.479</td>
</tr>
<tr>
<td>718</td>
<td>75.6</td>
<td>0.670</td>
<td>0.513</td>
</tr>
<tr>
<td>724</td>
<td>75.0</td>
<td>0.689</td>
<td>0.525</td>
</tr>
<tr>
<td>769</td>
<td>75.0</td>
<td>0.812</td>
<td>0.591</td>
</tr>
</tbody>
</table>

Table 6.2.5.
Results for 25% N\textsubscript{2} - 75% CO\textsubscript{2} mixture.
Figure 6.2.5.

Results for 75% Ni - 25% Co mixture.

Periodic line-source values of Westenberg and de Haas, Keys, Rothman and Bromley and Vines.

Correlation of results of theoretical values.

Thermal Diffusivity $\kappa$ (cm$^2$/sec).

Temperature $\theta$. 0 300 500 600 700 800 900 1000
Figure 6.2.6.

Results for 50% N₂ - 50% CO₂ mixture

Periodic line-source values.

Correlation of results of Westenberg and de Haas, Keyes, Rothman and Bronley, and Vines.

Theoretical values

Temperature °K

Thermal Diffusivity
K (cm²/sec)
Figure 6.2.7.

Thermal Diffusivity

Results for 25% N₂ - 75% CO₂ mixture

Periodic line-source values.

Correlation of results of Westenberg and de Haas, Keyes, Rothman and Bromley, and Vines.

Theoretical values.
section 2.6 c). The values of the self diffusion coefficients needed in the equations were calculated using the relation \( \frac{\varepsilon D}{\eta} = (6/5) A^* \) and the binary diffusion coefficients were calculated using the Mason-Merrick formula (58) which is

\[
\ln(pD_{ij}) = \ln A + s\ln T - (S/T).
\]

In this equation \( p \) is the pressure in atmospheres, set equal to unity for this work, and, for the case of nitrogen and carbon dioxide,

\[
A = 3.15 \times 10^{-5} \text{ atm. cm}^2 \text{ sec}^{-1} \text{ K}^{-s}
\]

\[
s = 1.570 \quad \text{and} \quad S = 113.6 \text{ K}.
\]

The values of \( \lambda_1^{(tr)} \), needed in equation 2.6.34, were calculated using equation 2.6.5, as originally recommended by Hirschfelder (42). The values of \( \lambda_1^{(int)} \), needed in equation 2.6.40, were then calculated using equation 2.6.41, T.P.R.C. values being used for \( \lambda_1^{(expt)} \). The alternative methods of selecting \( \lambda_1^{(tr)} \) and \( \lambda_1^{(int)} \) which were discussed in section 2.6 c) i.e. those suggested by Maczek and Gray (44), were not used because of the doubt about the values of \( D'(int) \). The use of these alternative methods would have caused \( f(tr) \) to be greater than 5/2 for carbon dioxide at the higher temperatures. This would be contrary to theory, which indicates that \( f(tr) \) is decreased below 5/2 for polyatomic gases. Finally, the values of \( \lambda_{ij} \), needed in equations 2.6.33 and 2.6.34, were calculated using equation 2.6.36.

The values of thermal conductivity obtained from equation 2.6.39 were converted into values of thermal diffusivity and the results of this process are indicated by the short dashed lines in figures 6.2.5, 6.2.6 and 6.2.7.
6.3 Discussion of the results.

The values of thermal diffusivity obtained using the periodic line-source technique have been shown to be in reasonably close agreement with other experimental values and with theoretical values. The mean deviation $\bar{d}$ of the points in figure 6.2.3 i.e. the results for nitrogen, is $+1\%$ and the mean absolute deviation $|\bar{d}|$ is $4\%$. The equivalent figures for carbon dioxide are $\bar{d} = 0.4\%$ and $|\bar{d}| = 3\%$. These figures indicate that the results of the periodic line-source measurements are slightly greater than the T.P.R.C. values but that the errors in the measurements are such that the difference is not very significant.

A closer examination of figure 6.2.3 reveals that, at the higher temperatures, there is a tendency for the experimental points to show more of a positive departure from the T.P.R.C. values than at the lower temperatures. However, this departure is less than the experimental errors so it can not be said that the results indicate a significant departure from the T.P.R.C. values, even at the higher temperatures. The results for carbon dioxide do not exhibit any trend of this kind.

The theoretical curves in figures 6.2.1 and 6.2.2 also show reasonable agreement with the experimental results. It is unfortunate that the experimental results are not sufficiently accurate to enable a more detailed comparison with the theory to be made so that the values of $Z(\text{rot})$ in equation 2.6.26 could be calculated. There needs to be a considerable improvement in the accuracy of experimental measurements if this task is to be attempted because, as was indicated in section 2.6, the value of $(\Lambda \tau/\Theta)$ is very insensitive to changes of $Z(\text{rot})$ because the last term in equation 2.6.26 is small in comparison
with the other terms.

The only significant discrepancy between the theoretical and experimental values of thermal diffusivity occurs at the higher temperatures of the carbon dioxide results. This, as was pointed out in the previous section, is probably due to an incorrect evaluation of $D'(\text{int})$.

The results for the mixtures of nitrogen and carbon dioxide also indicate reasonable agreement with theoretical values and with the results of other workers, though, here again, the agreement appears to become increasingly better with the increasing proportion of carbon dioxide in the mixture. The results plotted in figures 6.2.5, 6.2.6 and 6.2.7 have not taken into account the fact that the mixture proportions were not exactly those required, but the errors caused as a result of this are small because, as can be seen from the results, the thermal diffusivity does not change rapidly with changes of mixture content.

The Hirschfelder-Eucken equation, equation 2.6.39, which was used to calculate the theoretical values of thermal diffusivity, can be used in a variety of different ways, as was indicated in section 2.6. However, no matter which method is selected, the resulting values of thermal diffusivity are not vastly different. Consequently, because of the comparatively large experimental errors, it is not possible to select any one of these methods as giving better agreement with experimental results. A much more accurate technique of measuring thermal diffusivity is required for this purpose. It can be concluded, however, that in the temperature range studied, theoretical values of thermal diffusivity agree, to within 5%, with experimental values.
6.4 Analysis of the errors in the measurements.

The error in the measurement of the thermal diffusivity can be related to the errors in the individual measurements with the aid of equation 3.3.5. This is only an approximate equation but it is sufficiently accurate for the purposes of this analysis. Equation 3.3.5 shows that the thermal diffusivity \( K \) is given by

\[
K = \frac{m u^3}{(\omega_2^2 - \omega_1^2)}
\]

The percentage error in values of \( K \) can be calculated using the equation

\[
\frac{\Delta K}{K} = \left( \frac{\Delta m}{m} \right) + 3 \left( \frac{\Delta u}{u} \right) + 2 \frac{\Delta f}{(f_2^2 - f_1^2)}
\]

Substituting for the partial derivatives, and putting \( \Delta \omega_1 = \Delta \omega_2 = \Delta \omega = 2\pi \Delta f \) gives

\[
(\Delta K/K) = (\Delta m/m) + 3(\Delta u/u) + 2\Delta f/(f_2^2 - f_1^2)
\]

Typical values are

\[
(\Delta m/m) = 0.02 \quad (\Delta u/u) = 0.005 \quad \text{and} \quad \Delta f/(f_2^2 - f_1^2) = 0.002
\]

This gives a typical value for \( (\Delta K/K) \) of 0.04 which shows that the error in the measurement of the thermal diffusivity is approximately 4%, though it can vary from one set of measurements to another depending upon the conditions.

Other, systematic errors in the measurements are believed to be small. The consequences of approximations introduced in the theory in appendix I i.e. taking only the first two terms in the modified
Bessel function and assuming that \( u \) and \( K \) are both constant, are very
difficult to estimate. The effect of the variation of \( u \) and \( K \) was
studied in section 5.1 c). The effect may also be noticeable when
\( \ln(V_1/V_2) \) is plotted against \( x \), this being the method used to obtain
the value of the thermal diffusivity from equation 3.3.4. The effect
of the variation of \( u \) and \( K \) upon such a plot is to cause the line
joining the points to become curved rather than being straight, the
curvature being due to the decrease of the value of \( (K/u^2) \) with the
increase of the value of \( x \). One of the examples given in figure 6.1.1
exhibits curvature of this sort but the best straight line through the
points gives an average slope which is suitable for the calculation
of \( K \) since average values of the temperature and the velocity of the
gas in this same interval are used in the calculations.

It is very difficult to estimate the error that might be intro­
duced by the effects mentioned above but it is believed to be less
than 2%. Consequently, the overall accuracy of the measurements is
estimated to be in the region of 6%. The scatter of the results
plotted in the many figures in section 6.2 is consistent with the
accuracy figures given here, apart from an occasional stray point.
It seems that these few stray points must have been the result of
human error at some stage in the measurement procedure.

The error in the measurement of the temperature of the gas,
including the necessary corrections to the thermocouple measurements,
is believed to be less than 1%.
CHAPTER VII

CONCLUSIONS

The periodic line-source technique has been found to give reasonably accurate values of the thermal diffusivity of gases. The technique is particularly suited for high temperature measurements because there are no convection effects to consider. There are no radiation or end effects of any consequence, except that the measurement of the gas temperature requires a radiation correction, and there can be no conduction from the source to the detector via the apparatus itself. The technique is therefore free of many of the effects which can cause systematic errors to the results.

The disadvantages of the method are that it requires a flow of gas with a uniform velocity distribution, which can be difficult to obtain, and that, in the present form, large volumes of gas are needed since no recycling of the gas is possible. This means that the technique can only be used for measurements of the common gases, though it may be possible to devise some variation of the technique where the gas is not lost to the atmosphere. It would probably be possible to have a cell with a periodically varying source and a detector in a stationary gas, though the measurements may then be subject to convection effects.

Kestin (59) has recently cast doubt upon the results of many workers, suggesting that the effects of convection upon their results was greater than they had believed, and that their results, in some cases, were in error by as much as 9%. The discrepancy between the theoretical values and the experimental (T.P.R.C.) values for carbon
dioxide at the higher temperatures could be due to such errors rather than being due to an incorrect evaluation of $D'(\text{int})$, as was suggested in section 6.2 a) to be the cause of the discrepancy. However, the periodic line-source results are also greater than the theoretical values which suggests that the error lies in the evaluation of $D'(\text{int})$ rather than in the measurement of thermal conductivity, the periodic line-source method being free from the effects of convection. It should be pointed out, however, that the errors in the experimental measurements are sufficient to account for the discrepancy between the theoretical and experimental values, so no definite conclusions can be reached on this point.

Clearly, more accurate values of thermal conductivity of gases are needed to settle this problem. The technique described in this thesis could be improved if a more uniform gas flow could be obtained or if a different method of introducing the temperature perturbations into the gas flow could be found. Alternatively, it may be necessary to develop a new technique or to improve an already existing method in order to improve the accuracy of present measurements.
THE TEMPERATURE DISTRIBUTION DUE TO A PERIODIC LINE'SOURCE OF HEAT IN A MOVING GAS.

The temperature $T$ at any point $(x,y,z)$ in an infinite medium, in this case a gas, due to a quantity of heat $Q$, which is instantaneously generated at time $t=0$ at the origin of the co-ordinate system, i.e. at $x=y=z=0$, is given by the equation

$$T = \frac{Q}{8\pi\varepsilon c} (\pi\kappa t)^{-3/2} \exp\left[-\left(\frac{x^2 + y^2 + z^2}{4\kappa t}\right)\right]$$

where $\kappa = \lambda/\varepsilon c$ = the thermal diffusivity of the gas,
$\lambda$ = the thermal conductivity of the gas,
$\varepsilon$ = the density of the gas,
and $c$ = the specific heat (the heat capacity per unit mass) of the gas at constant pressure.

This equation, which is obtained from Carslaw and Jaeger (50), can be used to solve many heat conduction problems. If the instantaneous point source is replaced by a continuous point source, from which heat is liberated at the rate $\phi(t')$ per unit time from $t'=0$ to $t'=t$, the temperature $T$ at $(x,y,z)$ at time $t$ will be given by

$$T = \frac{Q}{8\pi\varepsilon c} (\pi\kappa)^{-3/2} \int_0^t \phi(t') \exp\left[-\frac{r^2}{4\kappa(t-t')}\right] (t-t')^{-3/2} dt'$$

where $r^2 = x^2 + y^2 + z^2$.

This equation gives the temperature distribution in a stationary gas. If the gas is flowing past the origin with uniform velocity $u$, parallel to the $x$-axis, the expression for the temperature $T$ at $(x,y,z)$
at time $t$, can be written down by replacing $'x'$ in equation A.2 by the expression $'[x - u(t - t')]'$. The expression for $T$ then becomes

$$T = (8\sigma c)^{-1} (\pi \kappa)^{-3/2} \int_0^t \phi(t') \exp[-((x-u(t-t'))^2 + y^2 + z^2)/4\kappa(t-t')] (t-t')^{-3/2}dt'. \quad A.3$$

Consider the case where $\phi(t') = A + B \exp(i\omega t')$

and substitute $p = (t-t')^{-3/2}$

so $dp = \frac{3}{2}(t-t')^{-3/2}dt'$

and $t' = t - p^{-2}$

Equation A.3 then becomes

$$T = (8\sigma c)^{-1} (\pi \kappa)^{-3/2} (I_1 + I_2) \quad A.4$$

where

$$I_1 = \int_{\frac{1}{2}}^{\infty} 2A \exp[-(x^2 + y^2 + z^2)p^2/4\kappa]dp$$

and

$$I_2 = \int_{\frac{1}{2}}^{\infty} 2B \exp[i\omega(t-p^{-2})-(x^2 + y^2 + z^2)p^{-2}/4\kappa]dp.$$

Now $I_1$ can be written as

$$I_1 = 2A \exp(ux/2\kappa) \int_{\frac{1}{2}}^{\infty} \exp[-(r^2 + u^2)p^2/4\kappa]dp$$

and the value of the integral in this equation can be obtained from equation 7.4.33 of Abramowitz and Stegun (60). The result is that

$$I_1 = 2A \exp(ux/2\kappa) \left[(\pi \kappa)^{\frac{3}{2}}/2r\right]$$

$$\left[\exp(-ur/2\kappa) \text{erfc}\left(\frac{1}{2}\sqrt{\kappa t}\right)^{-\frac{1}{2}} - \frac{3}{4}u(t/\kappa)^{\frac{1}{3}}\right] +$$

$$\exp(ur/2\kappa) \text{erfc}\left(\frac{1}{2}\sqrt{\kappa t}\right)^{-\frac{1}{2}} + \frac{3}{4}u(t/\kappa)^{\frac{1}{3}}\right].$$

This equation is obtained from equation 7.4.33 of reference (60) by simple substitution and by the use of the fact that $\text{erf}(\infty) = 1$ and
erfc(x) = 1 - erf(x).

For experimental purposes the steady-state solution is required, so $I_1$ must be evaluated for the case where $t \to \infty$. Now $\text{erfc}(\infty) = 0$ and $\text{erfc}(-\infty) = 2$, so the expression for $I_1$ as $t \to \infty$ is

$$I_1 = 2A \exp(ux/2\kappa) \left[ (\pi \omega)^{1/2} \right] 2 \exp(-ur/2\kappa)$$

$$= 2A \left[ (\pi \kappa)^{1/2} \right] \exp \left[ (x-r)u/2\kappa \right].$$

Likewise, $I_2$ can be written as

$$I_2 = 2B \exp(i\omega t + ux/2\kappa) \left[ (\pi \kappa)^{1/2} \right] \left\{ \int_0^\infty \exp\left[ -(r^2p^2 + u^2p^{-2} + 4kiwp^{-2})/4K \right] dp \right\}.$$

If $'(u^2 + 4ki\omega)'$ is replaced by $'v^2'$, the above integral can again be determined from equation 7.4.33 of reference (60) but it must be remembered that $\nu$ is a complex number. This, however, does not affect the evaluation of $I_2$ for the limiting case when $t \to \infty$. Therefore, as $t \to \infty$

$$I_2 = 2B \exp(i\omega t + ux/2\kappa) \left[ (\pi \kappa)^{1/2} \right] 2 \exp(-vr/2\kappa)$$

$$= 2B \left[ (\pi \kappa)^{1/2} \right] \exp \left[ (ux - vr)/2\kappa \right] \exp(i\omega t)$$

where $\nu = (u^2 + 4ki\omega)^{1/2}$.

It would be more convenient to write $\nu$ in the form

$$\nu = (\alpha + i\beta)u$$

for which it is necessary that

$$(\alpha^2 - \beta^2 + 2i\alpha\beta)u^2 = u^2 + 4ki\omega$$

i.e. $\alpha^2 - \beta^2 = 1$ and $\alpha\beta = 2K\omega/u^2$. 
The solution to these simultaneous equations is

\[ \alpha = \left[\frac{(R+1)/2}{2}\right]^2 \quad \text{and} \quad \beta = \left[\frac{(R-1)/2}{2}\right]^2 \quad \text{A.5} \]

where \( R = \left(1 + \frac{16K^2}{u^4}\right)^{1/2} \quad \text{A.6} \)

Using this notation, \( I_2 \) can be written as

\[ I_2 = \left[2B\left(\pi K^2/r\right)\right] \exp\left[(x-\alpha r)u/2K\right] \exp(iwt - i\sigma r/2K) \]

and the resulting expression for \( T \), obtained by substituting the expressions for \( I_1 \) and \( I_2 \) into equation A.4, is

\[ T = (4\pi GeKr)^{-1} A \exp\left[(x-r)u/2K\right] + \]

\[ (4\pi GeKr)^{-1} B \exp\left[(x-\alpha r)u/2K\right] \exp(iwt - i\sigma r/2K). \quad \text{A.7} \]

This is the solution for a point source of heat. It is an exact solution, as can be seen by substituting the expression for \( T \) into the appropriate differential equation of heat conduction, which is

\[ \kappa \left[ \frac{\Delta^2 T}{\Delta x^2} + \frac{\Delta^2 T}{\Delta y^2} + \frac{\Delta^2 T}{\Delta z^2} \right] = u \frac{\Delta T}{\Delta x} + \frac{\Delta T}{\Delta t} \]

The mathematics for this is quite simple, but tedious, and is not reproduced here. The reader is advised to follow a method similar to that given in appendix III if he should wish to test the solution.

The solution given by equation A.7 is the same as that given by both Podolsky (61) and Ritchie (62), though they used different methods of solving the problem.

To obtain the solution for a periodic line source, it is necessary to integrate the expression for the periodic point source over all \( z \) from \(-\infty\) to \(+\infty\). Integrating equation A.7 gives
\[ T = (4\pi e^\kappa)^{-1} (I_3 + I_4) \]

where

\[ I_3 = A \exp(ux/2K) \int_{-\infty}^{\infty} \exp\left[-(x^2 + y^2 + z^2)^{1/2}\left(x^2 + y^2 + z^2\right)^{-1/2}\right] \, dz \]

and

\[ I_4 = B \exp(ux/2K + i\omega t) \int_{-\infty}^{\infty} \exp\left[-(x^2 + y^2 + z^2)^{1/2}(\alpha + i\beta)u/2K\right] \, dz. \]

The integrals appearing in \( I_3 \) and \( I_4 \) can be determined from the expression given in appendix II. The resulting expressions for \( I_3 \) and \( I_4 \) are

\[ I_3 = A \exp(ux/2K) 2K_0 \left[ (x^2 + y^2)^{1/2} u/2K \right] \]

and

\[ I_4 = B \exp(ux/2K + i\omega t) 2K_0 \left[ (x^2 + y^2)^{1/2}(\alpha + i\beta)u/2K \right] \]

where \( K_0(\cdot) \) is the modified Bessel function of the second kind of zero order. Using equation 9.7.2 of Abramowitz and Stegun (60) the function \( K_0(z) \) can be approximated by the expression

\[ K_0(z) = (\pi/2z)^{3/2} \exp(-z) \left[ 1 - (8z)^{-1} + (9/128)z^{-2} - (75/1024)z^{-3} + \ldots \right] \]

though, for the purposes of this work, \( K_0(z) \) can be quite adequately approximated by the expression

\[ K_0(z) = (\pi/2z)^{1/2} \exp(-z) \left[ 1 - (8z)^{-1} \right] \]

subject to the condition that \(|z| \gg 1\).

Using this approximation, and redefining \( r \) as

\[ r = (x^2 + y^2)^{1/2}, \]

then

\[ K_0(\omega r/2K) = (\pi \kappa/\omega r)^{1/2} \left( 1 - \kappa/4\omega r \right) \exp(-\omega r/2K) \]

and

\[ K_0((\alpha + i\beta)\omega r/2K) = \left[ (\pi \kappa/\omega r(\alpha + i\beta))^2 \right] \left[ 1 - \kappa/\omega r(\alpha + i\beta) \right] \exp\left[-\omega r(\alpha + i\beta)/2K\right]. \]
It is now necessary to write \((\alpha + i\beta)^{1/2}\) in the form \((P - iQ)\).

For these two terms to be equal it is necessary that

\[ P = \left[\frac{R^2 + \alpha}{2R}\right]^{1/2} \quad \text{and} \quad Q = \left[\frac{R^2 - \alpha}{2R}\right]^{1/2} \]

where \(R\) is given by equation A.6. The expressions for \(I_3\) and \(I_4\) can, therefore, be written in the form

\[ I_3 = 2A (\pi \kappa/ur)^{1/2} \left(1 - \kappa/4ur\right) \exp[(x - r)u/2K] \]

and

\[ I_4 = 2B (\pi \kappa/ur)^{1/2} (P - iQ) \left[1 - \kappa/4ur(\alpha + i\beta)\right] \exp[(x - \alpha r)u/2K] \exp(\omega t - i\sigma ur/2K). \]

For convenience, the term \((P - iQ)/(\alpha + i\beta)\) is put equal to \((P' - iQ')\)

where \(P' = (\alpha P - \beta Q)/R\) and \(Q' = (\alpha Q + \beta P)/R\).

The expressions for \(I_3\) and \(I_4\) can now be substituted into equation A.8.

The resulting equation for \(T\) is

\[ T = \frac{A}{\rho c} (4\pi v ur)^{1/2} \left(1 - \kappa/4ur\right) \exp[(x - r)u/2K] + \]

\[ (B/\rho c) (4\pi v ur)^{1/2} \left[(P - iQ) - (P' - iQ')\right]/4ur \]

\[ \exp[(x - \alpha r)u/2K] \exp(\omega t - i\sigma ur/2K). \]  \hspace{1cm} \text{A.9} \]

This is the solution for a line source of heat for which

\(\phi(t) = A + B\exp(\omega t),\) where \(\phi(t)\) is an expression for the amount of heat transferred from the source to the gas, from unit length of the source, in unit time. It is not an exact solution because of the approximation used for expressing the modified Bessel function \(K_0( )\) as a power series, of which only the first two terms were used. This
approximation is valid provided that $ur/2K \gg 1$ or, more correctly, provided that $|ur(\alpha + i\beta)/2K| \gg 1$. Now $|ur(\alpha + i\beta)/2K| = ur^{1/2}/2K$ and since $R$ is of the order of unity, the condition amounts to saying that $ur \gg 2K$.

As a test for this solution it can be substituted into the differential equation of heat conduction applicable to the system, which is

$$K \left[ \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right] = u \frac{\partial T}{\partial x} + \frac{\partial T}{\partial t}.$$ 

This again is a tedious mathematical task, the method used and the result of the test is given in appendix III.

The solution given by equation A.9 is that for a source of heat for which $\phi(t) = A + B\exp(i\omega t)$. If the solution for the more practical case, where $\phi(t) = A + B\cos\omega t$, is required, then all that is needed is the real part of equation A.9. This will clearly involve a term

$$P \cos(\omega t - \beta ur/2K) + Q \sin(\omega t - \beta ur/2K)$$

and a similar term with $P'$ and $Q'$. The above expression can be written more conveniently as

$$(P^2 + Q^2)^{1/2} \sin(\omega t - \beta ur/2K + \theta) \quad \text{where} \quad \tan \theta = P/Q.$$

Now

$$P^2 + Q^2 = R^{-1/2} \quad \text{and} \quad P/Q = \frac{[(R^2 + \alpha)/(R^2 - \alpha)]^{1/2}}{\beta/(R^2 - \alpha)}.$$

Likewise

$$P'^2 + Q'^2 = R^{-2}(\alpha^2 P^2 + \beta^2 Q^2 + \alpha^2 Q^2 + \beta^2 P^2)$$

$$= R^{-2}(\alpha^2 + \beta^2)(P^2 + Q^2)$$

$$= R^{-3/2}.$$

The solution can now be written as
\[ T = \left( \frac{A}{gc} \right) (4\pi \kappa u r)^{-\frac{1}{2}} \left( 1 - \frac{\kappa}{4ur} \right) \exp \left[ \frac{(x - r)u}{2\kappa} \right] + \]
\[ \left( \frac{B}{gc} \right) (4\pi \kappa u r)^{-\frac{1}{2}} \exp \left[ \frac{(x - \kappa r)u}{2\kappa} \right] \]
\[ \left[ R^{-\frac{1}{2}} \sin(\omega t - \beta u r/2\kappa + \theta) - R^{-\frac{1}{2}}(\kappa/4ur) \sin(\omega t - \beta u r/2\kappa + \theta') \right] \]
where \( \tan \theta = \frac{P}{Q} = \beta / (R^{\frac{1}{2}} - \alpha) \)
and \( \tan \theta' = \frac{P'}{Q'} \)
\( \beta = (\alpha P/Q - \beta)/(\alpha + \beta P/Q) \)
\( \beta = (2\alpha - R^{\frac{1}{2}})/(\alpha R^{\frac{1}{2}} - 1) \)

The two sinusoidal terms in the above equation can be combined into one, the result being
\[ T = \left( \frac{A}{gc} \right) (4\pi \kappa u r)^{-\frac{1}{2}} \Delta_1 \exp \left[ \frac{(x - r)u}{2\kappa} \right] + \]
\[ \left( \frac{B}{gc} \right) (4\pi \kappa u r)^{-\frac{1}{2}} R^{-\frac{1}{2}} \Delta_2 \exp \left[ \frac{(x - \kappa r)u}{2\kappa} \right] \sin(\omega t - \beta u r/2\kappa + \theta - \gamma) \]
where \( \Delta_1 = (1 - \frac{\kappa}{4ur}) \)
\( \Delta_2 = \left[ 1 + w^2 - 2w \cos(\theta' - \theta) \right]^{\frac{1}{2}} \)
\( w = R^{-\frac{1}{2}}(\kappa/4ur) \)
and \( \tan \gamma = \left[ w \sin(\theta' - \theta) \right] / \left[ 1 - w \cos(\theta' - \theta) \right] \).

This is the required result which is used in the theory of chapter III.

The terms which appear in this expression and which were defined earlier in this derivation, are collected together below for convenience.
\[ \alpha = \left[ (R + 1)/2 \right]^{\frac{1}{2}} \]
\[ \beta = \left[ (R - 1)/2 \right]^{\frac{1}{2}} \]
\[ R = (1 + 16\kappa^2 \omega^2/u^4)^{\frac{1}{2}} \]
\[ \tan \theta = \beta / (R^{\frac{1}{2}} - \alpha) \]
and \( \tan \theta' = \beta(2\alpha - R^{\frac{1}{2}})/(\alpha R^{\frac{1}{2}} - 1) \).
APPENDIX II

EVALUATION OF INTEGRALS OF THE FORM

\[ I = \int_{-\infty}^{\infty} \left( x^2 + y^2 + z^2 \right)^{-\frac{1}{2}} \exp \left[ -(x^2 + y^2 + z^2) \frac{C}{2} \right] dz \]

We substitute into the above integral \( x^2 + y^2 = r^2 \)
and also \( z = r \sinh p \)
so \( dz = r \cosh p \, dp \)
Hence \( x^2 + y^2 + z^2 = r^2 + r^2 \sinh^2 p = r^2 \cosh^2 p \)
so \( I = \int_{-\infty}^{\infty} (r \cosh p)^{-1} \exp(-Cr \cosh p) \, r \cosh p \, dp \)
\[ = \int_{-\infty}^{\infty} \exp(-Cr \cosh p) \, dp \]
This integral can be evaluated using equation 9.6.24 of Abramowitz and
Stegun (60), the result being that \( I = 2 K_0(Cr) \) where \( K_0(\cdot) \) is the
modified Bessel function of the second kind of zero order. Thus we have
\[ I = 2 K_0 \left[ C(x^2 + y^2)^{\frac{1}{2}} \right] \]

It is easy to show that the integral given by
\[ y = \int_{0}^{\infty} \exp(-a \cosh p) \, dp \]
is a solution to the modified Bessel function of zero order by showing.
that it satisfies the appropriate differential equation which is
\[ (d^2y/da^2) + (dy/da)/a - y = 0 \]
We have \( (dy/da) = - \int_{0}^{\infty} \cosh p \, \exp(-a \cosh p) \, dp \)
and \( (d^2y/da^2) = \int_{0}^{\infty} \cosh^2 p \, \exp(-a \cosh p) \, dp \)
Integrating the expression for \((dy/da)\) by parts gives
\[ (dy/da) = - a \int_{0}^{\infty} \sinh^2 p \, \exp(-a \cosh p) \, dp \]
Thus, adding the expression for \((d^2y/da^2)\) to that for \((dy/da)/a\) can
be seen to give the expression for \( y \), which gives the required proof.
APPENDIX III

TEST OF SOLUTION OBTAINED IN APPENDIX I.

It is required to test that equation A.9 of appendix I satisfies the differential equation

\[ K \left( \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} \right) - \left[ u \frac{\partial T}{\partial x} + \frac{\partial T}{\partial y} \right] = 0 \quad \text{C.1} \]

Consider the general form

\[ T = f(r) \exp[\text{i}wt - iF(r)] \quad \text{C.2} \]

It is easy to show that

\[ \frac{\partial T}{\partial x} = T \left[ f^{-1} \frac{\partial f}{\partial x} + i \frac{\partial F}{\partial x} \right] \quad \text{C.3} \]

and that

\[ \frac{\partial^2 T}{\partial x^2} = T \left[ f^{-1} \frac{\partial^2 f}{\partial x^2} - \left( \frac{\partial F}{\partial x} \right)^2 - 2if^{-1} \frac{\partial f}{\partial x} \frac{\partial F}{\partial x} - i \frac{\partial^2 F}{\partial x^2} \right] \]

A similar expression results for \( \frac{\partial^2 T}{\partial y^2} \) so

\[ \frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} = T \left[ f^{-1} \left( \frac{\partial^2 f}{\partial x^2} + \frac{\partial^2 f}{\partial y^2} \right) - \left( \frac{\partial F}{\partial x} \right)^2 - \left( \frac{\partial F}{\partial y} \right)^2 \right. 
- \left. 2if^{-1} \left( \frac{\partial f}{\partial x} \frac{\partial F}{\partial x} + \frac{\partial f}{\partial y} \frac{\partial F}{\partial y} \right) - i \left( \frac{\partial^2 F}{\partial x^2} + \frac{\partial^2 F}{\partial y^2} \right) \right] \quad \text{C.4} \]

Also

\[ \frac{\partial T}{\partial t} = i\omega T \quad \text{C.5} \]

Taking \( f \) to be of the form

\[ f = C r^{(\frac{1}{2} - n)} \exp\left\{ (x - \omega t)u/2k \right\} \quad \text{C.6} \]

and using the fact that, since \( r^2 = x^2 + y^2 \), \( (\partial r/\partial x) = x/r \) and \( (\partial r/\partial y) = y/r \), then \( (\partial f/\partial x) \) and \( (\partial f/\partial y) \) are given by
\[
(\alpha f/\alpha x) = f\{(1 - \alpha x/r)u/2K + (\frac{1}{2} - n)x/r^2\}, \quad C.7
\]
\[
(\alpha f/\alpha y) = f\{(\frac{1}{2} - n)y/r^2 - \alpha uy/2Kr\}. \quad C.8
\]

Taking the second derivatives of these two equations and then adding the two together gives
\[
\frac{\delta^2 f}{\delta x^2} + \frac{\delta^2 f}{\delta y^2} = f\{(1 + \alpha^2 - 2\alpha x/r)u^2/4K^2 + (\frac{1}{2} - n)^2r^{-2} + (\frac{1}{2} - n)ux/kr^2 - (1 - n)\alpha u/kr\}. \quad C.9
\]

Taking \(F\) to be of the form
\[
F = (\alpha u/2K)r \quad C.10
\]
gives
\[
(\alpha F/\alpha x) = (\alpha u/2K)(x/r) \quad C.11
\]
\[
(\alpha F/\alpha y) = (\alpha u/2K)(y/r) \quad C.12
\]
\[
(\alpha^2 F/\alpha x^2) = (\alpha u/2K)(r^{-1} - x^2/r^3) \quad C.13
\]
\[
(\alpha^2 F/\alpha y^2) = (\alpha u/2K)(r^{-1} - y^2/r^3) \quad C.14
\]

It follows, from equations C.11 and C.12, that
\[
(\alpha F/\alpha x)^2 + (\alpha F/\alpha y)^2 = (\alpha u/2K)^2 \quad C.15
\]

and using equations C.7, C.8, C.11 and C.12 it can be shown that
\[
\frac{\delta f \; \delta F}{\delta x \; \delta x} + \frac{\delta f \; \delta F}{\delta y \; \delta y} = (\alpha u/2K)(f/r)\{(\frac{1}{2} - n) + ux/2K - \alpha ur/2K\}. \quad C.16
\]

It is clear, from equations C.13 and C.14, that
\[
(\alpha^2 F/\alpha x^2) + (\alpha^2 F/\alpha y^2) = (\alpha u/2K) r^{-1} \quad C.17
\]
Substituting equations C.9, C.15, C.16 and C.17 into equation C.4, and putting \((\alpha^2 - \beta^2) = 1\), gives

\[
\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} = T \left[ (1 - \alpha x/r)u^2/2k^2 + (\frac{1}{2} - n)^2 r^{-2} + (\frac{1}{2} - n)ux/kr^2 - (1 - n)xu/kr - i(\beta u/2k)(2 - 2n + ux/k - \alpha ur/k)/r \right]
\]

C.18

and substituting equations C.7 and C.11' into equation C.3 gives

\[
(\partial T/\partial x) = T \left[ (1 - \alpha x/r)u^2/2k + (\frac{1}{2} - n)x/r^2 - i(\beta u/2k)x/r \right]
\]

C.19

Putting \(\alpha\beta = 2\kappa w/u^2\), and combining equations C.5, C.18 and C.19 gives

\[
\frac{\partial^2 T}{\partial x^2} + \frac{\partial^2 T}{\partial y^2} - u \frac{\partial T}{\partial x} - \frac{\partial T}{\partial t} = T \left[ (\frac{1}{2} - n)^2 k/r^2 - (1 - n)(\alpha + i\beta)u/r \right]
\]

C.20

For \(n = 1\), the right hand side of this equation is

\[
T[4/4r^2].
\]

C.21

For \(n = 2\) it is \(T[9k/4r^2 + (\alpha + i\beta)u/r]\). \hspace{1cm} C.22

For \(n = 3\) it is \(T[25k/4r^2 + 2(\alpha + i\beta)u/r]\). \hspace{1cm} C.23

It is now possible to test equation A.9. The first part of equation A.9 is just a particular case of the second part of the equation, obtained by putting \(\alpha = 1\) and both \(\omega = 0\) and \(\beta = 0\). Consequently, it is only necessary to test the second part of the equation. By replacing \((P' - iQ')\) by \((P - iQ)/(\alpha + i\beta)\) and by substituting

\[
Z = (E/c)(4\pi ku)^{-1} (P - iQ) \exp[(x - \alpha r)u/2k + i\omega t - i\beta ur/2k]
\]

the second part of equation A.9 can be written as
\[ T = Z r^{-1} - Z r^{-3/2} \kappa/4 u(\alpha + i\beta) \]  \hspace{1cm} C.24

This equation can be regarded as two separate terms, and can be substituted, in turn, into the right hand side of equation C.20. For the first term, this gives

\[ Z r^{-5/2} \kappa/4 \]

and for the second term, it gives

\[ -9 Z r^{-7/2} \kappa^2/16 u (\alpha + i\beta) - Z r^{-5/2} \kappa/4 \]

Adding these two terms eliminates the terms in \( r^{-5/2} \) and leaves only the term in \( r^{-7/2} \). The inclusion of higher order terms in equation C.24 would eliminate the term in \( r^{-7/2} \) etc. and equation C.24 would then be a more exact solution to equation C.20. It is clear, however, that equation C.24, or equation A.9, is the required solution to equation C.20, being sufficiently accurate for the purposes of the theory of appendix A and chapter III.
REFERENCES.

   a) Chapters 7 and 8, 441 - 610.
   b) Chapter 9, 611 - 667.
   c) Table I - M, 1126 - 1127.


13. W. Leidenfrost "An attempt to measure the thermal conductivity of liquids, gases and vapours with a high degree of accuracy over wide ranges of temperature (-180 to 500 C) and pressure (vacuum to 500 atmospheres)", Intern. J. Heat Mass Transfer 7, 447-78 (1964).


