THE TEMPERATURE DEPENDENCE OF SOUND ATTENUATION IN GAS MIXTURES

by

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Thesis submitted for the degree of Doctor of Philosophy at the University of Surrey

1971
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Abstract

A resonance tube system has been used to study the propagation of sound in mixtures of gases.

The resonance tube consisted of a long duralumin tube terminated at one end by a fixed reflector and at the other by a plane diaphragm. The diaphragm was vibrated by a moving coil at an amplitude determined by an optical system using a laser, and the variation with frequency of the driving point impedance of the diaphragm-gas-column system was investigated in the neighbourhood of several natural modes of the tube. A computer was used to evaluate the sound attenuation and velocity from these measurements.

Measurements were made in oxygen containing up to 0.25% water vapour at six different temperatures in the range 298K to 410K, and in oxygen with up to 13% helium at 296K. These results are listed in the table below.

In addition sound attenuation and velocity measurements were made in pure dry oxygen in the temperature range 298K to 410K. From these measurements the Helmholtz-Kirchhoff coefficient was calculated and was found to be about 30% higher than the theoretical value. This difference increased with increasing temperature.

RESULTS

(a) \(\text{O}_2-\text{H}_2\text{O}\) mixtures

<table>
<thead>
<tr>
<th>TEMPERATURE K</th>
<th>FREQUENCY OF MAXIMUM ABSORPTION (f_o) (\mu\text{z atm}^{-1})</th>
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<tr>
<td>298</td>
<td>(f_o = 9+199h+115h^2)</td>
</tr>
<tr>
<td>323</td>
<td>(f_o = 12+234h+117h^2)</td>
</tr>
<tr>
<td>343</td>
<td>(f_o = 14+261h+107h^2)</td>
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<tr>
<td>363</td>
<td>(f_o = 15+235h+134h^2)</td>
</tr>
<tr>
<td>383</td>
<td>(f_o = 17+283h+105h^2)</td>
</tr>
<tr>
<td>408</td>
<td>(f_o = 21+325h+96h^2)</td>
</tr>
</tbody>
</table>
(b) \( \text{O}_2 - \text{He} \)

\[
296K \quad f_0 = 10 + 3.8h
\]

\( h \) is the mole fraction of impurity gas \( \times 10^3 \)
Chapter 1

Introduction

The classical theory of sound absorption based on viscous and thermal conductivity losses in a gas was developed by Stokes (1845) and Kirchhoff (1868). Kirchhoff further developed a theory for sound propagation in gases contained in tubes. Although the theory is not strictly true for a system in which standing waves are present, it is usually applied to work of the present type, although not assumed explicitly. The equations, known as the Helmholtz-Kirchhoff equations, give, for sound propagation in tubes:

\[ \alpha_{\text{tube}} = \frac{\beta(\pi f)^\frac{1}{2}}{V_t} \]  \hspace{1cm} \text{(1.1)}

\[ V_{\text{tube}} = V_o \left\{ 1 - \frac{\beta}{(4r^2\pi f)^\frac{1}{2}} \right\} \]  \hspace{1cm} \text{(1.2)}

where \( \beta \), known as the Helmholtz-Kirchhoff coefficient, is given by

\[ \beta = \left( \frac{\eta}{\gamma} \right)^\frac{1}{2} + (\gamma - 1) \left( \frac{K}{dC_p} \right)^\frac{1}{2} \]  \hspace{1cm} \text{(1.3)}

where:

- \( \alpha_{\text{tube}} = \) attenuation of sound in the gas column due to the presence of the tube
- \( V_{\text{tube}} = \) velocity of sound in the gas in the tube
- \( V_o = \) free space velocity of sound in the gas
- \( d = \) density of the gas
\[ \eta = \text{viscosity of the gas} \]
\[ \mu = \frac{\eta}{d} \]
\[ f = \text{frequency of the sound wave} \]
\[ \gamma = \text{ratio of the principal specific heats} \]
\[ K = \text{thermal conductivity of the gas} \]
\[ C_p = \text{specific heat of the gas at constant pressure} \]
\[ C_v = \text{specific heat of the gas at constant volume} \]

The classical attenuation, that due to the viscous and thermal conductivity losses in the bulk of the gas, is given by:

\[ \alpha_{\text{classical}} = 2\pi f^2 \frac{\eta \gamma^3}{f} \left\{ \frac{4\mu}{3} + \frac{K}{dC_V} + \frac{K}{dC_V \gamma} \right\} \quad \ldots \ldots \ldots (1.4) \]

Since the attenuations are small it is normal practice to assume they are directly additive. In the present work at low frequencies (\(<1,000 \text{ Hz}\)) the classical attenuation is negligible compared to that due to the tube.

**Absorption due to relaxation processes**

Jeans (1904) suggested that additional absorption was likely in polyatomic gases if the rate of transfer of energy between the different internal states of the molecules of the gas could not keep pace with the changes in translational energy produced by the sound wave. Experimental evidence of this came later with the work of Naklepa\(j ew\) (1911) on air and Pierce (1924) on carbon dioxide. Theoretical studies quickly followed this, the most widely used being that of Kneser (1931, 1933).

**The nature of the relaxation process**

The energy in a gas is distributed among the translational, vibrational, rotational and electronic degrees
of freedom of its molecules. In most molecules the electronic quanta are so large that only the ground state is populated at temperatures below about ten thousand degrees Kelvin. One can thus discuss the thermodynamic properties of a gas by considering only the contributions of translation, vibration and rotation. Energy transfer among the various modes occurs by collision. Exchange of translational energy between molecules occurs at every molecular collision, while the exchange of energy between translational and the vibrational and rotational modes occurs less readily. For a molecular collision to be effective in changing the vibrational energy of a molecule, the duration of the collision should be comparable to the period of the vibration. A typical molecular relative translational velocity at room temperature is $5 \times 10^2$ metres per sec., while the effective range of the intermolecular forces during a collision is of the order of $10^{-10}$ metres. Hence the time which two molecules spend closer than $10^{-10}$ metres, i.e. the duration of the collision, will be $4 \times 10^{-13}$ seconds. A typical molecular vibration frequency of $3 \times 10^{13}$ Hz has a period of about $3 \times 10^{-14}$ seconds. Thus only those molecular collisions in which the relative velocity is much higher than average will lead to vibrational-translational energy transfer. The probability of the transfer of a vibrational quantum in collision will increase with increasing temperature and translational velocity, with decreasing vibration frequency, and with increase in the steepness of the intermolecular potential energy function.
The period of a typical molecular rotation is much closer to the duration of a collision, and rotational-translational energy transfer in a collision has a much higher probability. The ease of rotational energy transfer can also promote vibrational energy transfer through the sequence: translation → rotation → vibration. The time taken for the redistribution of energy between translation and one of the internal modes is known as the relaxation time. The passage of a sound wave through a gas will upset the equilibrium energy distribution among the various modes. If the time taken to redistribute the energy among the modes is very short compared with the period of the sound wave, the modes will always be effectively in equilibrium and little absorption will occur. If, however, the times are comparable, significant amounts of acoustic energy will be absorbed and later released out of phase with the sound wave. Under these conditions considerable absorption will occur. Mathematical relations between these various factors are developed in the next chapter, where the relaxation phenomena just described are seen to cause the active specific heat of the gas to be dependent on the sound frequency.

Gas mixtures

Considerable work has been carried out on the relaxation phenomena associated with mixtures of gases, especially since it was discovered that some impurities, even in very small quantities, can greatly affect the relaxation time of the
gas to which they are added.

Consider a mixture of two gases A and B, in which A is the major constituent. If A has a long relaxation time then a large number of A-A collisions will occur before any internal change of the molecules occurs. That is the probability of an A-A collision causing energy transfer to an internal mode is low. If molecules B are much better at exciting or de-exciting the internal modes of A then a small quantity of B can greatly shorten the relaxation time of the mixture. In most cases the inverse of the relaxation time will increase linearly with the concentration of B, since for small concentrations the number of A-B collisions will be proportional to the number of B molecules, and the A-B collisions control the relaxation time.

In general the de-excitation efficiency of a molecule with a dipole moment is higher than one without and molecules able to form chemical bonds are usually extremely efficient. Molecules with small moments of inertia and high peripheral velocities of rotation are also efficient in de-excitation.

Helium and to a greater extent hydrogen are very efficient in de-exciting oxygen molecules due to their small masses and hence greater translational velocities. The inverse of the relaxation time, or the frequency at which maximum absorption occurs follows the usual linear dependence on concentration for both helium and hydrogen. However, with water vapour as the additive to oxygen the linear relationship is no longer found. The relaxation time is shortened even more by the presence of very small amounts of water vapour and the frequency of maximum absorption found to have a quadratic dependence on the water vapour concentration.
Tuesday and Boudart's (1955) theory of a resonant exchange process is now generally accepted to explain the effect. This is developed in detail in Chapter 2.

Other theories suggesting that the quadratic dependence on water vapour concentration was due to chemical affinity giving a reaction $O_2 + 2H_2O \rightleftharpoons 2H_2O_2$ have been disproved by Henderson et al (1965). Their results with heavy water ($D_2O$) show a linear effect on the frequency of maximum absorption, which makes the triple collision theory untenable, since the chemical bonds would be expected to play the same part in the $D_2O - O_2$ collisions.

The present work

There now seems reasonable agreement between various workers as to the behaviour of oxygen-water vapour mixtures at room temperature. The aims of the present work were firstly to obtain more data at room temperature for these mixtures and secondly to extend the measurements over a range of temperatures. Results of this kind will yield the temperature dependence of the various molecular rate constants involved in the energy exchange process, such information being of great theoretical importance to a subject which, as yet, is still far from understood.
Chapter 2

Theory of the Relaxation Effect

A general picture of the relaxation process can be obtained by considering a two state equilibrium

\[
\begin{align*}
  \frac{K_{12}}{K_{21}} & \quad 1 \xleftrightarrow{K_{21}} 2 \\
\end{align*}
\]

where \( K_{12} \) and \( K_{21} \) are the forward and backward rate constants. The energy of 2 is assumed to be greater than 1. 1 and 2 may be different chemical species, or 2 may be some excited state of 1. Let \( n_1 \) and \( n_2 \) be the actual number of particles of 1 and 2 at any instant, and \( N = n_1 + n_2 \) be the total number of particles. The rate of disappearance of species 2 at any instant is:

\[
\frac{dn_2}{dt} = K_{21}n_2 - K_{12}n_1 \tag{2.1}
\]

\[
= \left( \frac{K_{21} + K_{12}}{K_{21}} \right) n_2 - K_{12}N \tag{2.2}
\]

\[
= \left( \frac{K_{21} + K_{12}}{K_{21}} \right) \left[ n_2 - N \left( \frac{K_{21}}{K_{12}} + 1 \right)^{-1} \right] \tag{2.3}
\]

at equilibrium \( \frac{dn_2}{dt} = 0 \) and

\[
K_{21}n_2^o = K_{12}n_1^o \tag{2.4}
\]

the figure \( o \) indicating the equilibrium number. Substituting the value of \( \frac{K_{21}}{K_{12}} \) from equation (2.4) into equation (2.3) we obtain:

\[
\frac{dn_2}{dt} = \left( \frac{K_{21} + K_{12}}{K_{21}} \right) \left( n_2 - n_2^o \right) \tag{2.5}
\]

\[
= \left( n_2 - n_2^o \right) / \tau \tag{2.5}
\]

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where $\tau$ is defined by equation (2.5) as $\frac{1}{K_{21} + K_{12}}$

The significance of $\tau$ is shown by integrating equation (2.5) i.e.

$$\frac{dn_2}{n_2^0 - n_2} = \frac{dt}{\tau}$$

and hence:

$$\ln \left( \frac{1}{n_2^0 - n_2} \right) = \frac{t}{\tau} + \text{CONSTANT} \ldots (2.6)$$

at $t = 0$, $n_2$ equals its initial value $n_2^i$. Hence

$$\frac{t}{\tau} = \ln \left( \frac{n_2^o - n_2^i}{n_2^0 - n_2} \right) \ldots \ldots \ldots \ldots (2.7)$$

i.e. $e^{-\frac{t}{\tau}} = \frac{n_2 - n_2^o}{n_2^i - n_2^o}$

Hence the distance of the reaction from equilibrium falls exponentially with time, $\tau$ being a measure of the rate of this approach to equilibrium. After a time equal to the relaxation time $\tau$, the distance from equilibrium has fallen to $\frac{1}{e}$ of its initial value $n_2^i - n_2^o$

**Effective heat capacity of a relaxing medium**

We now consider the effect of the passage of a sound wave through the two-state system. On account of the temperature variations in the sound wave, the equilibrium population of the two states will change. If the frequency of the sound wave is sufficiently low, the local value of $n_2^o$ will remain in equilibrium with the local temperature in the sound wave. For a sinusoidal wave we can write
\[ n_2^o = L \exp(i\omega t) \] ...........(2.9)

where \( L \) is a constant.

As the sound frequency increases the local value of \( n_2 \) (written \( n_2^\omega \)) may be unable to follow the rapid temperature changes, if \( K_{21} \) or \( K_{12} \) is too small. \( n_2^\omega \) will relax towards the instantaneous equilibrium value \( n_2^o \) according to equation (2.5).

\[
- \frac{dn_2^\omega}{dt} = \frac{n_2^\omega - n_2^o}{\tau} \quad \ldots \ldots (2.10)
\]

For a sinusoidal variation such as in equation (2.9), \( \frac{dn_2^\omega}{dt} \) may be replaced by \( i\omega \)

\[ \therefore - i\omega n_2^\omega = n_2^\omega - n_2^o/\tau \]

or \[ n_2^\omega = \frac{n_2^o}{1 + i\omega \tau} = \frac{L \exp(i\omega t)}{1 + i\omega \tau} \quad \ldots \ldots (2.11) \]

To study these effects on a macroscopic scale we consider the heat capacity at constant volume of the system. Since the present work concerns vibrational relaxation in oxygen we apply the above considerations to a diatomic gas possessing one vibration of frequency \( \nu \) and energy \( E^{\text{vib}} = h\nu \). Under specific low-frequency conditions for the sound wave, the gas will exhibit an equilibrium heat capacity

\[ C_{V_0} = C_V^{\text{translational}} + C_V^{\text{rotational}} + C_V^{\text{vibrational}} \]

As the frequency is increased past a certain value the heat capacity associated with the vibration will not participate in the acoustic cycle and the gas will exhibit a limiting value of the heat capacity

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\[
C_{v\omega} = C_v^{\text{translational}} + C_v^{\text{rotational}} + C_v^{\text{vibrational}} \quad \text{having the frequency dependence predicted by equation (2.11) i.e.}
\]

\[
C_v^{(\omega)} = \frac{C_v^{\omega} - C_v^{\omega\omega}}{1 + i\omega\tau} \quad \text{.........(2.12)}
\]

from which the total heat capacity at any frequency \(\omega\) will be given by:

\[
C_v^{(\omega)} = C_v^{\omega\omega} + \frac{C_v^{\omega} - C_v^{\omega\omega}}{1 + i\omega\tau} \quad \text{.........(2.13)}
\]

Considering the equation for the velocity \(V\) of a sound wave in a perfect gas:

\[
V^2 = \frac{RT}{M} \left( 1 + \frac{R}{C_v} \right) \quad \text{.........(2.14)}
\]

\(V^2\) will be frequency dependent given by:

\[
V^{2(\omega)} = \frac{RT}{M} \left( 1 + \frac{R}{C_v} \frac{C_v^{\omega} + C_v^{\omega\omega} \omega^2 \tau^2}{C_v^{\omega\omega} + C_v^{\omega\omega} \omega^2 \tau^2} \right) \quad \text{.........(2.15)}
\]

For frequencies low compared with \(\frac{1}{\tau}\) i.e. \(\omega\tau \ll 1\)

\[
V^{2(\omega)} = V^{2\omega} = \frac{RT}{M} \left[ 1 + \frac{R}{C_v^{\omega}} \right] \quad \text{.........(2.16)}
\]

at higher frequencies where \(\omega\tau \gg 1\)

\[
V^{2(\omega)} = V^{2\omega} = \frac{RT}{M} \left[ 1 + \frac{R}{C_v^{\omega\omega}} \right] \quad \text{.........(2.17)}
\]

The form of the frequency dependence of the sound velocity for an ideal gas is shown in Fig. 2.1. This dispersion process is accompanied by a non-classical absorption of sound.
RELAXATION DISPERSION AND ABSORPTION AS A FUNCTION OF TEMPERATURE; QUALITATIVE

\[ V^2 \]

\[ \mu \]

\[ \log(f_p) \]

\[ \log(f_p) \]

\[ V_\infty^2 = \frac{RT}{M} \left(1 + \frac{R}{C_{V_\infty}}\right) \]

\[ V_o^2 = \frac{RT}{M} \left(1 + \frac{R}{C_{V_0}}\right) \]

\[ \mu_{\text{max}} = \frac{\pi R C}{C_{p_\infty} C_{V_\infty}} \]

VIBRATIONAL DISPERSION
rising to a maximum at a value of frequency/pressure in the centre of the dispersion zone.

The absorption coefficient associated with the relaxation process can be readily derived. Since it can be found in most books on the subject (i.e. Cottrell and McCoubrey (1961)) only the results will be quoted here.

The sound attenuation $\mu$ per wavelength where

$$\mu = 2a \lambda$$

$a$ being the absorption coefficient, is given by:

$$\mu = \frac{2\pi R C_i \tau}{(R + C_{vo})^2 + \omega^2 \tau^2} \frac{2}{(R + C_{vo}) C_{vo}} \cdots \cdots (2.18)$$

For the case of oxygen the vibrational specific heat ($C_i$) is very small $\approx 2.9 \times 10^{-2} R$ and hence $C_{vo} \approx C_{\infty}$

$$\therefore \mu = \frac{2\pi R C_i \tau}{C_{p\infty} C_{\infty} \left(1 + \omega^2 \tau^2\right)} \cdots \cdots (2.19)$$

where $C_{p\infty} = R + C_{\infty}$

Equation 2.19 can be written

$$\mu = \frac{2\pi R C_i}{C_{p\infty} C_{\infty}} \left(\frac{\omega \tau}{1 + \omega^2 \tau^2}\right) \cdots \cdots (2.20)$$

and $\mu$ has its maximum value when $\frac{\omega \tau}{1 + \omega^2 \tau^2}$ is a maximum.

This is when $\omega \tau = 1$ i.e.

$$\frac{\omega \tau}{1 + \omega^2 \tau^2} = \frac{1}{2}$$

$$\therefore \mu_{\text{max}} = \frac{\pi R C_i}{C_{p\infty} C_{\infty}} \cdots \cdots (2.21)$$

also $\omega_{\text{max}} = \frac{1}{\tau} = 2\pi f_0$ where $f_0$ is the frequency
of maximum absorption.

Since the sound intensity is proportional to the square of the amplitude, \( \mu = 2a^2 \), and the attenuation per cm can be written

\[
a = \frac{\pi RC_i f^2 f_0}{V C_{oo} C_{poo} f_0^2 + f^2} \quad \ldots \ldots \ldots (2.22)
\]

Although in this derivation only a single gas was considered, the quantities involved can be equally well defined for a mixture of gases. For the mixtures used in the present work with small impurity concentrations only \( f_0 \) varies significantly and hence equation (2.22) is still valid.

For gases that are not too complicated, the general character of the acoustic absorption spectrum is always the same. A rotational maximum is superimposed on the rise of the classical absorption and the vibrational maximum appears at lower values of \( \frac{f}{\lambda} \), \( \mu \) max becomes smaller as its position shifts further into the low-frequency region. This is qualitatively shown in Fig. 2.1 for two temperatures. Almost all the experience gathered to date shows that relaxation times decrease with rising temperature, i.e. the relaxation maxima are shifted to higher values of \( \frac{f}{\lambda} \). Fig. 2.1 shows the vibrational dispersion characteristics in more detail.

Theories of the relaxation process

Vibrational-translational energy transfer

Theories of vibrational-translation energy transfer have been treated both classically and quantum mechanically. The classical treatment assumes both the translational and
vibrational motions of the colliding molecules can be treated classically. In the semi-classical theory the vibrations are treated quantum mechanically while the translational motion is described classically. The simplest physical model is that of an end-on collision between a diatomic molecule and an atom. It is also applicable to energy transfer in a collision of two diatomic molecules since experiment has shown that the probability of energy transfer to the vibrational mode of a diatomic molecule is not significantly affected by the internal structure of the collision partner. The semi-classical treatment is discussed in Cottrell and McCoubrey (1961) and is based on the work of Landau and Teller (1936). This gives for the overall probability of vibrational de-excitation of a diatomic molecule in an end-on collision with an atom, for an exponential repulsive potential

\[ P_{10} = \frac{64 \pi \frac{5}{4} m^2 \nu}{h \alpha \frac{2}{2} \nu} \left( \frac{m v^2}{9 \alpha^2 K T} \right)^{1/6} \exp \left[ -\frac{54 \pi \nu^2}{2 \alpha K T} \right]^{1/3} \]

\[ \alpha = \frac{\text{reduced mass of the system}}{\text{relative velocity}} \]

Equation (2.23) shows that if the exponential term is dominant the log of the vibrational relaxation time is proportional to the two thirds power of the vibration.
frequency (v), the one-third power of the reduced mass (m), the inverse two-thirds power of the coefficient of the repulsive potential (\(a\)), and the inverse one-third power of the temperature T.

Modern quantum-mechanical theory treats the collision as a parallel stream of molecules, which may be regarded as a de Broglie wave, falling on a molecule regarded as stationary. Vibrational excitation corresponds to inelastic scattering of the wave. This was originally done for the one-dimensional case by Zener (1931) and Jackson and Mott (1932) and subsequently by Schwartz, Slawsky and Herzfeld (1952). The treatment by Schwartz et al has been developed in various ways which are discussed in detail by Herzfeld and Litovitz (1959). The transfer probability \(P_{10}\) is given by Schwartz and Herzfeld (1954) in the form

\[
P_{10} = 0.716 \left(1 + \frac{C}{T}\right)^{-1} \left(\frac{r_c}{r_0}\right)^{1/2} \left(\frac{\pi}{3}\right)^{\frac{1}{2}} \left(\frac{8\pi^3 m \nu}{\alpha^* h}\right)^{2/3} V_{10}^{2/3} \chi^\frac{2}{3} \chi \exp\left(-3\chi + \frac{h\nu}{2kT} + \frac{\varepsilon}{kT}\right)
\]

where \(V_{10}\) is the oscillatory 'matrix element' for the 0 \to 1 quantum jump, C is Sutherland's constant, \(r_c\) the distance of closest approach, \(r_0\) the zero of the intermolecular potential energy curve, m the reduced mass of the colliding particles, \(\alpha^*\) the particular value of the intermolecular repulsion potential corresponding to an exponential expression, \(V = V_0 \exp(-\alpha r) + \varepsilon\), \(\varepsilon\) being the depth of the minimum in the potential energy curve, and \(\chi = \left[\frac{2m^2(h\nu)^2}{\alpha h^2 kT}\right]^{\frac{1}{3}}\).
is very strongly dependent on the intermolecular repulsion parameter $\alpha^*$ and a critical factor in the calculation is the fitting of the exponential expression

$$ V = V_0 \exp (-\alpha r) + \varepsilon, $$

to an actual intermolecular potential function such as the Lennard-Jones. This problem is discussed in detail by Herzfeld and Litovitz (1959) who conclude that the best method involves making a 2 point fit between the exponential and Lennard-Jones curves.

Dickins and Ripamonti (1961) compared values of $\tau$ calculated by this method with some of the more reliable experimental values available, as has been done also by Millikan (1965). These results show that for the diatomic molecules there is general agreement between theory and experiment, and a fair approximation to the correct linear dependence of $\ln \tau$ and $T^{-\frac{1}{3}}$ is given, where experimental data are available over large ranges of temperature.

The Schwartz-Slawsky-Herzfeld treatment appears to be satisfactory for diatomic molecules provided an adequate fit is used for the intermolecular potential.

**Rotational-translational energy transfer**

In most molecules the rotational and translational velocities are comparable and energy transfer in a collision may be expected to occur readily. The corresponding relaxation times will be very short and since much higher frequencies than those used in the present work are required to detect them they will not be discussed further.

**Vibrational-rotational energy transfer**

In 1962 Cottrell and Matheson suggested that in molecules with low moments of inertia, the transfer of energy
from vibration to rotation and thence to translation could occur more readily than direct vibrational-translational energy transfer. They argued that vibrational-rotational energy transfer would be preferred when the peripheral velocity of rotation of a molecule is greater than its translational velocity.

Under such circumstances the probability of de-excitation of the first vibrationally excited level will be

\[ P_{10} = Z \int_{0}^{\infty} P_{10}(v_r)f(v_r)dv_r \]  \hspace{1cm} (2.25)

where \( Z \) is the collision frequency of the gas molecules, \( P_{10}(v_r) \) is the probability of vibrational-rotational energy transfer for a given peripheral velocity of rotation \( v_r \), and \( f(v_r) \) is the distribution function of rotation velocities. To calculate \( P_{10}(v_r) \) the semi-classical expression for translational-vibration energy transfer was used, with the relative translational velocity of the colliding molecules replaced by the peripheral velocity of rotation \( v_r \). The distribution function of rotational velocities may be obtained from the standard treatment of rotational energy levels (Herzberg 1945). By substituting these values of \( P_{10}(v_r) \) and \( f(v_r) \) into eq (2.25) an expression for the probability of vibrational-rotational energy transfer in a collision can be obtained which can be integrated numerically.

Cottrell and co-workers (1964) explored the rotational-vibration transfer further. They considered that the relative molecular translational velocities were the same as in an ordinary collision, while the rotating molecules were
assumed to have the classical angular rotational velocity given by \( \frac{1}{2} I \omega^2 = KT \) \hspace{1cm} (2.26)

Although the translational velocity determines the overall duration of the collision, the average rotational velocity during the collision is assumed to determine the probability of energy transfer. For the forces between the peripheral atoms of the 2 molecules, both a repulsive Lennard-Jones function and an exponential repulsion were considered. The time dependence of the intermolecular force field resulting from rotation was evaluated from an analysis of the detailed geometry of the collision and the resulting expressions substituted into eq (2.25) to give the probability of energy transfer.

Many workers have observed that NH\(_3\) and H\(_2\)O greatly increase the rate of deactivation of vibrationally excited O\(_2\). Both NH\(_3\) and H\(_2\)O have low moments of inertia and high peripheral velocities of rotation and if energy transfer takes place preferentially from vibrationally excited H\(_2\)O molecules then the rate of decay of vibrationally excited O\(_2\) molecules would be increased by the addition of small amounts of H\(_2\)O as observed. (This is discussed in more detail in Chapter 12).

Shields and Burks have made calculations of relaxation times for CO\(_2\) - H\(_2\)O and CO\(_2\) - D\(_2\)O mixtures assuming the bending mode of the CO\(_2\) vibration was exchanging energy with the rotational motion of the H\(_2\)O and D\(_2\)O molecules. They found it possible to explain qualitatively the three unusual effects of H\(_2\)O and D\(_2\)O on the relaxation of the CO\(_2\) (i.e. the high collision efficiency, inverse temperature
dependence and the large difference between the effectiveness of H\textsubscript{2}O and D\textsubscript{2}O. H\textsubscript{2}O was found to be more efficient than the slower rotating D\textsubscript{2}O in deactivating CO\textsubscript{2}. Similarly H\textsubscript{2}O has been found to be more efficient than D\textsubscript{2}O in deactivating vibrationally excited C\textsubscript{2}H\textsubscript{4} and N\textsubscript{2}O. cf. Hudson, McCoubrey and Ubbelohde (1961) and Wight (1956).

**Molecular transfer of vibrational energy**

If a gas A containing a two state vibration which is relaxing is mixed with a gas B which has no vibrational energy, vibrational-translational energy transfer in A can occur by two mechanisms, cf. Lambert J.D. (1967) Quart Rev. Chem. Soc. 21: 67

\[ \frac{K_{10}^{AA}}{K_{01}^{AA}} A^* + A \xrightarrow{AA} A + A \quad (\text{vib} \rightarrow \text{trans}) \]

\[ \frac{K_{10}^{AB}}{K_{01}^{AB}} A^* + B \xrightarrow{AB} A + B \quad (\text{vib} \rightarrow \text{trans}) \]

where * denotes a molecule vibrationally excited. By analogy with equation (2.5) page 11 the relaxation time \( \tau_1 \), observed in the mixture is given by

\[ \frac{1}{\tau_1} = K_{01}^{AA} + K_{01}^{AB} + K_{10}^{AA} + K_{10}^{AB} \quad \ldots \ldots (2.27) \]

where \( K_{01}^{AA} \) is the average number of 0-1 vibrational transitions in A-A collisions per molecule per second at one atmosphere. The other symbols have similar meanings. The value of \( K_{01}^{AA} + K_{10}^{AA} \) will decrease as the mole fraction of A, \( x_A \) decreases, giving

\[ K_{01}^{AA} + K_{10}^{AA} = \frac{x_A}{\tau_{AA}} = \frac{1 - x_B}{\tau_{AA}} \quad \ldots \ldots (2.28) \]
where $\tau_{AA}$ is the relaxation time of pure $A$ at one atmosphere, and $x_B$ is the mole fraction of $B$. Similarly

$$K_{01}^{AB} + K_{10}^{AB} = \frac{x_B}{\tau_{AB}} \quad \ldots \ldots (2.29)$$

where $\tau_{AB}$ is the relaxation time of a hypothetical mixture in which only $AB$ collisions cause transitions. Hence

$$\frac{1}{\tau_1} = \frac{1 - x_B}{\tau_{AA}} + \frac{x_B}{\tau_{AB}} \quad \ldots \ldots (2.30)$$

and a plot of $\frac{1}{\tau_1}$ vs. $x_B$ should be a straight line.

**Relative collision efficiencies**

Consideration of a pure gas $A$ in which only $A \rightarrow A$ collisions occur. We can by analogy with equation (2.5) again define $\tau$ by an equation

$$\tau_{AA} = Z_{AA}(tc)_{AA} \quad \ldots \ldots (2.31)$$

where $Z_{AA}$ is the average number of $AA$ collisions for energy transfer $(tc)_{AA}$ is the average time between intermolecular collisions. For the gas mixture $AB$ described on page 9 we can similarly write (cf. K. F. Herzfeld T. A. Litovitz Absorption and dispersion of Ultrasonic Waves 1959 page 206)

$$\tau_{AB} = Z_{AB}(tc)_{AB} \quad \ldots \ldots (2.32)$$

Equation (2.30) now takes the form:

$$\frac{1}{\tau_1} = \frac{1}{\tau_{AA}} \left[ 1 + x_B \left( \frac{Z_{AA}}{Z_{AB}} \frac{(tc)_{AA}}{(tc)_{AB}} - 1 \right) \right] \quad \ldots (2.33)$$

Hence if the observed relaxation time $\tau_1$ is measured and the relaxation time of the pure gas $A$ is known ($\tau_{AA}$) the relative collision efficiency $\frac{Z_{AA}}{Z_{AB}}$ can be calculated from
equation (2.33) if \( \frac{(tc)_{AA}}{(tc)_{AB}} \) is known. The collision times \((tc)\) are connected to the viscosity via the kinetic theory of gases. Herzfeld and Litovitz have derived an expression for \( \frac{(tc)_{AB}}{(tc)_{AA}} \) which is:

\[
\frac{(tc)_{AB}}{(tc)_{AA}} = \frac{4(T + C_A)}{T + (C_A C_B) \frac{1}{2}} \left( \frac{2N_B}{M_A + M_B} \right)^{\frac{1}{2}} \left[ 1 + \left( \frac{M_B}{M_A} \right)^{\frac{1}{2}} \left( \frac{\eta_A}{\eta_B} \right)^{\frac{1}{2}} \right] \times \left( \frac{T + C_A}{T + C_B} \right)^{\frac{1}{2}} \]...

\[\text{......(2.34)}\]

where \( T = \) absolute temperature

\( C_A = \) Sutherland's constants for molecules type A etc.

\( M_A = \) molecular weight for molecules type A etc.

\( \eta_A = \) the viscosity for molecules type A etc.

The collision efficiencies of various mixtures are given in Appendix I.

Returning to the gas mixture \( AB \), if \( A \) and \( B \) both have vibrational energy, there are now five possible energy transfer processes:

1. \( A^* + A \rightarrow A + A \) (vib \( \rightarrow \) trans) \[\text{......(2.35)}\]
2. \( A^* + B \rightarrow A + B \) (vib \( \rightarrow \) trans) \[\text{......(2.36)}\]
3. \( A^* + B \rightarrow A + B^* \) (vib \( \rightarrow \) vib \( \rightarrow \) trans) \[\text{......(2.37)}\]
4. \( B^* + B \rightarrow B + B \) (vib \( \rightarrow \) trans) \[\text{......(2.38)}\]
5. \( B^* + A \rightarrow B + A \) (vib \( \rightarrow \) trans) \[\text{......(2.39)}\]

In process (3) vibrational energy from a vibrationally excited molecule \( A \) is transferred in a collision to vibration of a \( B \) molecule; if the vibrational quanta
two molecules are not equal, the energy difference is equilibrated with translation. The mechanism of vibrational energy transfer now depends on the relative rates of processes (1) to (5). If (3) is very slow, then A and B will relax separately: the mixture will show a double dispersive region, and each of the relaxation times will vary with the composition of the mixture according to equation (2.30), i.e. we now have two separate relaxation times $\tau_1$, and $\tau_2$ given by

$$\frac{1}{\tau_1} = \frac{1 - x_B}{\tau_{AA}} + \frac{x_B}{\tau_{AB}} \quad \cdots \cdots (2.40)$$

and

$$\frac{1}{\tau_2} = \frac{x_B}{\tau_{BB}} + \frac{1 - x_B}{\tau_{BA}} \quad \cdots \cdots (2.41)$$

If process (3) is very rapid and vibrational energy is easily exchanged between A and B, the vibrational energy of both species will equilibrate with translation by a common mechanism with a single relaxation time. If the energy transfer is homomolecular, i.e. (1) or (4) the rate is proportional to $x^2$ and there should be near quadratic dependence of $\frac{1}{\tau}$ on $x^2$.

Vibrational-vibrational energy transfer has been observed in diatomic molecules. For example, the vibrational relaxation time of $N_2$ is greatly shortened by the addition of $CO_2$ on account of the transfer of energy from the $69.9 \times 10^{12}\text{Hz}$ state of nitrogen to the $70.4 \times 10^{12}\text{Hz}$ state of $CO_2$, cf. Henderson et al (1969), Taylor and Bitterman (1969a). A similar effect is observed on the addition of $CD_4$ to $N_2$ cf. Henderson, Burbank and Glatzel (1969b). Both the classical and quantum mechanical theories of energy transfer have been extended to such cases and the agreement between theory and experiment is good, cf. Sharma and Brain (1969), Berend and
The quadratic dependence on impurity content has also been found for mixtures of O$_2$ and H$_2$O and since this was the mixture used in the present work a more detailed description of the molecular processes follows. The most accepted theory at present to explain this effect is that due to Tuesday and Boudart (1955). The theory is based on the 'resonance transfer' effect where the vibration frequency of the oxygen molecule (wave number 1556 cm$^{-1}$, characteristic temperature $\theta = 2239$K) and the frequency of a bending vibration of the water molecule (wave number 1595 cm$^{-1}$, $\theta = 2295$K) are very similar. The deactivation of the oxygen molecule thus occurs most easily by transferring the internal energy not to translation, but to a bending vibration of the water molecule. We now have a set of reaction equations comparable to equations (2.35) to (2.39). Boudart writes:

$$0_2^* + O_2 \overset{k_{10}}{\underset{k_{01}}{\rightleftharpoons}} 0_2 + O_2 \quad \text{(vib} \rightleftharpoons \text{trans}) \quad \text{(2.42)}$$

$$0_2^* + H_2O \overset{k_{20}}{\underset{k_{02}}{\rightleftharpoons}} 0_2 + H_2O \quad \text{(vib} \rightleftharpoons \text{trans}) \quad \text{(2.43)}$$

$$0_2^* + H_2O \overset{k_{30}}{\underset{k_{03}}{\rightleftharpoons}} 0_2 + H_2O^* \quad \text{(vib} \rightleftharpoons \text{vib}) \quad \text{(2.44)}$$

$$H_2O^* + H_2O \overset{k_{46}}{\underset{k_{04}}{\rightleftharpoons}} H_2O + H_2O \quad \text{(vib} \rightleftharpoons \text{trans}) \quad \text{(2.45)}$$

$$H_2O^* + O_2 \overset{k_{50}}{\underset{k_{05}}{\rightleftharpoons}} H_2O + O_2 \quad \text{(vib} \rightleftharpoons \text{trans}) \quad \text{(2.46)}$$
The resonance process, whereby we have direct vibrational vibrational energy transfer is given by equation (2.44).

Tuesday and Boudart's theory is further developed and is given in detail in Herzfeld and Litovitz (1959). Let the mole fractions of \( \text{O}_2 \), \( \text{H}_2\text{O} \), \( \text{O}_2^* \) and \( \text{H}_2\text{O}^* \) be \((1-X), X, x_1, x_2\) respectively where \( X \gg x_1, X \gg x_2 \) and \( 1 \gg X \). \( N \) is the number of molecules per c.c.

They arrive at an expression:

\[
\frac{1}{\tau} = N k_{10} + N \left[ \frac{k_{20} - k_{10} + \frac{k_{30}k_{50}}{k_{03} + k_{50} - (k_{03}+k_{50}-k_{40})X}}{X} \right] + N \left[ \frac{k_{30}(k_{40}-k_{50})}{k_{03} + k_{50} - (k_{03}+k_{50}-k_{40})X} \right] X^2 \ldots (2.47)
\]

which is of the required quadratic form provided

\[
k_{03} + k_{50} \gg (k_{03} + k_{50} - k_{40})X
\]

Measurements of the relaxation frequency as a function of the mole fraction of water vapour enables one to deduce the various reaction rates from equation (2.47). The application of experimental results to this equation will be discussed in more detail in Chapter 12).
The Resonance Tube Method

The theory of the present method is based on that of Reay (1950) and was employed by both Kitching (1962) and Nolan (1967), the two previous workers from this laboratory. Since the technique is well established only an outline of the theory will be presented here. A more detailed derivation can be obtained by reference to any of the above named authors.

Consider a gas, of density $\rho$, contained in a rigid cylindrical metal tube of length $l$ and cross-sectional area $s$, in which longitudinal vibrations are excited by a plane diaphragm, vibrating parallel to the axis of the tube. The tube is terminated by a reflector which is assumed to be perfectly rigid. If the particle velocity at a distance $x$ from the diaphragm is

$$\xi = A \exp \left[ -ax + j(\omega t - qx) \right] + B \exp \left[ ax + j(\omega t + qx) \right]$$

and the periodic force driving the piston-like diaphragm is $\psi = \psi_0 e^{j\omega t}$ then it may be shown, by using the appropriate boundary conditions, that the mechanical impedance of the system at the driving point is

$$Z_{oo} = \psi_0 \left. \frac{\xi}{\psi_0} \right|_{x=0} = Z_0 + \coth(a + jq)l \quad \ldots \ldots (3.2)$$

where $Z_0$ is the impedance of the diaphragm alone and the unit of impedance is taken as spv where $v$ is the sound velocity, $q$ is the propagation constant $= \frac{2\pi}{\lambda} = \frac{2\pi f}{v}$ and $a$ is the attenuation coefficient.
We now proceed to examine the variation of $Z_{oo}$ over a small range of frequency containing one of the natural frequencies of the gas column. Over such a range $Z_{oo}$ moves rapidly through a maximum and a minimum value. Equation (3.2) can be represented on an Argand diagram as is shown in Figure 3.1, page 31. $Z_o$ may be represented by a vector $P'O$, while the application of familiar transformations associated with the circle diagrams used in transmission line theory shows that the locus of $\coth(a + jq)\ell$, represented by the vector $OP$, is a circle of radius $1/\sinh a\ell$. The vector $PP'$ represents $Z_{oo}$, and $OM$ and $OL$ are given by
\[
\frac{\sinh 2a\ell}{\cosh 2a\ell - 1} \quad \text{and} \quad \frac{\sinh 2a\ell}{\cosh 2a\ell + 1}
\]
respectively.

$OM$ represents the impedance of the gas column at a frequency such that $2q\ell = 2N\pi$, where $N$ is an integer. Successive integral values of $N$ correspond to natural modes of the gas column, for which its length is an integral number of half wavelengths. $OL$ represents the impedance at a frequency midway between two such natural modes, this being an anti-resonant frequency for which the length is an odd number of quarter wavelengths. To a first approximation $OL$ can be neglected since $a\ell$ is small and $O$ and $L$ may be regarded as coincident.

As the frequency increases from an anti-resonant value, $P$ moves anti-clockwise from $L$ round the circle and $Z_{oo}$ after first increasing to a maximum $P'P_2$ rapidly decreases to a minimum value $P'P_1$ and then increases slowly again. In the present work values of the impedance $|Z_{oo}|$ in arbitrary units were determined experimentally in the neighbourhood of a particular resonant frequency of the gas column and a curve such as that shown in Fig. 3.1 was obtained. From such a
CIRCLE DIAGRAM

VARIATION OF $|Z_{oo}|$ WITH FREQUENCY
curve the vector locus diagram can be readily derived, since

\[ QT = P_1P_2, \quad O'S = P'C \text{ where } S \text{ is the midpoint of } QT, \text{ and} \]

\[ O'U = OP'. \] Values of \( |Z_0| \) and frequency taken from the curve establish the positions of \( P \) on the circle at either side of the resonance point, and the phase angle \( \phi \) can be measured for each of these frequencies. \( \tan \phi \) is given by

\[ \tan \phi = \frac{\sin 2q \lambda}{\sinh 2a \lambda} \]

For a small range of frequency on either side of the resonance point a graph of \( \tan \phi \) against \( f \) is to a good approximation a straight line, the slope of which, when \( \tan \phi = 0 \), is given by

\[ \text{Slope} = \frac{4 \pi \lambda}{V} \cdot \frac{1}{\sinh 2a \lambda} \]

which since \( 2a \lambda \) is small, gives

\[ a = \frac{2\pi}{V \times \text{Slope}} \approx \frac{2\pi}{V} \]

approximately \( \ldots \ldots (3.3) \)

The resonant frequency \( f_N \) is given when \( 2q \lambda = 2N \)

\[ \text{since} \quad q = \frac{2\pi}{\lambda} = \frac{2\pi f_N}{V} \]

\[ \therefore \quad \frac{2\pi f_N \lambda}{V} = F \pi \]

giving \( V = \frac{2f_N \lambda}{N} \)

\( \ldots \ldots (3.4) \)

Hence both the attenuation coefficient \( \alpha \), and the velocity in the tube \( V \) may be calculated from equations (3.3) and (3.4).

It is important to note that two assumptions have been made in this derivation. These being that both \( \alpha \) and \( Z_0 \) are
constant over the small frequency either side of the natural mode. However, previous experience has shown that these assumptions do not produce any significant errors. In the present work OL was initially neglected and a value of $a$ obtained from the second circle diagram. This value of $a$ was then used to calculate OL and the true circle diagram constructed. In practice the value of $/Z_0/$ given as $0'U$ in Fig. 3.1 was initially estimated by measuring the driving point impedance at the two anti-resonant frequencies on either side of $f_N$, where the measured impedance differs only slightly from $/Z_0/$, and assuming it to have a linear relationship with frequency between these two points. In practice a small range of values of $/Z_0/$ about the experimental value was used, the one yielding the best $\tan \phi$ against frequency line being taken as the true value.

**Measurement of the driving point impedance**

When the diaphragm is excited by a periodic force

$$\psi = \psi_0 e^{j\omega t}$$

the particle velocity of its centre is given by

$$\psi_0$$

In the present apparatus the diaphragm was driven by

$$/Z_{oo}/$$

passing an alternating current through a moving coil attached to it, the driving force being proportional to the current. If $I$ is the root mean square value of the current which produces some pre-assigned value $\xi$ of the amplitude, then

$$/Z_{oo}/ = \frac{DI}{f}$$

where $D$ is a constant. Hence relative values of

the driving point impedance, which are all that are needed in the foregoing theory, may be obtained by measuring the current required to maintain a constant assigned amplitude,
together with the appropriate frequency. The required constant amplitude is achieved by using the optical effect described by Smith (1945) which is discussed in detail in Chapter 4.

The computer programme

The analysis of the present work by the circle diagram method was done automatically by the University's I.C.L. computer.

From the experimentally obtained \( |Z_0| \) against frequency curve the basic quantities necessary for the construction of the Argand diagram were obtained. By the use of co-ordinate geometry and the cosine formula values of \( \tan \phi \) were calculated for a range of frequencies about the resonant value \( f_N \). A least squares best fit to the \( \tan \phi \) and frequency points was then obtained. The above procedure was performed for a range of possible values of \( |Z_0| \) lying about the estimated value. The one which yielded the best straight line was taken as the true value. An example of this is shown in Chapter 10. The slope of this line was calculated and the attenuation and tube velocity calculated from equations (3.3) and (3.4).

In practice the above procedure was initially performed by neglecting the small distance \( OL \left( = \frac{\sinh 2aL}{\cosh 2aL + 1} \right) \) and a value of the attenuation calculated from equation (3.3). The procedure was then repeated including the length \( OL \) calculated using the value of \( a \) just obtained, and a new value of the attenuation coefficient found.

From the total attenuation coefficient thus found the relaxation attenuation was determined by subtracting the
previously determined tube absorption. This complete
procedure is illustrated in more detail in Chapter 10 which
gives a specimen calculation for an actual set of measurements
taken on March 16, 1971.
The Resonance Tube Assembly

The resonance tube system was based on that previously used by Kitching (1962) and Nolan (1967). Major modifications were made to the design enabling the system to be used at higher temperatures. It consisted of a rigid duralumin tube, closed at one end by a massive steel reflector, and at the other by a plane aluminium diaphragm. The construction of the system was such that both the reflector and diaphragm were flat and perpendicular to the axis of the tube, the tube walls being smooth and free from flaws. In addition it was necessary that the system could be evacuated to a low pressure and filled with a gas mixture of known composition.

The tube

The tube used was a seamless duralumin tube having a clean smooth inner surface. It was approximately 220 cm. long and 11.5 cm. in internal diameter. The ends of the tube were threaded to take the stainless steel flanges for the reflector and loudspeaker sections. Before measurements of the tube length and diameter were made, the tube was heated to 350°C for twelve hours and then cooled very slowly back to room temperature to relieve internal stresses and strains. The internal diameter of the tube was measured with a travelling microscope to \( \pm 0.001 \text{ cm} \). Four measurements of the diameter were made at each end of the tube. These results are shown in Table 4.1.

The diameter of the tube sets an upper limit to the frequency range that can be used.
### Table 4.1

**Tube Dimensions**

#### (i) Length at 28°C

<table>
<thead>
<tr>
<th>Orientation</th>
<th>Tube length (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0°</td>
<td>218.7825</td>
</tr>
<tr>
<td>90°</td>
<td>218.7870</td>
</tr>
<tr>
<td>180°</td>
<td>218.7920</td>
</tr>
<tr>
<td>270°</td>
<td>218.7865</td>
</tr>
</tbody>
</table>

The following values were added to these readings:

(i) 0.002 (T-20) cm. for gauge expansion

(ii) 0.086 cm. for distance between end of tube and diaphragm.

This gives length of gas column = **218.889 ± 0.005 cm. at 28°C**

#### (ii) Diameter

<table>
<thead>
<tr>
<th>Tube diameter (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reflector end</td>
</tr>
<tr>
<td>11.417</td>
</tr>
<tr>
<td>11.420</td>
</tr>
<tr>
<td>11.410</td>
</tr>
<tr>
<td>11.416</td>
</tr>
<tr>
<td>Orientation</td>
</tr>
<tr>
<td>0</td>
</tr>
<tr>
<td>90°</td>
</tr>
<tr>
<td>180°</td>
</tr>
<tr>
<td>270°</td>
</tr>
<tr>
<td>L/S end</td>
</tr>
<tr>
<td>11.416</td>
</tr>
<tr>
<td>11.423</td>
</tr>
<tr>
<td>11.408</td>
</tr>
<tr>
<td>11.415</td>
</tr>
</tbody>
</table>

Mean diameter = **11.416 ± 0.008 cm.**
According to Lamb (1925), providing the wavelength is greater than 1.7 times the tube diameter transverse vibrations cannot be propagated, the wavefront is plane and the Helmholtz-Kirchhoff theory is applicable, although in the present work it is not assumed explicitly. In the present case the upper limit of frequency was about 1,700 Hz.

The length of the tube, measured from the reflector end to the loudspeaker end, which was open, was determined using a set of measuring rods with a micrometer attachment. In order to verify that the reflector was perpendicular to the tube, four readings were taken around the circumference of the tube. Preliminary readings showed that the reflector was slightly out of alignment. This was corrected by tightening the appropriate bolts securing flange B to flange A on the reflector assembly (see Fig. 4.6). The results of the length measurements are shown in Table 4.1. Corrections were applied to the measurements to allow for the expansion of the gauge due to its temperature change. The small distance between the end of the tube and the diaphragm had to be added to give the exact length of the gas column.

It was felt desirable to measure the coefficient of linear expansion of the duralumin of the tube, and to investigate its temperature dependence, since the exact composition of the tube material was not known. A comparator technique, using a fused silica rod was employed. The rod was supplied by Thermal Syndicate Limited. It was 220 cm. long and 6 mm. diameter with a mean coefficient of linear expansion of $0.6 \times 10^{-6}$ °C$^{-1}$ in the temperature range 20 to 400°C. The apparatus used to measure the expansion of the tube is shown in Figs. 4.1 and 4.2.
FIG. 41.

TECHNIQUE USED TO MEASURE THE EXPANSION OF THE RESONANCE TUBE
The resonance tube with the reflector end fitted was placed on its trolley in the furnace. The silica rod was pushed into the tube to meet the face of the reflector. In this position approximately 2 cm. of the rod protruded from the open end of the tube. By means of a wire attached to the trolley the resonance tube could be pulled from the centre of the furnace to the entrance. The furnace entrance was sealed with an asbestos plug which had a hole just large enough to allow the resonance tube to pass through. Just beyond the asbestos plug a piece of dexion was fixed to act as a stop (see Fig. 4.2). By means of two probes, each running on a vernier scale bolted to a rigid wooden base, the difference between the length of the tube and the rod could be measured. The inside of the open end of the resonance tube was packed with fibre glass insulation to keep the heat losses at that end to a minimum. The technique used was to push the resonance tube into the centre of the furnace and bring it to a steady temperature. This was measured by six chromel-alumel thermocouples equally spaced along the length of the tube (shown as $\bullet$ in Fig. 4.1). Their outputs were recorded on a six channel chart recorder which gave a continuous reading of the temperature. When the temperature along the tube was uniform to within $\pm$ 0.5°C the tube was pulled from the centre of the furnace to the end stop. The two probes were quickly pushed into contact with the tube and silica rod respectively taking care that the far end of the silica rod was in contact with the reflector face. The two probes were made of asbestos so that their own expansions could be neglected. The verniers of the two probes were read at each temperature and subtracted from
their initial readings at room temperature. The expansion 
of the silica rod was determined at each temperature from 
the data supplied by the manufacturers.

With reference to Fig. 4.3 the procedure for the 
calculation of the coefficient of linear expansion \( \alpha \) of the 
material of the resonance tube was as follows:-

- \( b_1 \) = initial reading of tube probe at \( t_1 \) °C
- \( a_1 \) = initial reading of rod probe at \( t_1 \) °C
- \( b_2 \) = final reading of tube probe at \( t_2 \) °C
- \( a_2 \) = final reading of rod probe at \( t_2 \) °C

Expansion of silica rod 
\[
\delta l_R = l_R(T_1) \alpha_R (t_2 - t_1) \text{ (cm)}
\]

where \( l_R = 220 \text{ cms. at } 21\degree C \)

\( \alpha_R \) = coefficient of linear expansion of silica rod given 
as \( 0.6 \times 10^{-6} \degree C^{-1} \)

\[
\delta l_R = 1.32 \times 10^{-4} (t_2 - 21) \text{ (cm)}
\]

Let \( l_1 \) = length of resonance tube at \( t_1 \) °C

- \( l_2 \) = length of resonance tube at \( t_2 \) °C
- \( l_R \) = length of silica rod at \( t_1 \) °C

\( S \) = arbitrary distance

Considering Fig. 4.3 we have

\[
S + l_1 + b_1 = l_2 + b_2 \quad \text{........(4.1)}
\]

\[
S + l_R + a_1 = l_R + \delta l_R + a_2 \quad \text{........(4.2)}
\]

Eliminating \( S \) from equations (4.1 and 4.2) we have

\[
l_2 - l_1 = (a_2 - a_1) - (b_2 - b_1) + \delta l_R
\]

or \( \delta l = \delta a - \delta b + \delta l_R \) 

\text{........(4.3)}

If we assume that over the temperature range \((t_2 - t_1)\) \degree C \( \alpha \) has 
a linear dependence on temperature then we can define

\[
\alpha = \frac{l_2 - l_1}{l_1(t_2 - t_1)} \degree C^{-1} \quad \text{........(4.4)}
\]
FIG. 4.3.

CALCULATION OF THE RESONANCE TUBE EXPANSION

\[ \text{TUBE} \]

\[ \text{TEMP. } T_1 \]

\[ s \]

\[ l_R \]

\[ \text{TEMP. } T_2 \]

\[ b_1 \]

\[ b_2 \]

\[ a_1 \]

\[ a_2 \]
So from equation (4.3)

\[
a = \frac{\delta a - \delta b + \delta L}{\xi(t_2-t_1)} \quad \xi = 1 \quad \ldots \ldots (4.5)
\]

The change in length \((\xi_2 - \xi_1)\) with respect to \(21^\circ C\) was calculated from the experimental measurements using equation (4.3). The value of \(\xi_1\) at \(21^\circ C\) was calculated from the measured length at \(28^\circ C\) with an estimated value for \(a\). \(\delta \xi\) was plotted against temperature (Fig. 4.4). The measured points lie on a shallow curve which is as to be expected since the variation of \(\delta \xi\) with temperature is only linear to a first approximation. Average values of \(a\) in the temperature ranges \(21 - 100^\circ C\), \(21 - 150^\circ C\), \(21 - 200^\circ C\) and \(21 - 250^\circ C\) were obtained by assuming a linear dependence between \(\delta \xi\) and \(t\) and calculating \(a\) from equation (4.4) using the slopes of the lines shown in Fig. 4.4. M. Steel (1959) using a duralumin tube of known composition estimated values for \(a\) from results of a number of different workers. The results were taken regardless of the heat treatment of the specimen and average values of the expansion coefficient between \(20 - 100^\circ C\), \(20 - 200^\circ C\), \(20 - 300^\circ C\) were taken. Table 4.2 gives the values used together with the maximum deviation from the average value, the number of values averaged and references to the relevant workers.

The results of individual observers often differed by \(2\%\) even with specimens of similar compositions subjected to similar heat treatment, thus an overall average of the results for each temperature yields a reasonable estimate for \(a\). Too stringent a comparison is not really justified since the exact composition of the present tube was not known.
FIG. 4.4.

RESONANCE TUBE EXPANSION AGAINST TEMPERATURE

\[ \delta l \text{ (cm)} \]

\[ T \text{ (°C)} \]

(a) \( \alpha_{21-250} = 24.3 \times 10^{-6} \text{ (°C)} \)

(b) \( \alpha_{21-200} = 23.7 \times 10^{-6} \text{ (°C)} \)

(c) \( \alpha_{21-150} = 22.7 \times 10^{-6} \text{ (°C)} \)

(d) \( \alpha_{21-100} = 22.0 \times 10^{-6} \text{ (°C)} \)
<table>
<thead>
<tr>
<th>Temperature Range °C</th>
<th>Number of values averaged</th>
<th>Maximum deviation from average value ( \times 10^{-6} ) °C</th>
<th>Observers</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 - 100</td>
<td>51</td>
<td>+ 0.6</td>
<td>Hidnert (1925)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Kempf (1933)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Ebert (1938)</td>
</tr>
<tr>
<td>20 - 200</td>
<td>51</td>
<td>+ 0.6</td>
<td>Willey and Fink (1945)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Barber (1949)</td>
</tr>
<tr>
<td>20 - 300</td>
<td>40</td>
<td>+ 0.6</td>
<td>Hidnert (1952)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>High Duty Alloys (1957)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Zeelerder (1958)</td>
</tr>
</tbody>
</table>
However, the slightly poorer agreement for $\omega_{21-100}$ could possibly be due to experimental errors since in this temperature range changes in length were smaller and hence more difficult to measure accurately. However, the error in the total length of the tube introduced by this disagreement is only about 0.01% which would lead to an error in subsequent velocity determinations of approximately $3\text{cm.sec}^{-1}$ which is negligible.

The reflector

The reflector is illustrated in Figs. 4.5 and 4.6. Three stainless steel flanges A, B and C formed the main assembly. Flange A screwed directly onto the tube. Flange B was secured to A by means of eight bolts. B was $1\frac{1}{4}$ in. thick with a smooth inner surface. Flange C was bolted to B by six bolts. To produce gas tight joints, thin copper gaskets were sheared between the mating flanges AB and BC. The performance of this type of high temperature vacuum seal is reported by Brymner and Steckelmacher (1959). Fig. 4.7 (a) and (b) shows the formation of the seal. This type of seal does not rely on compression, although this must still exist, but on surface shear brought about by the large frictional forces involved. Two stages exist in the making of the seal:

(i) The gasket is formed, by the drawing operation, to the shape of the cone of the male mating surface.

(ii) Further pressure from the bolts produces the surface-shearing action which forms the vacuum seal.

The seals were independent of temperature changes since the flanges, being of the same material, expanded and contracted...
FIG. 45.

THE REFLECTOR

supporting framework

resonance tube

resistance thermometer
FIG. 46.

gas entry system
not in plane of bolts

scale = \( \frac{1}{2} \) full size

THE REFLECTOR
THE VACUUM SEALS

(a)

(b)
radially by equal amounts maintaining the frictional forces across the sealing surface. The design for the seals used in the present work was based on recommended dimensions given by Brymner and Steckelmacher. The copper gaskets were nickel plated before use to prevent oxidization of the copper from contaminating the system. To enable gas to enter and leave the tube, a movable plunger system was incorporated as illustrated. The stainless steel plunger D moved in the central hole, and when closed fitted flush with the small hole in the centre of B. With no force on the plunger the spring S would maintain it in the open position enabling the passage of gas between the tube and the vertical hole in C. Pressure could be exerted on D via the stainless steel bellows E, closing the gas passage between the tube and C. A length of brass studding G and the clamping arrangement H enabled the bellows to be fixed open or closed from a suitably distant position from the reflector. The gas entry to the reflector was via \( \frac{1}{4} \) in. diameter stainless steel tubing which was cemented into the vertical hole in C, using high temperature cement (see appendix II).

The loudspeaker

The loudspeaker assembly is shown in Figs. 4.8 and 4.9. The stainless steel flange A screwed directly onto the tube about two inches from the end. Another stainless steel flange B was bolted to A so that it fitted flush with the end of the tube. This flange incorporated the gas inlet system which is shown in more detail in Fig. 4.11(a). The mild steel flange C bolted onto B. This carried the six bolts used to clamp the diaphragm flush with the end of the tube. This is shown in more detail in Fig. 4.10.
FIG. 48.

Supporting frame
Glass disc
Diaphragm
Clamping bolts
Leads to coil
Resonance tube
The loudspeaker
FIG. 4.10.

THE DIAPHRAGM CLAMPING SYSTEM
The diaphragm was clamped between two circular asbestos gaskets. One was housed in a recess cut into flange B, the other being carried by a circular brass holder controlled by the six clamping bolts.

The cylindrical magnet G was bolted between the mild steel flanges C and D. The mild steel section E slid into the hole in D to which it was bolted, and left a narrow annular gap between it and the flange C. The symmetry of the gap was checked using a travelling microscope, and adjustments could be made by tightening the appropriate bolts securing E to D. The loudspeaker coil was situated in this annular gap, and hence in the magnetic field produced in the magnetic loop G - C - E - D - G. The inner surface of E was partly threaded such that the stainless steel section F could be screwed into position. One end of F carried the lens and lens holder used to produce Newton's rings. (see Fig. 5.2). E was closed by the stainless steel section H which had a flat glass disc cemented directly onto one end.

The gas entry system is shown in Fig. 4.11(a). A vertical plunger was housed in the stainless steel bellows. Compression of the bellows was achieved by the action of the screw S which located in a small metal disc. The screw assembly was supported by a flat T-piece structure which bolted onto the back face of flange B. Compression of the bellows was achieved via the chain and cog system. As with the reflector system a strong spring returned the plunger to the open position when the pressure on the bellows was removed. The gas entry was through the side tube into which a \( \frac{1}{4} \)in. stainless steel tube was cemented. To ensure that the entire system was gas tight vacuum seals described earlier were incorporated.
GAS INLET SYSTEM

THE DIAPHRAGM AND COIL
between the mating flanges. Where these seals were impractical to use, as with the gas inlet tubes and where the end flanges screwed directly onto the tube, sealing was achieved with a high temperature cement. This cement and its preparation is described in appendix II.

The vacuum seals on all the flanges except that between the flanges B and C on the loudspeaker system, proved satisfactory. This last seal however was a constant source of trouble throughout the period of the research. Even with a replacement seal the trouble was not cured. Further discussion of this trouble and a short review on future design to improve the system is given in appendix III.

The diaphragm

The first diaphragm employed was that used by Nolan, the previous worker from this laboratory. It consisted of two discs of duralumin 0.91 mm. thick and 4.5 in. and 7.5 in. diameter respectively. They were joined together using a vacuum leak sealant which when cured formed a very strong bond. However, experiments with this diaphragm showed it to have a prohibitively high impedance at the lower frequencies.

An alternative diaphragm was made, which is shown in Fig. 4.11(b). This was of the same dimensions as the previous one, except that it was made from one piece of duralumin. In order to be sure that the diaphragm was flat, and to relieve internal stresses it was heated to 300°C between heavy steel plates and maintained at that temperature for 24 hours. It was then cooled very slowly for the next 24 hours.

The loudspeaker coil

The coil consisted of 150 turns of 34 s.w.g. enamel covered constantan wire wound onto an asbestos former. It is
shown in Fig. 4.11(b) attached to the diaphragm. The coil was made in two layers. One layer of asbestos paper was wound onto a specially constructed brass former. The surface of the paper was coated with a thin layer of high temperature cement, and the entire assembly fixed into a coil winding machine. One layer of turns was wound onto the paper while the cement was still wet, causing the cement to rise up between the turns, giving added insulation between the windings. Another thin layer of cement was applied over these windings and a piece of asbestos paper fixed over them. This was similarly coated with cement and a further layer of turns wound, in the same direction, onto the paper. The cement that had risen between the turns was smoothed away and the entire coil heated to 250°C for twelve hours to cure the cement. When the curing was completed the base of the coil was cut to form castellations which were bent at right angles to the axis of the coil. The castellations on the inner surface were bent towards the coil centre and those on the outside away from the centre. This gave a large surface of contact for adhesion to the diaphragm surface. The completed coil was 4 cm. outside diameter and 3 cm. long with 0.1 cm. wall thickness. The coil was seated in position on the diaphragm and some leak sealant applied to the asbestos castellations and allowed to soak through to the diaphragm surface.

One side of an optically flat borosilicate glass disc 3/4 in. in diameter was roughened and coated with graphite. This was then attached to the centre of the diaphragm using the leak sealant. The entire system was then cured at 200°C for twelve hours and then cooled very slowly.
Great care was necessary when assembling the loudspeaker system, to prevent damage to the coil and diaphragm. The technique used was to place the assembled loudspeaker sections C G D E flat on a bench with the copper sealing gasket in position. The six clamping bolts, brass ring and asbestos gasket were also in position so they could support the diaphragm. The leads from the coil, after being insulated with high temperature sleeving, were fed through the holes in C. Three pieces of thread were laid across the annular gap, one end of each piece passing down the central hole in E. The diaphragm was then carefully put in place, the coil being held in the centre of the gap by the threads placed around it. Section B, complete with asbestos gasket was placed in position above C. The eight bolts were placed in position, and adjacent bolts tightened by equal amounts until the seal had been sufficiently deformed. The threads locating the coil were then carefully withdrawn through the hole in E. The six clamping bolts were then carefully screwed up until the diaphragm was securely clamped between the two asbestos gaskets. The lens holder system F could then be screwed into place, and the end section H slid into position. The coil leads in the holes in C were attached to metal-ceramic lead-throughs which were cemented into position on the flange surface.
Chapter 5

The Measuring Systems

The method used to determine the amplitude of vibration of the diaphragm was first described by Smith (1945) and involves Newton's rings formed between a vibrating glass disc on the diaphragm and a stationary lens. If the diaphragm is set into sinusoidal vibration and the amplitude is gradually increased, the bright and dark fringes interchange their identities, in passing through a state of zero visibility, at a series of critical amplitudes. The first eight critical amplitudes are: $0.1914 \lambda$, $0.4393 \lambda$, $0.6886 \lambda$, $0.9383 \lambda$, $1.1882 \lambda$, $1.4380 \lambda$, $1.6880 \lambda$, and $1.9379 \lambda$ where $\lambda$ is the wavelength of the light used. The transition through a critical amplitude was marked by an interchange of the bright and dark fringes, providing a sensitive method of setting. The first disappearance in light from a helium-neon gas laser, $\lambda = 6328 \AA$ was employed throughout the present measurements of sound attenuation, so that the constant amplitude used was $1.211 \times 10^{-5} \text{cm}$.

For the initial calibrations of the loudspeaker a system using mercury green light was employed. This method proved unsatisfactory however when applied to the loudspeaker in its working position and was replaced by the laser system described on page 71 which was then used for all subsequent measurements.

The mercury green light system is illustrated in Fig. 5.1. Light from the D.C. mercury lamp was focussed on to the stop C by the condenser lens. It then passed through the converging collimator lens via a green gelatine filter E onto a glass plate which reflected it through the opening in G. Suitable
FIG. 61.

MERCURY LAMP
condenser lens
$f = 2$ cm.
collimator lens
$f = 2$ cm.
glass plate

telescope

-61-
positioning of the components ensured that the emergent beam was accurately parallel. This parallel beam was directed through the inclined glass plate on H (see Fig. 5.2) along the tube F to the lens and glass disc, between which the Newton's rings were formed. The glass plate on H and the back face of the lens were inclined to the axis to prevent them reflecting light into the field of view. The inner surfaces of H and F were painted with high temperature matt black paint to minimize any reflections from them.

The lens was plano-convex, 0.8 cm. in diameter, 0.5 cm. long with a radius of curvature of 100 cm. The orientation of the lens could be altered by the three supporting screws in the lens holder, and in this way it was possible to centralize the fringe pattern. The fringes could then be viewed through the telescope. The power supply to provide direct current to the mercury lamp was that used by Nolan (1967). Direct current was used to avoid beats being produced between the vibrating diaphragm and the periodic illumination.

An important advantage of this technique is that it provides very sensitive checks on the diaphragm performance. If the diaphragm is not vibrating uniformly the fringes do not disappear from the entire field of view at the same time, but instead a band of uniform illumination crosses the field of view as the amplitude of vibration is increased. The amplitude should be proportional to the current through the coil and this was verified by measuring the current required to produce successive fringe disappearances. It was also important that the loudspeaker impedance had a smooth variation with frequency. Therefore it was necessary to perform these initial checks before the loudspeaker could be considered satisfactory. The
FORMATION OF NEWTON'S RINGS

![Diagram of Newton's rings experiment]

- coil
- glass disc
- lens holder
- adjusting screws
- lens
- F
- H
- E
- diaphragm
results of these initial checks are shown in Figs. 5.3, 5.4 and 5.5. Fig. 5.3 shows the graph of current against amplitude of vibration. This was measured at four different frequencies and linear relationship both at high and low temperatures was found.

The diaphragm was clamped independently by six bolts and the impedance spectrum was found to be quite sensitive to the clamping pressure. It was necessary to adjust the clamping pressure by slowly tightening the six bolts by equal amounts until a satisfactory smooth variation of impedance with frequency was obtained. Although it was a tedious procedure it was possible to achieve a very smooth variation in the frequency range 60 - 800Hz. Outside this range the impedance was too large for satisfactory measurements to be made. Figs. 5.4 and 5.5 show the impedance spectrum obtained at the two temperatures of 296K and 497K. Measurements were made at five temperatures within this range and the curves fell within the two limiting ones shown in the figures. This is better illustrated in Fig. 5.6 where the impedance is shown against temperature for 9 different frequencies.

Measurements at the different temperatures were performed by placing the loudspeaker assembly into a thermostatically controlled oven. The back face of the oven was packed with fibre-glass to avoid standing waves being set up. The oven had a glass window in the door which enabled the optical system to be used directly without upsetting the temperature. Reliable measurements were thus possible over the temperature range 295K - 520K. Over this temperature range the fringe pattern changed its position by only a very small amount and there was no need for any adjustment to the lens.
GRAPH OF CURRENT AGAINST AMPLITUDE OF VIBRATION

- 65 -
FIG. 54.
DIAPHRAGM IMPEDANCE AT LOW FREQUENCIES

frequency (Hz)
FIG. 55

DIAPHRAGM IMPEDANCE AT HIGH FREQUENCIES

impedance (arb. units)

frequency (Hz)

600
800
900

397 K
296 K
impedance (arb. units)

200 Hz

900 Hz

300 Hz

500 Hz

temperature (K)

273 293 333 373 413 453 493

VARIATION OF IMPEDANCE WITH TEMPERATURE
To ensure that the temperature variation of the loudspeaker impedance was not due to any design fault a further investigation was made of:

(a) The discontinuity occurring at about 150 Hz,

(b) The decrease in the resonant frequency (≈ 450 Hz) of the loudspeaker with increasing temperature.

(a) This was thought to be due to some resonance occurring behind the diaphragm. The following approximate calculation bears this out.

If we assume the wavelength \( \lambda \) associated with the resonance is constant, depending only on a dimension of the enclosure behind the diaphragm then \( f_{\text{resonance}} \propto V_T \) where \( V_T \) is the sound velocity at temperature \( T \). From Fig. 5.4 at the temperatures of 296 K and 497 K the discontinuities occur at approximately 130 Hz and 170 Hz respectively.

Assuming \( V_T \sqrt{T} \), then:

\[
\frac{f_{\text{resonance}}}{V_T} = \sqrt{T}
\]

Therefore \( \frac{130}{170} \) should be approximately equal to \( \sqrt{\frac{296}{497}} \). These two ratios give values of 0.765 and 0.772 which shows good agreement.

(b) For the case of the temperature dependence of the resonant frequency of the loudspeaker we consider an equation given by Rayleigh for the resonant frequency of a circular disc clamped at its perimeter. This applies, to a first approximation, to the present system. The equation given by Rayleigh (1877) is:-

\[
F_o = \frac{2.96h}{2\pi \rho} \sqrt{\frac{E}{\rho (1-\sigma^2)}}
\]

......(5.1)
where \( F_0 \) is the resonant frequency
\( r' \) is the radius of the disc
\( h \) is the thickness of the disc
\( E \) is Young's Modulus
\( \sigma \) is Poisson's ratio = \( \frac{E}{2n} - 1 \)
\( \rho \) is the density
\( n \) is the rigidity

Therefore equation (5.1) can be written

\[
F_0 \alpha \sqrt{\frac{E}{(1-\sigma^2)}} \quad \text{.........}(5.2)
\]

or
\[
F_0 \alpha \sqrt{\frac{E}{1 - (\frac{E}{2n} - 1)^2}} \quad \text{.........}(5.3)
\]

If we consider the temperature dependence of equation (5.3) assuming \( \rho, r \) and \( h \) are approximately constant in the range we consider then:

\[
F_0(t) \alpha \sqrt{\frac{2n_0 (1-\alpha_n t)}{(4\mu_0 - E_0) - (\alpha_E E_0 - 4\mu_0 n)t}} \quad \text{.........}(5.4)
\]

where \( E(t) = E_0(1 - \alpha_E t) \)
\( \mu_t = \mu_0(1 - \alpha_n t) \) to a first approximation

Now for duralumin: (cf. Kaye and Laby 1966)
\( n_0 = 2.6 \times 10^{10} \text{ N.m}^{-2} \)
\( E_0 = 7 \times 10^{10} \text{ N.m}^{-2} \)
\( \alpha_n = 5.2 \times 10^{-4} \text{ °C}^{-1} \)
\( \alpha_E = 48 \times 10^{-4} \text{ °C}^{-1} \)

Now \( 4\mu_0 - E_0 \approx 10^{10} \) and \( \alpha_E E_0 - 4\mu_0 \alpha_n \approx 10^6 \)

\( \Rightarrow \) In the temperature range considered

\[
(4\mu_0 - E_0) \geq (\alpha_E E_0 - 4\mu_0 \alpha_n)t
\]
therefore, to a first approximation

\[
2\no(1 - \alpha_n t) \\
\frac{4\no - E_0}{4\no - E_0}
\]

i.e. \( \frac{F_o(t)}{a} = 1 - \alpha_n t \) \hspace{1cm} (5.5)

or \( F_o(t) = A(1 - \alpha_n t) \) \hspace{1cm} (5.6)

At eleven different temperatures in the range 25°C to 200°C the loudspeaker resonant frequency was determined, being taken as the frequency at which the minimum current was required to vibrate the diaphragm at the first critical amplitude. This point was found to within \( \pm 0.5 \)Hz. A far greater accuracy was possible but not really necessary for the present measurements. The results are shown in Fig. 5.7 where the points lie reasonably well on a straight line as predicted by equation (5.6). The experimental line has an intercept \(- 468 \)Hz and slope \( 0.267 \) Hz °C\(^{-1}\)

From equation (5.6) this gives:

\[
\begin{align*}
A &= 468 \text{ Hz} \\
A\alpha_n &= 0.267 \text{ Hz °C}^{-1}
\end{align*}
\]

\[\therefore \alpha_n = \frac{0.267}{468} \approx 5.71 \times 10^{-4} \text{ °C}^{-1}\]

which shows fair agreement to the value of \( 5.2 \times 10^{-4} \) °C\(^{-1}\) taken from tables. From these two checks it was concluded that the diaphragm was vibrating correctly and was satisfactory for use in the temperature range 25°C - 250°C.

**The laser system**

The optical system previously described proved successful for the preliminary measurements of the loudspeaker characteristics. However, in its working position in the furnace the
VARIATION OF THE RESONANT FREQUENCY OF THE LOUDSPEAKER WITH TEMPERATURE
The loudspeaker was two feet from the furnace entrance. Using the mercury light source the intensity of the ring pattern was so reduced as to make very accurate measurements impossible. It was therefore necessary to employ a different optical arrangement. This consisted of a low powered gas laser which, as well as giving a sufficiently intense beam to allow for the increased distance between the loudspeaker and source, enabled the rings to be projected onto a screen.

The laser system is illustrated in Fig. 5.8. The laser was supplied by Scientific and Cook Electronics Ltd. and was a helium neon laser of one milliwatt output with a wavelength of 6328 Å. It produced a very parallel beam of 2.5 mm. diameter with a divergence of approximately 0.8 milliradian. The beam was too narrow for the present work so two diverging lenses (a) and (b) were used to produce a slightly broader beam. The beam was then reflected by a face silvered totally reflecting mirror (c) into the loudspeaker assembly. The reflected beam from the loudspeaker was similarly reflected by a surface reflecting mirror (d) on the far wall of the dark room, onto a screen. The laser together with the lenses (a) and (b) and the mirror (c) were mounted on adjustable riders running on the optical bench L. This made the system very flexible and it was possible to scan the complete fringe pattern and examine any particular section in more detail. A brass tube, whose inner surface was painted with high temperature matt black paint to avoid reflection, was fixed in the furnace as shown in Fig. 5.8. The letters D, S, A, R and O represent the digital ammeter, oscilloscope, amplifier resistance box and oscillator, respectively. The circuit diagram of the loudspeaker circuit is shown in Fig. 5.9. The
BLOCK DIAGRAM OF LOUDSPEAKER CIRCUIT
signal was obtained from an Adret model 201 frequency generator which could give output frequencies at 0.1 Hz increments in the range 0.1 Hz to 1 MHz. The quoted frequency stability was 2 parts in 10^9 after seventy-two hours of operation. The signal was then amplified by an audio power amplifier, and a Racal universal counter timer used to check the frequency reading. In practice the reliability of the oscillator was such that only occasional spot checks were made. The amplified signal was fed through a non-inductive resistance box and a multi-range Solartron digital meter to the loudspeaker coil. The A.C. ammeter ranges were 0-2 mA, 0-20 mA and 0-200 mA. An oscilloscope was incorporated to check that no distortion of the signal occurred. As is shown in Fig. 5,8 the apparatus was grouped about the dark room so that it could be reached while sitting in a suitable position to view the fringes. When taking readings the procedure was firstly to spend about ten minutes in the dark room to accustom oneself to the darkness. During this time adjustments could be made to the fringe pattern to obtain rings of maximum contrast. Alignment of the various optical components was fairly simple; scattering of the light beam from cigarette smoke enabled the path to be seen clearly, which greatly increased the speed at which the system could be adjusted. Once this had been done, a suitable frequency was selected on the oscillator and the current through the coil adjusted by means of the series resistance for course control and the output control on the oscillator for fine adjustment. The current at the critical amplitude was measured on the digital ammeter; the values of current so measured were reproducible to within 1%. Similar readings
were taken at 0.1 Hz intervals about the resonant frequency of that particular mode of the tube, generally about thirty readings in all. This method of measuring the driving point impedance of the diaphragm proved very successful and was used for all the subsequent results.
The Control and Measurement of Temperature

In work of this type it is very important to control the temperature of the gas mixture to a high degree of accuracy. Any temperature gradient is likely to cause a non-uniform distribution of water vapour in the mixture, and this is important because of the very critical dependence of the relaxation time on the water vapour content. Since measurements of each impedance against frequency curve took about thirty minutes, it was also important that no drift in the temperature occurred during this period which would distort the curve obtained. Because of these requirements it was necessary to construct a furnace which would produce a stable and uniform temperature over a volume large enough to contain the resonance tube assembly.

The furnace

The construction of the furnace is shown in Figs. 6.1 and 6.2. Two tubes 335 cm. long, 48 cm. and 38 cm. diameter of 0.159 cm. thick mild steel, were sealed concentrically by two 0.635 cm. thick mild steel plates at each end. The 5 cm. annular space between them could be evacuated, and formed the vacuum jacket of the furnace. An additional seven square plates were cut and fitted over the outer tube to which they were brazed. These acted as supports to prevent possible collapse of the outer tube during evacuation. Inside the vacuum jacket another 335 cm. tube of 35.6 cm. diameter was fitted. It was supported in position by two 1.3 cm. thick mild steel rings fitted around the ends. On to the outer surface of this tube was wound the furnace heating elements. Two thin slabs of P.T.F.E. were attached at either end of
the inner tube, on to the steel rings, so that it could be easily slid into position inside the vacuum jacket. The resonance tube assembly was mounted on to a specially constructed trolley (see Fig. 6.2) which ran along the inner surface of the tube. In its working position the resonance tube was overlapped by approximately 46 cm. of the furnace at both ends. This allowed ample space in which to compensate for the maximum heat losses at the furnace ends. The outside of the vacuum jacket was filled with fibre-glass insulation and the complete furnace then sealed in an asbestos box. Both ends of the furnace were also packed with fibre-glass and closed with removable 5 cm. thick asbestos plugs. These had suitable holes to take the various inlet and outlet tubes to the resonance tube. A brass tube on a dexian frame was fixed in front of the loudspeaker assembly inside the furnace which allowed the laser beam to pass unrestricted to the loudspeaker.

The dark room, built at one end of the laboratory, enclosed about 1½ feet of the furnace at the loudspeaker end. The entire furnace system was mounted onto the top of a movable 'speed frame' trolley which also accommodated all the ancillary equipment.

The vacuum jacket pumping system (see Fig. 7.1) was positioned directly below the furnace, and after treating the welded joints with lacquer the system could be evacuated to a pressure of a few microns.

The heating elements

The heating elements of the furnace were wound on to the outside of the inner furnace cylinder. Two types of heating systems were used. One system was manually controlled and used to bring the furnace close to its working temperature.
The second system was automatically controlled, and used to stabilise the temperature and produce a uniform temperature over the length of the resonance tube.

(a) **Manually controlled heaters**

These were used such that the working temperature of the furnace could be obtained quickly. They were controlled by variacs and ran directly from the mains supply. They were wound directly on top of the temperature controllers separated by a layer of fibre-glass matting. Three separate heaters were used.

(i) **End heaters**

These were wound circumferentially to cover a length of one foot of the furnace tube at each end. They were made of 75 ft. of 24 s.w.g. eureka wire giving a maximum power output at each end of 1.5 kw.

(ii) **Central heater**

This was wound in a similar manner to cover the central 9 ft. of the furnace tube. It was constructed of 130 ft. of 20 s.w.g. eureka wire giving a maximum power output of 2 kw.

The three heaters thus had a maximum total power output of 5 kw.

(b) **Temperature controllers**

The design of the controllers was a modification of that first reported by Barnes (1951) where the heating elements also act as the sensing elements for the control. Three identical units were used, each covering one third of the furnace tube area. The principle of the control is illustrated in Fig. 6.3(a). \( R_1 \) and \( R_2 \) are the resistances of the heating elements and the bridge is balanced when:-
If $X_3/X_4$ remains constant and equal to $A$ (say) and $R_1$ and $R_2$ have different temperature coefficients of resistance, then the balance point will be determined by the equation

$$\frac{R_{01}(1 + \alpha_1 t_1)}{R_{02}(1 + \alpha_2 t_2)} = A \quad \ldots \ldots \ldots \ldots \ldots \ldots (6.3)$$

where $R_0$ signifies the resistance value at $0^\circ C$, $\alpha$ the temperature coefficient of resistance, and $t$ the temperature. The balance of the bridge is thus a function of $t_1$ and $t_2$. If either $\alpha_2 = 0$ or $t_1 = t_2$ then

$$(\alpha_2 = 0) \quad \frac{R_{10}(1 + \alpha_1 t_1)}{R_{02}} = A \quad \ldots \ldots \ldots \ldots \ldots \ldots (6.4)$$

$$(t_1 = t_2) \quad \frac{R_{01}(1 + \alpha_1 t_1)}{R_{02}(1 + \alpha_2 t_1)} = A \quad \ldots \ldots \ldots \ldots \ldots \ldots (6.5)$$

in each case the equation is satisfied at one particular temperature only. The bridge system thus has a unique balance temperature $t_1$, unaffected by external conditions.

**Construction**

Platinum and nickel-chrome wires were used for the resistance arms 1 and 2 respectively, as they are both stable at high temperatures and have widely different temperature coefficients of resistance, giving the bridge high sensitivity. The temperature coefficient of the nickel-chrome ($\alpha_2$) although
(a) Nickel-chrome furnace tube

(b) 103 Ω

Nickle-chrome  Platinum

(c) furnace tube

--- platinum wire

--- nickle-chrom wire
small, is not zero, so that equation (6.4) is not quite satisfied. However, by having the two lengths of wire side by side, their separation is made small and therefore their temperatures are nearly equal so that equation (6.5) is almost satisfied. The individual wires were insulated with thin flexible high temperature sleeving and laid lengthwise along the outer surface of the furnace tube, as shown in Fig. 6.3(c). This meant that the temperature of the metal surface of the cylinder was very near to the controlled temperature of the wires, keeping the thermal insulation between the tube and the wires to a minimum. It also ensured mechanical support for the windings and gave two resistance arms of low inductance. In order to have sufficient length of windings to cover the surface of the furnace tube, and also to ensure a sufficient power output, the two bridge arms were constructed as illustrated in Fig. 6.3(b). The arm R₁ was constructed with two parallel nickel-chrome elements each 26 s.w.g. and 15.3 metres long, resistance of each arm being 103 ohms. The arm R₂ was made of 7 metres of 33 s.w.g. platinum wire having a total resistance of 15.2 Ω. As there was approximately four times the length of nickel-chrome wire as platinum, the procedure was firstly to fix the platinum wire in position around the furnace tube and then space the nickel-chrome wire around this, as illustrated in Fig. 6.3(c). Once the three controllers had been fixed in position on the tube, a layer of fibre-glass matting was bound over them which, as well as giving added insulation between the controller elements and the manual heaters, helped to give support to the windings. The manual heating elements were then wound onto the matting as described previously. The entire system was then bound
with asbestos tape and the furnace tube slid into the vacuum jacket of the furnace.

The circuit

The control circuit has two functions

(i) to amplify any out of balance signal across the detector

(ii) to sense whether the out of balance signal is due to a higher or lower temperature in the windings, relative to the set temperature, and adjust the power supplied to the heater accordingly.

Fig. 6.4(a) and Fig. 6.5 show the complete circuit in which the dummy ratio arms of the bridge were made of a sufficiently low enough impedance to enable the use of a small mains transformer to be used as the detector of the out of balance signal from the bridge. A step down transformer configuration was used to supply current drive to a negative feedback amplifier comprising transistors T5 to T7 (see Fig. 6.5).

The output of the detector amplifier is then fed into a phase sensitive rectifier and compared with a reference signal derived also from the mains supply but shifted in phase by 90 degrees. The phase sensitive rectifier is thus able to detect the phase of the out of balance signal from the bridge circuit.

The output of the phase sensitive rectifier is fed into an integrating circuit in order to smooth the net positive or negative output signal into a steady d.c. level which is used to operate a relay. The contacts of the relay, when 'made', short out a current limiting resistor in series with the supply to the heating element and enable full power to be applied to the heaters.
OSCILLATION OF WINDING TEMPERATURE

TEMP. OF WINDING

TIME

ON
OFF

RELAY CONTACTS

MAINS VOLTAGE HIGH AND SMALL LOSS OF HEAT

RELAY CONTACTS

MAINS VOLTAGE LOW AND LARGE LOSS OF HEAT
When the heaters have reached the set temperature and slightly overshot it, the out of balance signal reverses its phase causing the relay contacts to open. A lower power is then supplied to the heaters through the current limiting resistor, resulting in a gradual decrease of temperature until the hysteresis of the control circuit is overcome and the relay contacts close again. Thus the set temperature is attained by time averaging the oscillations of the heater winding (see Fig. 6.4(b)). The limits of the temperature oscillations are such that the thermal insulation provided by the fibre-glass sleeving is sufficient to damp out the temperature fluctuations. Overshooting of the temperature limits is unlikely to be appreciable because of the rapid response of the whole system to changes in both temperature and power input to mains voltage variations. The temperature against time curve has an approximately triangular shape as shown in Fig. 6.4(b); a change in either the supply voltage or in the rate of loss of heat from the furnace merely changes the rates of rise and fall of the curve, leading to a change in the on/off ratio of the relay. Thus the mean power input to the heaters remains equal to the rate of loss of heat at the desired temperature.

**Temperature measurement**

Two different systems were used to indicate the temperature of the gas enclosed in the resonance tube.

The first system consisted of six chromel-alumel thermocouples equally spaced along the length of the resonance tube surface. Their outputs were displayed on a six channel chart recorder giving a continuous record of the temperature distribution along the tube. The six thermocouples were firstly
calibrated against each other in the temperature range 25 - 300°C. A maximum variation of 0.3% between individual couples was found. This was an acceptable error since the thermocouples were not used to measure the absolute temperature of the system. This was measured by three platinum resistance thermometers fixed at each end and the centre of the resonance tube. The thermometers were supplied by the Rosemount Engineering Company, calibrated at the ice, steam and zinc points. The response of the thermometer elements over the temperature range -189°C to 630°C is given by the Callendar-Van Dusen equation:

$$\frac{R_t}{R_0} = 1 + \alpha \left[ t - \delta \left( \frac{t}{100} - 1 \right) \frac{t}{100} - \beta \left( \frac{t}{100} - 1 \right)^3 \right]$$

......(6.6)

where $R_t$ is the element resistance at $t^\circ C$

$R_0$ is the element resistance at 0°C

$\alpha$, $\beta$ and $\delta$ are characteristic constants for each sensor.

In October 1968 a revised form of the International practical temperature scale was adopted by the international committee of weights and measures. The new scale, known as I.P.T.S.-68 to distinguish it from the previous I.P.T.S.-48, has been in use at the National Physical Laboratory since January 1967.

The changes in the range of temperatures covered by resistance thermometry, involve a considerably more complicated resistance temperature relationship than the Callendar-Van Dusen equations of the I.P.T.S.-48 scale. Temperatures measured in the present work were on the I.P.T.S.-48 scale and a small correction from tables supplied by the manufacturers was used to convert them to the I.P.T.S.-68 scale.
As an example, 200.000°C on the '48 scale becomes 200.043°C on the '68 scale. The calibration of the three thermometers is given in Table 6.1. Each thermometer was sealed in a tubular ceramic casing two inches long and 0.125 in. in diameter. Four platinum lead out wires enabled both current and potential measurements to be made. This is illustrated in Fig. 6.6. Gold leads were spot welded on to the platinum wires, which then connected into the resistance measuring system. The platinum thermometers were attached to the tube by means of three specially constructed cylindrical brass holders. Each holder was 2\frac{1}{2} in. long and \frac{3}{4} in. in diameter. One side was curved to fit flush with the resonance tube surface and a central hole made in each contained the complete length of the thermometer. They are illustrated in Fig. 6.6. The holders provided good mechanical support for the fragile thermometers and ensured good thermal contact with the surface of the resonance tube. A low contact resistance switch supplied by Pye Unicam Ltd. was used to enable easy switching between each element and the measuring system. The switch had a contact resistance variation of less than 20 \mu \Omega and a drift of less than \pm 50 \mu \Omega per 10^8 operations.

**Measurement of the element resistance**

The resistance values of the platinum elements were measured on a Smith's difference bridge supplied by the Cambridge Instrument Company. The bridge, designed for the accurate measurement of temperature, is based on the second method described by Smith (1913). The thermometer resistance is measured in a Wheatstone bridge in which three arms are fixed, and the fourth contains the thermometer in series with a continuously variable precision resistance. An increase
<table>
<thead>
<tr>
<th>Thermometer</th>
<th>Resistance at ice point (Ω)</th>
<th>Resistance at steam point (Ω)</th>
<th>Resistance at zinc point (Ω)</th>
<th>α</th>
<th>δ</th>
<th>β</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>25.4812</td>
<td>35.4809</td>
<td>65.4303</td>
<td>0.0039243</td>
<td>1.492</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>25.4785</td>
<td>35.4711</td>
<td>65.3972</td>
<td>0.0039270</td>
<td>1.494</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>25.4998</td>
<td>35.5088</td>
<td>65.4848</td>
<td>0.0039251</td>
<td>1.493</td>
<td>0</td>
</tr>
</tbody>
</table>
The Platinum Thermometers

Front sectional view

End view

The Platinum Thermometer Holders
in thermometer resistance is balanced by a corresponding decrease in the variable resistor. A switch is provided for short circuiting the thermometer on the bridge so that the bridge zero may be checked at any time. A commutator is provided which interchanges the ratios and alters the thermometer connections so that by taking the mean of the two measurements the resistance of the thermometer leads and any departure from equality of the ratio arms is eliminated from measurement. To avoid stray variations due to contacts and thermal e.m.fs etc. the design of the bridge is such that:-

(i) No slide wire is used, but a continuously variable two terminal resistance arm designed to avoid contact variations and thermal e.m.fs.

(ii) The galvanometer circuit is always closed so that any thermal e.m.f. associated with this circuit appears only as a shift in its mechanical zero.

(iii) The current in the thermometer is the same at all temperatures, since the bridge arms are always restored to the same resistance at balance.

(iv) The bridge was oil filled to ensure a constant uniform temperature of the network. Inlet and outlet nipples to the oil tank allowed for oil circulation and oil temperature control.

The complete measuring system used is illustrated in Fig. 6.7. The entire assembly was mounted on a dexion trolley. Oil from the tank was pumped to the oil bath of the bridge and gravity fed from the overflow back to the tank. As the furnace was likely to cause temperature fluctuations in the laboratory the oil temperature was thermostatically controlled.
FIG. 6.7.

Diagram showing a system with a "smith's bridge", an "oil bath", a "stirrer", a "motor", an "oil inlet", a "one way valve", a "metal disc", an "on off switch", a "thermostat control unit", an "oil tank", a "pump", a "heater", and a "cork float". The diagram is labeled "oil out" and "supply".
a few degrees higher than ambient. The temperature of the oil bath as measured on a mercury in glass thermometer was never seen to change by more than an estimated 0.2°C during operation of the thermostat system. A cut-off switch for the pump controlled by the metal disc and float assembly was used to prevent the level in the tank falling below a certain limit. A one-way valve in the pumping line prevented the oil running back from the oil bath and causing the tank to overflow when the system was not in use. In practice when the system was running the pumping line was restricted sufficiently to keep the levels in the bath and tank approximately the same.

The bridge galvanometer was separately mounted to avoid vibrations. The choice of galvanometer was such that it had approximately critical damping when connected to the bridge circuit. In practice it was found that resistance values could be accurately measured to 0.001 Ω corresponding to approximately 0.01 K.

Because of the large thermal inertia the tube system was very slow to respond to temperature changes and the measured shift during a set of frequency against impedance measurements was always better than 0.03 K. By careful manipulation of the furnace heaters the temperature distribution along the tube could be controlled to within ± 0.2 K.
Chapter 7

The Gas Handling System

In work of the present type great care is necessary in the mixture preparation to eliminate all possibility of active impurities contaminating the mixture. To achieve these requirements the apparatus was designed so that it could be evacuated to a low pressure, and flushed with a pure dry sample of the gas to be used.

Because of the technique used to determine the percentage of water vapour, the system also had to maintain a low pressure for a considerable period.

The resonance tube pumping system is shown in Fig. 7.1. It was constructed from 1 in. copper tubing, all the connections being made with commercial couplings. The inlet tubes to the loudspeaker and reflector were $\frac{1}{4}$ in. stainless steel. Two flexible couplings (a) and (b) were used to allow easy mating between the 1 in. and $\frac{1}{4}$ in. systems and to allow for changes in length as the temperature was increased. Two additional systems illustrated in Fig. 7.2 were incorporated in the gas handling system and connected into the main 1 in. system at the points indicated in the Figures.

The pumping system consisted of an Edwards two stage rotary pump backing an oil diffusion pump. The pressure of the system during evacuation was measured on the dial gauges at the higher pressures and the pirani and penning gauges at the lower pressures. It was important that no pressure difference developed across the diaphragm during evacuation, and hence a careful observation was made of the two dial gauges at either ends of the resonance tube. A more sensitive
THE VACUUM SYSTEMS

Fig. 71.

- 0-760 dial gauge
- Oil manometer
- Vacuum gauge heads
- Resonance tube pumping system
- Furnace pumping system
- MERCURY bubble

To gas purification system

Valves (0)
check was to observe the displayed ring pattern, any pressure
difference being shown up by a movement of the rings across
the field of view. This usually occurred when the pumping
speed was too fast, gas being taken from either side of the
diaphragm at an unequal rate. By slowing the pumping speed
the pressure differential could easily be corrected. When
the systems were being filled with oxygen, the latter was
firstly passed through the gas purification system shown in
Fig. 7.2. Any traces of carbon dioxide were removed by the
passage over a commercial absorbant trade name 'Sofnolite'.
Drying the gas was achieved by passing it over four two-feet
lengths of phosphorous pentoxide. Two cold traps C₁ and
C₂, cooled by solid carbon dioxide-acetone mixtures condensed
any vapour present. The gas then entered the 1 in. system
at C. The gas purification system was constructed of pyrex
glass with ground glass connections and some small lengths
of high quality P.V.C. tubing to provide flexibility. The
'Sofnolite' and phosphorous pentoxide were contained in
pyrex boats seated inside the cylindrical tubes. A dial
gauge and pirani gauge measured the pressure in this system.

A second system also shown in Fig. 7.2 was used for the
accurate measurement of the gas pressure in the tube. A
mercury manometer measured the difference between the final
gas pressure and atmospheric pressure. A closed arm oil
manometer was used to measure the water vapour pressure. The
oven was incorporated so that the oxygen could be preheated
when necessary before entering the tube. The water holder,
which is shown in more detail in Fig. 7.3, enabled water to
be evaporated directly into the resonance tube via valves
5, 6 and 7. The holder consisted of 10 cm. of 2 mm. diameter
capillary tube closed by stopcocks A and B. Above A the holder connected directly to the pressure measuring system by a conical ground glass joint. Before filling the holder, the capillary tube was initially evacuated through stopcock A. A was then closed and distilled water, which had previously been boiled to remove any entrained gases, was added to the space above A. Stopcock A was then slowly opened and a column of water was drawn down the capillary tube to B. A was then closed and any remaining water left above A carefully removed. When the holder was fixed in position any volume of water could be drawn out of the capillary, by manipulation of the stopcock A, and evaporated into the system. The water was drawn out in stages as too rapid an evaporation caused the water to freeze. Once the holder had been filled it usually contained sufficient water for a complete set of measurements at one particular temperature.

The method of preparing a specific gas mixture was firstly to evacuate all the systems, then fill and flush with dry oxygen for several hours. The systems were then evacuated again, isolated from the pumps and water evaporated directly into the resonance tube. The tube was then filled to the final working pressure with dry oxygen. Before each set of new runs the system was evacuated for about twenty-four hours at a temperature about ten to fifteen degrees higher than the required working temperature. This kept the outgassing rate at the working temperature to a minimum. A more detailed account of the use of the gas systems is given in the next Chapter.
Chapter 8

Measurements in Pure Oxygen

At each temperature preliminary measurements were made with pure dry oxygen in order to establish that the apparatus was operating correctly and also to determine the component of the absorption due to the tube.

In the frequency range used losses due to viscous and thermal conduction effects in the body of the gas, and to relaxation effects, can be neglected. The major source of attenuation is the result of the effects of viscosity and heat conductivity in the interaction of the plane sound waves with the walls of the tube. The generally accepted theory accounting for these losses is that of Helmholtz and Kirchhoff which gives for the sound absorption coefficient:

$$\alpha_w = \left[ \frac{\pi}{13.6 \times 981.3 \ r^2 \ y} \right]^{\frac{1}{2}} \left[ \frac{\eta}{\nu} + (\gamma - 1) \left( \frac{K}{C_p} \right) \right] \left( \frac{\nu}{\rho} \right)^{\frac{1}{2}}$$

\[\ldots\ldots(8.1)\]

where $\alpha_w$ is the attenuation coefficient per cm. due to tube walls

$f$ is the frequency of sound in Hz

$p$ is the gas pressure in cm. Hg

$r$ is the tube radius in cm.

$\gamma$ is the ratio of the principal specific heats of the gas

$\eta$ is the viscosity of the gas in poise

$K$ is the thermal conductivity of the gas in cal. cm. $^{-1}$ K$^{-1}$

$C_p$ is the specific heat at constant pressure in Joules K$^{-1}$
In addition to this, attenuation occurs as the wave is reflected, and to compare its value with $a_w$, a mean value per cm. of the tube can be calculated. Using an approximation given by Parker (1961) we obtain:

$$
\alpha_e = \frac{2}{l} \left[ \frac{\pi}{13.6 \times 981.3 \gamma} \right]^{\frac{1}{2}} \left[ \frac{K}{(\gamma - 1)} \frac{(f_p)^{\frac{3}{2}}}{(C_p)} \right]
$$

\[
\text{(8.2)}
\]

where $\alpha_e$ is the attenuation on reflection per cm. of tube.

$l$ is the length of the tube in cm.

Combining equations 8.1 + 8.2 we obtain an equation of the form

$$
a_{\text{tube}} = \chi \left( \frac{f_p}{C_p} \right)^{\frac{3}{2}}
$$

\[
\text{(8.3)}
\]

where $\chi$ is a constant for a particular gas and tube and $a_t$ is the total attenuation due to the tube. Hence a plot of the total attenuation coefficient $a_t$ against $\left( \frac{f_p}{C_p} \right)^{\frac{3}{2}}$ should give a straight line through the origin with a slope determined from the above equations. Graphs of $a_t$ against $\left( \frac{f_p}{C_p} \right)^{\frac{3}{2}}$ are shown in Figs. 8.1 to 8.5, and the corresponding slopes quoted in Table 8.1, column 8.

The oxygen used was supplied by Air Products Limited who supplied the following analysis:

- Oxygen 99.7% per volume
- Argon 0.3% per volume
- Nitrogen 0.05% per volume
- Carbon dioxide < 0.003% per volume
- Carbon monoxide < 0.002% per volume
- Carbonacious Compounds .008% per volume

Nitrogen and Argon were the only gases present in any significant amounts. Holmes, Smith and Tempest (1963)
FIG. 8.1.

\( a \) AGAINST \( \left( \frac{f_p}{P} \right)^{\frac{1}{2}} \) FOR PURE DRY \( O_2 \) AT 298 K

\( a \times 10^4 \) (cm\(^{-1}\))

\( (f_p)^{\frac{1}{2}} \) \( (Hz)^{\frac{1}{2}} \) \( (\text{cmHg})^{\frac{1}{2}} \)

- \( P = 68.1 \) cm
- \( P = 75.2 \) cm
Fig. 8.2.

a AGAINST \((\frac{f}{p})^{\frac{1}{2}}\) FOR PURE DRY \(O_2\) AT 319 K

\[ P = 77.96 \text{ cm Hg} \]

\[ 2 \left( \frac{f}{p} \right)^{\frac{1}{2}} \left( \text{cm Hg} \right) \]

\[ a \times 10^{-6} \left( \text{cm} \right)^4 \]

-106-
$\alpha$ AGAINST $(f/p)^{\frac{1}{2}}$ FOR PURE DRY $O_2$ AT 342 K

$$P = 75.0 \text{ cm Hg}$$
$a$ AGAINST $(f_p/HZ)^{\frac{3}{2}}$ FOR PURE DRY O$_2$, AT 366 K AND 386 K.

$366 \text{ K}$  $P = 72.10 \text{ cm Hg}$

$386 \text{ K}$  $P = 74.57 \text{ cm Hg}$
a Against (f/p)^{1/2} for pure dry O_2 at 408 K
<table>
<thead>
<tr>
<th>Total Gas Pressure (cm Hg)</th>
<th>Tube Radius (cm)</th>
<th>Temperature (T) (K)</th>
<th>Method 1</th>
<th>Method 2</th>
<th>√T (K) $rac{1}{2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Vt $f_0$ $^{1/2}$ m sec$^{-1}$ Hz$^{1/2}$</td>
<td>2r(π)$^{1/2}$ sec</td>
<td>β (at 1 atm) cm sec$^{-1}$</td>
<td>a$_{tube}$</td>
</tr>
<tr>
<td>68.1</td>
<td>5.710</td>
<td>11.54</td>
<td>6.172</td>
<td>0.674</td>
<td>328.1</td>
</tr>
<tr>
<td>77.96</td>
<td>5.713</td>
<td>15.33</td>
<td>5.953</td>
<td>0.925</td>
<td>340.3</td>
</tr>
<tr>
<td>75.0</td>
<td>5.716</td>
<td>15.52</td>
<td>5.755</td>
<td>0.887</td>
<td>352.2</td>
</tr>
<tr>
<td>72.10</td>
<td>5.719</td>
<td>16.14</td>
<td>5.557</td>
<td>0.874</td>
<td>364.9</td>
</tr>
<tr>
<td>74.57</td>
<td>5.721</td>
<td>19.96</td>
<td>5.406</td>
<td>1.069</td>
<td>375.3</td>
</tr>
<tr>
<td>76.26</td>
<td>5.723</td>
<td>20.76</td>
<td>5.247</td>
<td>1.091</td>
<td>386.8</td>
</tr>
</tbody>
</table>
investigated the possible effects of argon and nitrogen impurities on the relaxation time of oxygen. Measurements on samples of oxygen with 10% argon and 0.5% nitrogen gave such small effects that for the much smaller amounts present in the oxygen used here the effects will be completely negligible.

Any traces of carbon dioxide and water vapour were removed by the purification system.

It was found in practice that while the measured absorption in the non-relaxing gas had the \( \frac{f_p}{f} \) dependence predicted by equation (8.3) the values of \( \chi \) were always between 30% to 50% higher than the theoretical value, the difference increasing with increasing temperature. This is discussed in more detail later.

**Velocity measurements in pure oxygen**

The velocity of sound in the gas in the tube was determined at each mode of the tube. The tube velocity \( V_t \) was plotted against \( \left( \frac{f}{f_0} \right)^\frac{3}{2} \) in accordance with equation (1.2), Chapter 1, i.e.

\[
V_t = V_0 \frac{\beta}{(4\pi f^2 f_0)^{\frac{3}{2}}} \quad \cdots \cdots \cdots (8.4)
\]

which should give a straight line with intercept \( V_0 \), where \( V_0 \) is the free gas velocity.

These results are shown in Figs. 8.6 to 8.8. A least squares best fit to the measured points was used to calculate \( V_0 \) and the slope of the line at each temperature. These values are shown in Table 8.1, columns 7 and 4. \( V_0 \) is plotted as a function of temperature in Fig. 8.9. Considering the results of other workers, i.e. Abbey and Barlow (1948)
FIG. 8.6,

\[ T = 296.46 \text{ K} \]
\[ V_0 = 328.07 \text{ m/sec}^{-1} \]
\[ \text{slope} = 11.54 \text{ m/sec(Hz)}^{-\frac{1}{2}} \]

\[ T = 319.08 \text{ K} \]
\[ V = 340.30 \text{ m/sec}^{-1} \]
\[ \text{slope} = 15.33 \text{ m/sec(Hz)}^{-\frac{1}{2}} \]
GRAPHS OF $V_T$ AGAINST $1/f$ AT 342 AND 360 K

**FIG. 8.7**

$T = 341.62$ K

$V_0 = 352.23$ m/sec

Slope $= 15.52$ m/(sec Hz)$^{1/2}$

$T = 366.43$ K

$V_0 = 364.94$ m/sec

Slope $= 16.14$ m/(sec Hz)$^{1/2}$
GRAPHS OF $V_T$ AGAINST $(1/f)^2$ AT 387 AND 411 K

At $T = 386.60$ K

$V_T = 375.29$ m/sec$^{-1}$

Slope = 19.96 m/sec(Hz)$^{-1/2}$

At $T = 410.52$ K

$V_T = 386.75$ m/sec$^{-1}$

Slope = 20.76 m/sec(Hz)$^{-1/2}$
FIG. 8.9.

GRAPH OF FREE SPACE VELOCITY AGAINST TEMPERATURE

$V_0 \left( \frac{m}{sec} \right)$

TEMPERATURE (K)

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Knotzel and Knotzel (1948), Koehler (1950), Smith and Wintle (1959) find values for $V_0$ at 1 atmosphere and 303K in the range 331.3 to 331.8 m.sec$^{-1}$. The present measured value of $V_0$ at 296.46K is 328.07 m.sec$^{-1}$ which, assuming $V_0 \propto \sqrt{T}$ gives $V_0 = 331.7$ m.sec$^{-1}$ at 303K. An estimated error from the spread of the experimental points gives

$V_0 = (331.7 \pm 0.1)$ m sec$^{-1}$ at 303 K

If $V_0$ is plotted as a function of $T^{\frac{1}{2}}$ over the temperature range used in the present work, a least squares best fit to a straight line gives an equation to the measured points of

$$V_0 = 19.32 \sqrt{T} - 4.75$$

where $V_0$ is in m.sec$^{-1}$

$T$ is in kelvin

with an almost perfect correlation.

The Helmholtz-Kirchhoff coefficient

The Helmholtz-Kirchhoff coefficient $\beta$ was calculated at each temperature from both velocity and attenuation measurements in pure oxygen. From the velocity measurements described earlier $\beta$ was calculated from the slope and intercept of the respective $V_t$ against $(1/T)^{\frac{1}{2}}$ graphs. From the attenuation measurements $\beta$ was calculated by considering equation (1.1), i.e.

$$a_t = \frac{\beta(\pi f)^{\frac{1}{2}}}{V_0 r}$$

Hence from the previous $a_t$ against $(f/p)^{\frac{1}{2}}$ graphs $\beta$ could be calculated directly from the slope, the value of $V_0$ being obtained from the velocity measurements. The values of $\beta$ so obtained were corrected to a pressure of 1 atmosphere, and

- 116 -
the results shown in Table 8.1.

Table 8.2 gives a brief summary of the differences found by other workers between the measured absorption and that predicted by the Helmholtz-Kirchhoff theory. Results available over a range of temperatures are shown together with the present work in Fig. 8.10.

The results of the present work are seen to yield higher values of $\beta$ than the majority of other workers. At 300K $\beta$ experimental is approximately 30% greater than the theoretical value, this difference increasing to 50% at 400K. In practice the tube absorption is calculated by the Helmholtz-Kirchhoff equation and an empirical correction applied to it by using pure gases.

Contrary to the usual assumption that the correction is independent of the gas used, Parker (1961) found discrepancies varying between 6 and 30% which were functions of the molecular weight; the heavy gases such as oxygen and argon showing the larger discrepancies. In 1962 Parker developed a theory to try and account for the excess absorption in terms of adsorption of the gas molecules onto the tube surfaces. The theory however is not easy to test on practical systems since the adsorption process is very dependent on surface conditions, which, particularly with water vapour, is difficult to determine.

The results of Shields and Langeman (1957) are unusual in that they found no discrepancies, but their system did not use standing waves which means that the Helmholtz-Kirchhoff theory is strictly applicable to their work.

Although the present tube absorption was found to be rather larger than average, it had the predicted $(f/p)$
Table 8.2

<table>
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<tr>
<th>Observer</th>
<th>Gases Used</th>
<th>Difference %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Knotzel and Knotzel (1948)</td>
<td>O₂</td>
<td>15</td>
</tr>
<tr>
<td>Harlow (1954)</td>
<td>Air, N₂, Ar</td>
<td>17-23</td>
</tr>
<tr>
<td>Parker (1961)</td>
<td>He, Ne, Ar, H₂; CO₂, N₂, O₂</td>
<td>6-30</td>
</tr>
<tr>
<td>Holmes, Smith &amp; Tempest (1963)</td>
<td>Ar, N₂, O₂</td>
<td>30-40</td>
</tr>
<tr>
<td>Nolan (1967)</td>
<td>Air, N₂, O₂</td>
<td>18-20</td>
</tr>
<tr>
<td>Shields and Langeman (1957)</td>
<td>Ar, N₂, CO₂</td>
<td>0</td>
</tr>
<tr>
<td>Present work</td>
<td>O₂</td>
<td>30</td>
</tr>
</tbody>
</table>

The percentage difference is taken as:

\[ \frac{\beta_{\text{experimental}} - \beta_{\text{theoretical}}}{\beta_{\text{theoretical}}} \times 100 \]
FIG. 8.10. VARIATION OF $\beta$ WITH TEMPERATURE
dependence at each temperature, and also the magnitude of
the relaxation absorption at room temperature agreed well
with other workers suggesting that the apparatus was working
correctly.
Measurements in Mixtures of Oxygen and Water Vapour

Since the early measurements of Knudsen (1933) many workers have measured sound absorption in mixtures of oxygen and water vapour. Although the majority found a quadratic dependence of the frequency of maximum absorption on the water vapour concentration, considerable differences were reported as to its exact behaviour. In more recent years, results of Knotzel and Knotzel (1948) Harris and Tempest (1964) Henderson et al (1965) and Harlow and Nolan (1967) show good agreement. The combined data of Knotzel and Knotzel, Harris and Tempest, and Henderson, Clark and Lintz gives:

\[ f_0 = 7 + 183h + 132h^2 \text{ at } 1 \text{ atm.} \]

and data of Harlow and Nolan obtained from this laboratory gave:

\[ f_0 = 9 + 162h + 144h^2 \text{ at } 1 \text{ atm.} \]

where \( f_0 \) is the frequency of maximum absorption in Hz

\( h \) is the mole fraction of water vapour \( \times 10^3 \)

The aims of the present work were to obtain more data at room temperature and investigate the temperature dependence of the relationship between \( f_0 \) and \( h \). The major difficulty in obtaining reliable results is in the preparation of mixtures of accurately known composition. A small quantity of water vapour shifts the frequency of maximum absorption considerably and at low frequencies only very small concentrations can be used if \( f_0 \) is to lie within the frequency range of the present investigation. These concentrations are correspondingly difficult to measure.

Many of the earlier workers employed wet and dry bulb
thermometers to determine the water content but these are not very accurate for the low concentrations used in the present work. More recent workers such as Harlow and Kitching (1964) and Tuesday and Boudart (1955) determined the water content directly from the mass added. Later work showed that this technique leads to values of \( h \) which are much too high as considerable quantities of the water are adsorbed by the tube walls.

Henderson and his co-workers (1962, 1963, 1965) used a high pressure resonance tube in which they prepared a saturated mixture of oxygen and water vapour at pressures up to 100 atmospheres, making corrections for non-ideal behaviour of the gas and for the dependence of the saturated vapour pressure on the pressure.

Harris and Tempest (1964) circulated the oxygen through a saturator maintained at a constant temperature, so that water vapour was distributed throughout the system. Bypassing the saturator and maintaining the circulation enabled an equilibrium condition to be reached and the humidity was then measured with an electrical hygrometer.

Knotzel and Knotzel (1948) determined the water concentration by measuring the mass of water recovered from a metered volume of gas as the system was emptied.

Harlow and Nolan (1967) using similar apparatus to the present, determined \( h \) by three methods. The first and most successful was to measure the water vapour pressure directly by means of a closed arm oil manometer. This was the technique employed in the present work and is described in detail in Chapter 10. The one limitation to the accuracy of this technique is the possibility of air leakage into the system.
when the water vapour pressure is being determined.

The second technique used by Harlow and Nolan was to measure the mass of water recovered from 90% of the gas by passing it through a system of drying towers containing phosphorous Pentoxide. From the increase in weight of the towers, the known volume of the resonance tube and the change in pressure of the gas, the water vapour content was calculated. Although this technique did not prove very reliable it did give moderate agreement with the results obtained from the first method.

The third technique was to determine the water content directly from the mass of water added. This gave values very much greater than the previous methods suggesting that considerable quantities of water were adsorbed by the tube surfaces.

**Preparation of the mixtures used in the present work**

The technique used to measure the water content was that developed by Harlow and Nolan (1967) where water is evaporated directly into the resonance tube and the pressure measured on a manometer. An account of the practical details of this method is given in Chapter 10. As an additional check a sample of the gas was drawn through an electrical hygrometer, after a set of measurements had been taken. The construction of the water holder (Fig. 7.3) enabled the mass of water added to the system to be evaluated and it was of interest to calculate the water content by this method to see how much surface adsorption occurred. The possible sources of error introduced using the oil manometer technique are now considered.
Contamination of the mixture due to the oil is negligible since the oil used was Apiezon B whose vapour pressure is $10^{-7}$ mm.Hg. at 15°C giving a maximum concentration of about 1 part in $10^9$. Ammonia would have the greatest effect on $f_0$, but 1 part in $10^9$ would only change $f_0$ by about 0.3 Hz (Knudsen and Obert (1936)).

Readings of the water vapour pressure at both ends of the tube were always very similar, suggesting that no pressure gradients existed in the system. The effect on the equilibrium pressure of the water vapour of the addition of oxygen is likely to be negligible since Henderson (1963) quotes that at 100 atmospheres the correction to the saturated vapour pressure is only 8%, and the pressures used in the present work are only 1 atmosphere.

A more serious problem could arise from any water vapour being swept into or out of the system when filling with oxygen. Since the connecting tubes themselves had been flushed with dry oxygen prior to evacuation it was unlikely that they contained any water vapour. Also they constituted less than three per cent of the total volume of the system so that the effect would be very small. When the tube was being filled with oxygen the pressure outside the resonance tube was always maintained at approximately 1 atmosphere, so it was very unlikely that any water vapour was drawn out of the tube.

The most important limitation on the accuracy of the technique was the possibility of air leakage into the system when the water vapour pressure was being determined. Since it took over an hour for the water vapour to reach equilibrium it was very important that the system was vacuum tight.
This requirement caused considerable difficulties. Small leaks were a constant problem throughout the period of the research and considerable time was spent on their detection and elimination. When a leak developed the entire furnace system had to be shut down and the resonance tube assembly removed. Leak rates greater than 50 microns per hour were not tolerated and in practice they were usually much smaller than this. Assuming two hours were required to measure the water vapour pressure and that the leakage into the system was all water vapour, this would introduce a maximum error in h of 6%. Since it was highly unlikely that the leakage into the tube was only water and also in most cases the leak rate was much smaller than 50 microns per hour, the error in h was probably considerably less than 6%.

Outgassing of the system occurred as the temperature was increased and this was eliminated by evacuating the system for twenty-four hours at about 10 to 15 degrees above its working temperature. The measurements of the mixture composition based on a sample of the gas drawn out of the resonance tube were initially in good agreement with the method just described, but unfortunately after only a few measurements were made the hygrometer became contaminated and no longer functioned correctly. However, the results that were obtained served to show the validity of the pressure measuring technique which was used for all subsequent determinations of the water vapour content.

During the first set of runs at room temperature the total mass of water added to the system was recorded. The mass of water adsorbed could be determined by comparing this with the water vapour pressure measured with the oil manometer.
The results are shown in Fig. 9.1 where the mass adsorbed is plotted against the mass added. It can be seen from the figure that approximately 75% of the added water is adsorbed, this percentage decreasing as the system tends towards saturation at the higher added masses of water. It is interesting to compare this with Nolan's work using apparatus similar to the present. Here approximately 60% is adsorbed, (see Fig. 9.1). The extra adsorption of the present system is probably due to the presence of the asbestos gaskets clamping the diaphragm, which will have considerable hygroscopic properties, and the larger surface area of the present tube. Since the two tubes were of the same diameter their surface areas are in the same ratio as their lengths. Nolan used a tube of 168 cm. length and since the present tube was 218 cm. long, the ratio of the surface areas is \( \frac{168}{218} = 0.77 \). The corresponding ratio of the percentages of water absorbed is approximately \( \frac{60}{75} = 0.8 \) which is of the same order as the ratio of surface areas. These results confirm the serious errors introduced by deducing the water vapour pressure directly from the mass of water added.

The results for oxygen-water vapour mixtures

At each temperature six separate mixtures of oxygen and water vapour were prepared with molar fractions of water vapour ranging from \( 0.4 \times 10^{-3} \) to \( 2.4 \times 10^{-3} \). Readings were taken to determine the impedance curve in the neighbourhood of each of about 7 to 8 different modes of the tube. The curves obtained were analysed by computer to yield the sound attenuation and velocity. The measured attenuation included components from the tube as well as from the relaxation processes. To determine the latter the assumption of linear
addition was made: \( a = a_{\text{tube}} + a_r \) \( \ldots \ldots (9.1) \)

where \( a \) is the total measured attenuation

\( a_{\text{tube}} \) is the tube attenuation

\( a_r \) is the attenuation due to relaxation.

The attenuation due to the tube was found from the previous results with pure oxygen. The frequency of maximum absorption \( f_0 \) can be determined by using a method described by Parker (1962). In Chapter 2 it was shown in equation (2.22) that

\[
\frac{a_r}{\pi} = \frac{RC_i f_0^2}{V C_p \omega C_v} \frac{f_0^2 + f^2}{f_0^2 + f^2} \ldots \ldots (9.2)
\]

re-arranging we have

\[
\frac{f^2}{a_r} = \frac{V C_p \omega C_v}{\pi RC_i f_0} \frac{f_0^2 + f^2}{f_0} \ldots \ldots (9.3)
\]

Thus by plotting \( \frac{f^2}{a_r} \) against \( f^2 \) we should obtain a straight line with a slope \( S \) given by:

\[
S = \frac{V C_p \omega C_v}{\pi RC_i} \cdot \frac{1}{f_0} \ldots \ldots (9.4)
\]

If we let \( K = \frac{V C_p \omega C_v}{\pi RC_i} \)

we have \( S = \frac{K}{f_0} \ldots \ldots (9.5) \)

The intercept \( I \) will be given by

\[ I = K f_0 \ldots \ldots (9.6) \]

and thus from equations (9.5) and (9.6)

\[ f_0 = \left( \frac{I}{S} \right)^{\frac{1}{2}} \ldots \ldots (9.7) \]
Thus for the majority of sets of results \( f^{2}_{\lambda} \) was plotted against \( f^{2} \). A least squares best fit to the measured points yielded the slope \( S \) and intercept \( I \) from which \( f_{0} \) was calculated using equation (9.7). These results are shown in Table 9.1.

At the higher molar fractions of water vapour this method became too insensitive as \( f_{0} \) was much higher than the highest frequency used. In such cases the method described below was used to determine \( f_{0} \) from the measured absorption.

It can be seen from equations (9.9) and (9.6) that graphs of \( \frac{1}{S} \) against \( f_{0} \) and \( I \) against \( f_{0} \) should be straight lines with slopes \( \frac{1}{K} \) and \( K \) respectively. These lines were plotted at each temperature to check the consistency of the measurements and also to determine \( K \) which was required in the determination of \( f_{0} \) when the first method became insensitive. Examples of the experimental points obtained are shown in Figs. 9.2 to 9.6 where the \( f^{2}_{\lambda} \) against \( f^{2} \) lines, and \( \frac{1}{S} \) against \( f_{0} \) and \( I \) against \( f_{0} \) lines are shown for the two temperatures 298K and 408K respectively, \( h' \) being the mole fraction of water vapour.

Calculation of \( f_{0} \) for \( f_{0} \gg f \)

When the values of \( h \) were such that \( f_{0} \) was outside the range of measurable frequencies, the first technique used to calculate \( f_{0} \) became too insensitive. Considering equation (9.2) where

\[
ar = \frac{1}{K} \cdot \frac{f_{0}f^{2}}{f_{0}^{2} + f^{2}}
\]
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<th>Temperature (K)</th>
<th>Correlation Coefficient</th>
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<th>Total Tube Pressure (cm. Hg)</th>
<th>Water Vapour Pressure (cm. Hg)</th>
<th>Mole Fraction of Water Vapour ( \times 10^{-3} )</th>
<th>( f_{AX}^2 ) vs ( f^2 ) lines</th>
<th>( f_0 ) at 1 atm.</th>
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- 130 -
RESULTS FOR $\text{U}_2\text{H}_2\text{U}$ MIXTURES AT 298 K

\[ h' = 0.696 \times 10^{-3} \]

\[ h' = 0.974 \times 10^{-3} \]
RESULTS FOR $O_2/H_2O$ MIXTURES AT 298 K

- $h' = 1.44 \times 10^3$
- $h' = 1.65 \times 10^3$
- $h' = 2.52 \times 10^3$
RESULTS FOR $\text{O}_2$-$\text{H}_2\text{O}$ MIXTURES AT 408 K
RESULTS FOR O$_2$-H$_2$O MIXTURES AT 400 K

\[ h' = 0.985 \times 10^3 \]

\[ h' = 1.103 \times 10^3 \]

\[ h' = 1.493 \times 10^3 \]
GRAPHS OF $\frac{1}{S}$ AND $I$ AGAINST $f_0$

$T = 298 \, K$

\[
\frac{1}{S} \times 10^3 \quad I \times 10^{-8} \\
(cm)^{-1} \quad cm(Hz^2)
\]

\[
\begin{array}{c}
0.2 \\
40 \\
0 \\
\end{array}
\]

\[
\begin{array}{c}
0 \\
200 \\
400 \\
600 \\
\end{array}
\]

\[
\text{slope} = 3.25 \times 10^6 \, cm Hz
\]

$T = 408 \, K$

\[
\frac{1}{S} \times 10^3 \quad I \times 10^{-8} \\
(cm)^{-1} \quad cm(Hz^2)
\]

\[
\begin{array}{c}
0.2 \\
40 \\
0 \\
\end{array}
\]

\[
\begin{array}{c}
0 \\
200 \\
400 \\
600 \\
\end{array}
\]

\[
\text{slope} = 2.51 \times 10^6 \, cm Hz
\]
\[ \text{when } f_0 \gg f \quad a_r \approx \frac{1}{K f_0^2} \]

Therefore \( a_r \) should show a linear dependence on \( f^2 \) at the lower frequencies with a slope given by \( \frac{1}{K f_0} \). For frequencies below about 400Hz the error introduced by neglecting \( f^2 \) in comparison with \( f_0^2 \) will be small. Assuming \( f_0 \) to be of the order of 1,300Hz the error at 400Hz will be about 9% falling to 2% at 200Hz. Hence by plotting the variation of \( a_r \) with \( f^2 \) from 80 - 400Hz the slope of the line obtained can be used to give a value for \( f_0 \) with an estimated error of the order of 4%.

The value of \( K \) was found from the previous \( I \) against \( f^2 \) and \( \frac{1}{S} \) against \( f_0 \) graphs. The results of plotting \( a_r \) against \( f^2 \) are shown in Fig. 9.7 and the values of \( f_0 \) shown in Table 9.2. To check that this method was satisfactory \( f_0 \) was calculated at 298K for \( h' = 2.52 \times 10^{-3} \) by both methods.

From the \( \frac{f^2}{a_r} \) against \( f^2 \) graph a value for the intercept and slope were \( 26 \times 10^8 \text{ Hz}^2 \text{cm.} \) and \( 19.25 \times 10^3 \text{ cm.} \) respectively, giving \( f_0 \) at 1 atm. = 1,245 Hz. The result for \( f_0 \) by the second method gives \( f_0 = 1,239 \text{ Hz} \) showing satisfactory agreement.

An objective assessment of the errors involved is quite difficult. From the scatter of the results in the \( \frac{f^2}{a_r} \) against \( f^2 \) graphs the error in \( f_0 \) will be of the order 2 \( \rightarrow \) 3%. The probable error in the mixture composition will be of the same order suggesting a total error of about 5%.

The frequency of maximum absorption (\( f_0 \)) at one atmosphere is plotted against the molar fraction of water vapour \( x \times 10^3 \) (\( h \)) in Figs. 9.8 to 9.10 at each temperature.
Table 9.2

Results for $f_0$ where $f_0 \gg f$

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>$h \times 10^3$</th>
<th>Slope of $a_T$ vs. $f^2$ graph (cm$^{-1}$Hz$^{-2}$)</th>
<th>$K$ (cm Hz)</th>
<th>$f_0$ (Hz)</th>
<th>$f_0/\text{Atm}$ Hz atm$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>2.52</td>
<td>$0.25 \times 10^{-9}$</td>
<td>$3.25 \times 10^6$</td>
<td>1230</td>
<td>1239</td>
</tr>
<tr>
<td>323</td>
<td>2.39</td>
<td>$0.27 \times 10^{-9}$</td>
<td>$3.22 \times 10^6$</td>
<td>1150</td>
<td>1219</td>
</tr>
<tr>
<td>343</td>
<td>2.45</td>
<td>$0.293 \times 10^{-9}$</td>
<td>$2.80 \times 10^6$</td>
<td>1219</td>
<td>1292</td>
</tr>
<tr>
<td>363</td>
<td>2.29</td>
<td>$0.285 \times 10^{-9}$</td>
<td>$2.93 \times 10^6$</td>
<td>1198</td>
<td>1263</td>
</tr>
<tr>
<td>383</td>
<td>2.01</td>
<td>$0.376 \times 10^{-9}$</td>
<td>$2.90 \times 10^6$</td>
<td>916</td>
<td>982</td>
</tr>
<tr>
<td>408</td>
<td>1.78</td>
<td>$0.47 \times 10^{-9}$</td>
<td>$2.50 \times 10^6$</td>
<td>851</td>
<td>892</td>
</tr>
</tbody>
</table>
\( T = 343 \, \text{K} \)

\( T = 363 \, \text{K} \)
The solid curve on each graph represents a least squares best fit to the combined data of Knotzel and Knotzel (1948), Harris and Tempest (1964) and Henderson et al (1965) at room temperature. The present results at 298K are seen to be in excellent agreement with the above, as was the previous work from this laboratory by Nolan (1967). A least squares best fit direct to the present data is not very satisfactory since there are too few points at small values of h. However, if we make the assumption that \( f_0 = 10 \)Hz for pure oxygen (Holmes Smith and Tempest (1963)), and this point is weighted 10 times with respect to the others, we arrive at an equation:

\[
 f_0 = 9 + 199h + 115h^2 \quad \text{at 1 atm.}
\]

The combined results of Knotzel et al give:

\[
 f_0 = 7 + 183h + 132h^2 \quad \text{at 1 atm.}
\]

Those of Nolan give:

\[
 f_0 = 9 + 162h + 144h^2 \quad \text{at 1 atm.}
\]

At the higher temperatures the experimental points are shown in comparison to the room temperature curve. A least squares best fit to the experimental data at the higher temperatures poses an additional problem since the variation of \( f_0 \) for pure O\(_2\) with temperature is not accurately known over this temperature range.

As a first approximation the fairly well established linear relationship between \( \ln \tau \) and \( T^{-\frac{1}{2}} \) was used to give an estimation of \( f_0 \) for pure oxygen at the higher temperatures. When this is done and the \( h = 0 \) point weighted ten times, as was done with the result for 298K, we obtain by the least
squares best fit method the following equations:

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>$f_0 = a_0 + a_1 h + a_2 h^2$</th>
<th>weighted $h = 0$ point</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>$f_0 = 9 + 199 h + 115 h^2$</td>
<td>$f_0 = 10$ Hz</td>
</tr>
<tr>
<td>323</td>
<td>$f_0 = 11 + 235 h + 116 h^2$</td>
<td>$f_0 = 10.7$ Hz</td>
</tr>
<tr>
<td>343</td>
<td>$f_0 = 12 + 263 h + 106 h^2$</td>
<td>$f_0 = 11.2$ Hz</td>
</tr>
<tr>
<td>363</td>
<td>$f_0 = 13 + 239 h + 132 h^2$</td>
<td>$f_0 = 11.7$ Hz</td>
</tr>
<tr>
<td>383</td>
<td>$f_0 = 13 + 289 h + 102 h^2$</td>
<td>$f_0 = 12.2$ Hz</td>
</tr>
<tr>
<td>408</td>
<td>$f_0 = 14 + 336 h + 91 h^2$</td>
<td>$f_0 = 12.9$ Hz</td>
</tr>
</tbody>
</table>

The $a_0$ terms are taken to the nearest whole number. The third column shows the values of $f_0$ for pure oxygen calculated assuming $t \propto T^{-\frac{1}{3}}$ and $f_0 = 10$ Hz for pure oxygen at 298K.

It can be seen from these results that even with the $h = 0$ point weighted 10 times the experimental points make the $a_0$ values larger than those calculated. This suggests that $f_0$ for pure oxygen should vary at a greater rate than calculated. This is further born out by considering Fig. 9.11 where $\ln \tau$ is plotted against $T^{-\frac{1}{3}}$ for various values of $h$ where $\tau$ is the measured relaxation time of the mixture. These points were obtained using the equations above and assuming $\tau = \frac{1}{2 \pi f_0^2}$. It can be seen that the slope of the $h = 0$ line is not consistent with the others, the slopes showing a tendency to decrease as $h$ is increased. If we extend the $T^{-\frac{1}{3}}$ axis as is done in Fig. 9.12 the lines show a tendency to converge at one point. This clearly shows our underestimation of the variation of $\ln \tau$ with $T^{-\frac{1}{3}}$, and as a second attempt to verify this we extrapolate back from the convergence point to the point corresponding to $f_0 = 10$ Hz at 298K. The values of $f_0$ are now calculated assuming the variation of $\tau$ with temperature follows
(a) \( h = 0 \times 10^{-3} \)
(b) \( h = 0.2 \)
(c) \( h = 0.5 \)
(d) \( h = 1.0 \)
(e) \( h = 1.5 \)
(f) \( h = 2.0 \)

\[
\begin{align*}
\{ & \tau = 4.5 \times 10^{-5} \text{ sec} \\
& \tau^{\frac{1}{3}} (K^{\frac{1}{3}}) = 0.038 \end{align*}
\]
When this is done the points are seen to be in excellent agreement with Parker and Swope (1964) over the present temperature range. Parker and Swope find a definite change in slope of the $\ln \tau$ against $T^{-\frac{1}{2}}$ at about 400K (see Fig. 9.13). Unfortunately this lies just outside the range of the present work and so we cannot add any support to these points. However, the results of Parker and Swope within the temperature range of the present measurements show good agreement, and the present points (see Fig. 9.14) are an excellent fit to the theoretical curve presented by Parker (1964). Further discussion of this is given later in Chapter 12.

On the assumption that the temperature variation of $f_0$ for pure oxygen is of the right order we can recalculate the equations relating $f_0$ to $h$ at each temperature. This was done in the same way as before, the $h = 0$ points given the weight factor 10. The equations now become:

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>$f_0 = a_0 + a_1 h + a_2 h^2$</th>
<th>weighted $h = 0$ point</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>$f_0 = 9 + 199h + 115h^2$</td>
<td>$f_0^* = 10$ Hz</td>
</tr>
<tr>
<td>323</td>
<td>$f_0 = 12 + 234h + 117h^2$</td>
<td>$f_0^* = 11$ Hz</td>
</tr>
<tr>
<td>343</td>
<td>$f_0 = 14 + 261h + 107h^2$</td>
<td>$f_0 = 13$ Hz</td>
</tr>
<tr>
<td>363</td>
<td>$f_0 = 15 + 235h + 134h^2$</td>
<td>$f_0 = 15$ Hz</td>
</tr>
<tr>
<td>383</td>
<td>$f_0 = 17 + 283h + 105h^2$</td>
<td>$f_0 = 16$ Hz</td>
</tr>
<tr>
<td>408</td>
<td>$f_0 = 21 + 325h + 96h^2$</td>
<td>$f_0 = 19$ Hz</td>
</tr>
</tbody>
</table>

These equations, except for the $c_0$ terms, show very little change to the equations given on page 143. Except for the results at 363K the constants $a_1$ and $a_2$ show a consistent variation with temperature. This is illustrated in Fig. 9.15.
VIBRATIONAL COLLISION NUMBER

$Z_v$

$T (K)$

517 434 370 319 278

THEORETICAL CURVES FROM PARKER (1964)

- PARKER AND SWOPE (1965)
- SHIELDS AND LEE (1963)
- PARKER (1961)
- HOLMES SMITH AND TEMPEST (1963)
- PRESENT WORK
\[ f_0(T) = C_0 + C_1 A_1 T + C_2 A_2 T^2 \]
(a) $T = 298$ K
(b) $T = 323$ K
(c) $T = 343$ K
(d) $T = 383$ K
(e) $T = 408$ K
These equations for $f_0$ are plotted by computer and shown in Fig. 9.16. The result for $T = 363K$ is omitted since it is not consistent with the other results.
Specimen of Procedure and Calculation

To illustrate the operating procedure in more detail, this chapter gives a description of the experimental methods employed for the preparation of a mixture of oxygen and water vapour at 70°C carried out on 16th March 1971. Also included is an outline of the determination of the sound absorption from the measured values of impedance and frequency at one of the natural modes of the resonance tube.

On the evening of 14 March the previous charge of gas was evacuated from the system. The pressure measuring system (see Fig. 7.2) was firstly evacuated by the vacuum furnace pumping system by connection at B. This was to remove any excess water vapour that was likely to have collected in this system and to prevent it being swept into the resonance tube. After a time this system was opened to the resonance tube vacuum system and pumping continued. The entire system was then left to pump overnight and reached an ultimate pressure of about 2 microns. During all these operations the furnace was set at its working temperature.

On the following morning of March 15th the oven in the pressure measuring system was set at about 30 degrees above the furnace temperature, and the three cold traps C₁, C₂ and C₃ were filled with solid carbon dioxide-acetone mixtures. The systems were isolated from the pumps by closing valve 13 (see Fig. 7.1) and the entire system slowly filled with oxygen. A careful watch was kept on the ring pattern to ensure that no pressure difference developed across the diaphragm. When the system was filled to approximately atmospheric pressure, valves 12 and 14 were closed and valve 11
opened. The entire system was then flushed for about three hours with pure dry oxygen via valves 1 - 2 - 3 - 4 - 5 - 6 - 7 - 8 - 9 - 10 - 11, to leave the system at the mercury bubble isolated by the cold trap C3 to prevent any back diffusion of air into the system. Preheating the gas in the oven prevented any cooling of the resonance tube system during the flushing procedure. After flushing, valves 3 and 4 were closed to isolate the preheating system and the rest of the system was again evacuated during the evening and night of March 15. During evacuation the two oil manometers were vigorously shaken in the horizontal position to remove any trapped oxygen.

The following morning of March 16, the two oil manometers were fixed in their vertical positions and two travelling microscopes fixed in position to enable the heights of the oil columns to be read. The furnace temperature was checked both on the six thermocouples and the three platinum resistance thermometers to ensure that the temperature distribution along the tube was within the acceptable limits. The two cold traps C1 and C2 were filled. The resonance tube was then isolated from the pumps by closing valves 8 and 14 and readings of pressure against time on each oil manometer were taken over a period of about ten minutes. The stopcock A on the top of the water holder (see Fig. 7.3) was then carefully opened to allow a small column of water into the system via valves 5, 6 and 7. Stopcock A and valve 5 were closed when sufficient water had entered the system, and frequent pressure-time measurements were made on each manometer. The system reached equilibrium in about one hour but readings were continued for a further hour to ensure that the true equilibrium had been reached.
and to provide data needed to extrapolate back to zero time to compensate for any small leakage into the system. Since it took about one hour for the water to reach equilibrium it was assumed that in that period the water reached the furnace temperature and the measured pressure was the true water vapour pressure at the working temperature.

Fig. 10.1 shows the two graphs obtained for the pressure against time measurements on both manometers. The displacement of the two curves is due to the difference in zero levels of the two manometers. Extrapolating the curves back to zero time gives pressures of:

(i) Reflector manometer Pressure = 2.020 cm. oil
(ii) Loudspeaker manometer Pressure = 2.073 cm. oil

Subtracting the zero pressure readings from these results gives pressures of 1.997 and 2.023 cm. oil for the reflector and loudspeaker manometers respectively. The average of these readings gives the water vapour pressure =

\[(2.01 \pm 0.01) \text{ cm. oil.}\]

\[= (12.90 \pm 0.06) \times 10^{-2} \text{ cm. Hg}\]

Similar differences between the readings of the two oil manometers were obtained with every mixture used, and represent about a 0.5% uncertainty in the value of the water vapour pressure.

While the water vapour pressure measurements were being made valve 10 was closed, isolating the gas purification system and connecting tubes up to valves 8 and 14 from the pumps, and the system was filled with oxygen to approximately atmospheric pressure. When the water vapour pressure readings were finished the two oil manometers were isolated.
FIG. 10.1. GRAPH OF PRESSURE AGAINST TIME

READINGS TAKEN ON MARCH 16th, 1971

water vapour pressure
(cm oil)

introduction of water

--- dotted line --- manometer on loudspeaker

--- solid line --- manometer on reflector
from the system and valve 14 opened slightly so that oxygen was slowly bled into the resonance tube. It took approximately one hour to fill the tube, the pressure of the oxygen on the inlet side to the resonance tube always being maintained at approximately atmospheric pressure to prevent any back diffusion of water vapour out of the tube. The saturated vapour pressure of water at 20°C is 1.75 cm.Hg and since the maximum water vapour pressure used was 0.2 cm. Hg no vapour was likely to condense out of the resonance tube into the colder systems. The tube was filled to its final working pressure and valve 14 was then closed. The system was then left for about thirty minutes and the difference between the total gas pressure and atmospheric pressure measured on the mercury manometer and found to be \(-2.65\) cm. Hg. The atmospheric pressure measured on a fortin barometer was \(74.41\) cm. Hg giving a total gas pressure of \(71.76\) cm. Hg.

The molar fraction of water vapour \(h'\) was thus \(1.80 \times 10^{-3}\).

The plungers in the reflector and loudspeaker assemblies were then closed and the system left for a further thirty minutes to reach equilibrium. The apparatus was now ready and the readings necessary to determine the impedance against frequency curves at about eight of the natural modes of the resonance tube could be taken. The optical system and electronics had been adjusted previously and were ready for use. At each mode of the tube the temperature as indicated by the platinum resistance thermometers was noted. Also during all the measurements the thermocouple recorder was set running giving a continuous record of the temperature distribution along the tube.

The readings were taken in the dark room, the illumination
from the instruments being sufficient to enable the results to be recorded. The frequency was set to the required values by the digital oscillator and the current was adjusted by its output control in conjunction with a series resistance box. Readings of the current required to set the diaphragm vibrating at the first critical amplitude were taken at 0.1 Hz intervals about the resonant frequency of the particular mode of the tube; usually between 30 and 40 readings in all. These measurements took about thirty minutes at each mode, but to avoid undue eyestrain a rest of up to half an hour between successive sets was essential.

A detailed description of the measurements and results at the seventh mode will be sufficient to show the procedure adopted. The average temperature, as recorded by the three platinum resistance thermometers, at the beginning of the set of measurements was 71.16 ±0.03°C. Readings of the critical current were taken at 43 different frequencies at intervals of 0.1 Hz. The result of plotting the impedance against frequency is shown in Fig. 10.2 with a smooth curve drawn through the measured points.

This provided the basic data for the computer. The other data required were:-

(i) The length of the resonating gas column. This was calculated from the measured temperature and the appropriate value of the expansion coefficient previously determined.

(ii) A set of values of \( Z_0 \) to enable the best \( \tan \phi \) against frequency graph to be determined. A range of possible values of \( Z_0 \) at intervals of 0.05 units was fed into the computer which then calculated each corresponding
FIG. 10.2  PLOT OF IMPEDANCE AGAINST FREQUENCY

READINGS AT 7th MODE TAKEN ON MARCH 16th, 1971

impedance
(arbitrary units)

-158 -
2.0 -
2.4 -
2.8 -
3.2 -

frequency (Hz)

562 563 564 565 566
tan \( \theta \) against frequency graph. A least squares analysis to these computed points yielded the best straight line and hence the correct value of \( Z_0 \).

From the slope and intercept of the line the total absorption, resonant frequency and tube velocity were calculated. Fig. 10.3 shows the computed \( \tan \theta \) against frequency points, the best line corresponding \( Z_0 = 2.2 \) units. Other values of \( Z_0 \) gave points which lay on shallow curves, the curvature of which increased as the difference between \( Z_0 \) and its true value was increased. Two examples of this are illustrated in Fig. 10.3 for values of \( Z_0 = 2.0 \) and 2.4 units. They produce shallow curves about the best fit line \( Z_0 = 2.2 \), the curvature changing sign as \( Z_0 \) moves through its true value. From the best fit line the computer yielded the following results:

Total attenuation \( = 3.21 \times 10^{-4} \text{ cm}^{-1} \)

Velocity of sound in the tube \( = 352.83 \text{ m.sec}^{-1} \)

Resonant frequency \( = 563.66 \text{ Hz} \)

The tube absorption from previous measurements on pure oxygen was \( 1.94 \times 10^{-4} \text{ cm}^{-1} \) giving the relaxation absorption \( = 1.27 \times 10^{-4} \text{ cm}^{-1} \).
Fig. 10.3

Graphs of tan θ against frequency

-160-
Chapter 11

Measurements in mixtures of Oxygen and Helium

It was considered desirable to study the effect of helium on the relaxation time of oxygen since previous work from this laboratory (Nolan 1967) was limited to only one mixture, and the result found to be lower than expected.

In 1933 Knudsen found:

\[ f_0 = 6.4 \text{Hz} \text{ at } 1 \text{ atmosphere} \]

where \( h \) is the mole fraction of helium \( x \times 10^3 \)

Parker (1961) found:

\[ f_0 = 8.8 + 4.6 \text{Hz} \text{ at } 1 \text{ atmosphere} \]

where the term 8.8 was deduced from his other measurements on oxygen and hydrogen.

Nolan (1967) using one mixture of 2.51% helium found

\[ f_0 = 9 + 3.6 \text{Hz} \text{ at } 1 \text{ atmosphere}. \]

This is only 0.78 times the effect found by Parker. Nolan suggested that the discrepancy may well have been caused by air diluting the helium, as it was obtained by evaporating liquid helium. However, the difference was considerably larger than expected.

In the present work the helium used was supplied by British Oxygen with a purity better than 99.95%. Since helium is very much less effective than water vapour in exciting oxygen much larger concentrations are required.

Four different mixtures were used with molar fractions of helium of between \( 50 \times 10^{-3} \) and \( 130 \times 10^{-3} \). At this time the system had a leak rate which was too large for very reliable oxygen-water vapour mixtures. This is why the results with
oxygen-water vapour mixtures were only carried out up to 140°C. Since the time involved in finding and reducing the leak to a tolerable rate would, from previous experience, have been considerable it was decided to work with oxygen-helium mixtures. In this case, since the helium will be present in far greater quantities, it can be added to the system at atmospheric pressure where any leakage into or out of the system will be very small.

The method used to prepare the mixtures was firstly to evacuate the complete systems for about 24 hours. Because of the increased leak rate the ultimate vacuum obtainable was only about 25 microns compared to the usual vacuum of about 2 microns. Even if the pressure of 25 microns was completely due to the presence of water vapour in the system this would only affect $f_0$ by about 6 Hz. Since this is unlikely the expected error in $f_0$ from this source would probably be considerably less, and therefore negligible. After the system had been evacuated it was filled and flushed for three to four hours with pure oxygen. After flushing the resonance tube was isolated from the purification systems by closing valve (a) (see Fig. 11.1) and the total oxygen pressure could be measured on the open arm manometer $M_1$. The purification system and connecting tubes up to valve (a) were then evacuated again for several hours to a pressure of better than 1 micron. They were then filled to a pressure of about 90 cm. Hg with helium which was measured on the manometer $M_2$. The oxygen pressure in the resonance tube was about one cm. Hg above atmospheric. This pressure differential was measured accurately using a cathetometer to $\pm 0.001$ cm. Hg. Valve (a)
PREPARATION OF O$_2$-He MIXTURES
was opened slowly and helium forced into the resonance tube. When the pressure of the helium in the connecting tubes was reduced to about 4 cm. Hg above the pressure of the mixture in the tube, valve (a) was closed and the helium side was pressurised up to about 10 cm. Hg above the mixture pressure. This procedure was repeated until sufficient helium was forced into the tube. By maintaining the helium side always above the pressure in the tube it was unlikely that any oxygen was drawn out. When sufficient helium had entered the tube the mixture pressure was measured on the manometer M1. From these measurements and a knowledge of atmospheric pressure the composition of the mixture could be determined. Since the system was known to have a small leak it was necessary to check the total gas pressure after each set of measurements was completed to see if any leakage out of the system had occurred. In fact measurements indicated a small drop in total gas pressure of about 0.3% after a complete set of measurements for the mixture. However, if we assume that the total leakage out of the system is only helium then the error in h will be approximately 6%. This condition is possible since helium is much lighter than oxygen and will diffuse out of a leak more readily. However it is unlikely that no oxygen at all escaped so perhaps a more optimistic error would be four to five per cent. The value of h taken was then the average value of these two limits. The results obtained are shown in Table 11.1.

As with the oxygen water vapour mixtures the values of $f_0$ were determined from the slope and intercept of the corresponding $f^2/A_r$ against $f^2$ graph. These are plotted in Fig. 11.2. Fig. 11.3 shows the result of plotting I against
### Results for C₂ - He mixtures

<table>
<thead>
<tr>
<th>Total gas pressure (cm Hg)</th>
<th>Mole fraction of He x10²</th>
<th>Results of ( f²/α_r ) against ( f² ) graphs</th>
<th>( 1/α ) cm⁻¹</th>
<th>( f² ) at 1 atm.</th>
</tr>
</thead>
<tbody>
<tr>
<td>81.65</td>
<td>58.4</td>
<td>( 8.0 \times 10^8 )</td>
<td>1.2 x 10⁴</td>
<td>0.83 x 10⁻³</td>
</tr>
<tr>
<td>83.42</td>
<td>84.8</td>
<td>( 10.1 \times 10^8 )</td>
<td>0.88 x 10⁴</td>
<td>1.14 x 10⁻³</td>
</tr>
<tr>
<td>84.30</td>
<td>101</td>
<td>( 13.0 \times 10^8 )</td>
<td>0.73 x 10⁴</td>
<td>1.36 x 10⁻³</td>
</tr>
<tr>
<td>87.64</td>
<td>129</td>
<td>( 19.7 \times 10^8 )</td>
<td>0.56 x 10⁴</td>
<td>1.78 x 10⁻³</td>
</tr>
</tbody>
</table>

Best fit line to \( I \) vs \( f_0 \) graph gives \( K = 31.98 \times 10^6 \)
with \( 'r' = 0.99 \)

Best fit line to \( 1/α \) vs \( f_0 \) graph gives \( K = 31.96 \times 10^6 \)
with \( 'r' = 0.99 \)

giving average value of \( K = 3.2 \times 10^6 \) cm Hz
RESULTS FOR O$_2$-H$_2$ MIXTURES AT 258 K
O₂-He MIXTURES AT 296 K

---

- - - - Parker (1961)
---

- - - - Present work

---

\[ f_0 \]

\[ H_z (\text{atm}^{-1}) \]

\[ h \times 10^{-3} \]

\[ f_0 \] Hz

\[ I \times 10^{-8} \] cm (Hz²)

\[ \nu_s \times 10^{3} \] cm⁻¹ (Hz²)
fo and \( \frac{I}{S} \) against \( f_0 \). The slopes of these lines are in close agreement with the previous work on oxygen water vapour mixtures at 298K. Also in Fig. 11.3 the frequency of maximum absorption at one atmosphere is plotted against the water vapour content. A least squares fit direct to the measured points is not very satisfactory and a small negative intercept is obtained. However, if, as with the previous work, the point \( f_0 = 10 \text{ Hz} \) for \( h = 0 \) is weighted ten times, the best fit line becomes

\[
f_0 = 10 + 3.8h \text{ Hz} \quad \text{at 1 atm.}
\]

with a correlation coefficient \( r = 0.998 \)

where \( h = \) molar fraction of helium \( \times 10^3 \)

This is a little higher than Nolan's result but is still only 0.83 times the effect found by Parker. However, Holmes Smith and Tempest (1962) give a value for \( \frac{Z_{AA}}{Z_{AB}} \) for oxygen-helium mixtures as \( (2.8 \pm 0.6) \times 10^2 \). Using equation (2.29) page 22 where \( \frac{Z_{AA}}{Z_{AB}} = 280, \ x_B = h \times 10^{-3}, \ \tau_1 = \frac{1}{2 \pi f_0} \) and

\[
\tau_{AA} = \frac{1}{2 \pi 10} \quad \text{and} \quad \frac{(tc)_{AB}}{(tc)_{AA}} \quad \text{is calculated from equation (2.30) we arrive at equation}
\]

\[
f_0 = 10 + 3.7h \quad \text{at 1 atm.}
\]

which shows excellent agreement with the present work suggesting that the results of Parker are a little high.
Chapter 12

Discussion of the Results and Suggestions for Further Work

This Chapter is concerned with a more detailed analysis of the results obtained in the previous Chapters, and in particular to their relationship with some of the recent theoretical studies.

On a purely empirical basis it is of interest to compare the results of this work to a study made by Millikan and White (1963). They collected a large amount of data for vibrational relaxation times ($p \tau_V$ atm. sec.) of simple systems. When $p \tau_V$ values are plotted logarithmically against $T^{-\frac{3}{2}}$ they found them well represented by straight lines, the majority of which intersected at a common point, $p \tau_V = 10^{-8}$ atm. sec. $T^{-\frac{3}{2}} = 0.03 K^{-\frac{3}{2}}$.

Fig. 12.1 shows a selection of the systems considered. Systems designated by a single species refer to relaxation in the pure gas. Those labelled with two components refer to relaxation of the first species with a small fraction of the second named gas present, at a total pressure of $p$ atm. Thus from measurements on the mixture $AB$, where $B$ is the gas with no vibrational energy, the value of $\tau_{AB}$ is calculated from equation (2.26) Chapter 2.

\[ \frac{1}{\tau_1} = \frac{1}{\tau_{AA}} + \frac{x_B}{\tau_{AB}} \quad \ldots \ldots \ldots (12.1) \]

The results of the present work where applicable (i.e. $O_2 - O_2$ and $O_2 - H_e$) are shown in Fig. 12.1. The plotting of the results for $O_2 - H_2O$ mixture for $x = 1 \times 10^{-3}$ is not strictly
\[ \text{T (K)} \]

\[ 8000 \quad 2000 \quad 1000 \quad 500 \quad 300 \]

\[ P\gamma v \quad \text{(atmsec)} \]

\[ 10^{-2} \quad 10^{-4} \quad 10^{-6} \quad 10^{-8} \]

\[ T^{-1/3} \quad K^{-1/3} \quad 0.05 \quad 0.10 \quad 0.15 \]

\[ \times \text{ present work} \]
\[ \circ \text{ Parker and Swope (1965)} \]
\[ \triangledown \text{ Holmes Smith and Tempest (O}_2\text{ 1963  O}_2\text{He 1962)} \]
\[ \triangledown \text{ Shields and Lee (1963)} \]
\[ \triangle \text{ Losev and Generalov (1963)} \]
\[ \triangle \bullet \text{ White and Millikan (1963)} \]
\[ \triangledown \text{ Parker 1961} \]

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applicable since the $O_2 - H_2O$ system is complicated by
vibrational-vibrational resonant exchange and the use of
equation (12.1) is not completely valid as it implies a
linear relationship between $\frac{1}{\tau}$ and $x$. However, the results
do show the high efficiency of water in respect to other
gases in decreasing the relaxation time of oxygen.

The results for pure oxygen show clearly the difference
in slope between fitting a line to the high temperature
data as is done by Millikan, and to results in the present
temperature range. There is the possibility that this
difference is due to small amounts of impurities as they
would have their greatest effect at low temperatures.
However, most recent workers using oxygen of high purity
and taking extreme precautions to avoid impurities, find
consistent relaxation times which agree with the low tempera­
ture line. The existence of the transition region predicted
and found experimentally by Parker and Swope (1965) would
appear to be real and suggests a transition between different
modes of the molecule.

It is interesting to refer to Fig. 9.12. Here the
measured relaxation time $\tau$ of the mixture was plotted against
$T^{-\frac{1}{3}}$ for increasing values of the mole fraction of water
vapour. Although the relaxation time scales are not compar­
able, the common intersection point obtained by extending the
$T^{-\frac{1}{3}}$ axis occurs, within the limits of each extrapolation,
at approximately the same value of $T^{-\frac{1}{3}}$. This would seem
reasonable as there must be some temperature for every
collision to be effective for energy transfer and molecular
details are then no longer important. However, even with
forcing Millikan and White could not make the light mass
cases such as $O_2 - H_e$ and $CO - H_e$ (not shown in Fig. 12.1)
extrapolate to the common point. They overcome this by making the high-temperature intercept a function of the reduced mass. By then relating the slopes of the lines to the characteristic temperature $\theta$ of the gas concerned they obtain the empirical equation:

$$\log_{10}(\tau_T) = (5.0 \times 10^{-4}) \mu^{1/2} \theta^{4/3} \left[ T^{-3/2} - 0.015 \mu^{1/4} \right]^{-8} \ldots (12.2)$$

where $\mu$ is the reduced mass. This equation is found to reproduce the measured times within 50% for systems as diverse as $N_2$, $I_2$, $O_2 - H_2$. The calculations of Dickens and Ripamonti (1961) show that the Schwartz-Slawsky-Herzfeld theory, if suitably tied to experimental results will probably give relaxation times with about the same accuracy. It is unfortunate that the present results with oxygen and water vapour were not able to be extended beyond 410K, as it would be of great interest to see if any comparable change in slope occurs in this region as was found by Parker and Swope (1965) with pure oxygen. If one looks at the low temperature results for oxygen-helium mixtures, then the results of Parker and to a lesser extent the present work, fall below the line predicted from the results at higher temperatures. This leads to the implication that a transition region may also exist for this mixture somewhere in the temperature range between. However, this is purely speculative and there is an obvious need for more detailed experimental data in this region.

We now go on to consider the oxygen-water vapour results with special regard to the theory of Tuesday and Boudart (1955) described in Chapter 2 where it was shown that
\[
\frac{1}{\tau} = Nk_{10} + N \left[ \frac{k_{20} - k_{10} + \frac{k_{30}k_{50}}{k_{03} + k_{50} - (k_{03} + k_{50} - k_{40})} X}{k_{03} + k_{50} - (k_{03} + k_{50} - k_{40})} \right]
\]

where \( X \) is the mole fraction of water vapour and the \( k_{10} \) etc. are defined by the respective collision equations in Chapter 2. In the case of \( O_2 - H_2O \) we can make several simplifications

i.e. \( 1 - X \approx 1 \)

and \( k_{10} \) the rate constant for \( O_2 - O_2 \) collisions will be very much less than \( k_{20} \), the rate constant for \( O_2 - H_2O \) collisions, i.e. \( k_{10} \ll k_{20} \)

For the resonant exchange process equation 2.40 page 26, the ratio of the reaction rates will be given by:

\[
\frac{k_{30}}{k_{03}} = \frac{\exp (-\theta_{H_2O}/T)}{\exp (-\theta_{O_2}/T)}
\]

where \( \theta \) is the characteristic temperature, \( T \) the absolute temperature. Then if we take \( T = 300K \)

\[
\frac{k_{30}}{k_{03}} = 0.83
\]

Assuming the resonant exchanges are very much faster than the non-resonant exchange in equation (2.42) we have

\( k_{30} \gg k_{50} \)

Using these simplifications, equation (12.3) becomes
\[
\tau = Nk_{10} + N(k_{20} + 0.83k_{50})X + 0.83 N(k_{40} - k_{50}) X^2
\]

assuming \(Xk_{40}\) is small compared to other quantities. This is to be compared with our experimental results of:

\[
fo = 9 + 199h + 115h^2 = \frac{1}{2\pi} \quad \ldots \ldots (12.4)
\]

Now when \(h = 0\)

\[
fo = 9 \text{ Hz} = \frac{1}{2\pi}
\]

.. \(Nk_{10} = 18\pi = 57\)

\(h = \text{molar fraction of water } \times 10^3\) and the linear term of equation 12.4 is 199 hence:

\[
N(0.83k_{50} + k_{20}) = 2\pi \times 199 \times 10^3 = 1.25 \times 10^6
\]

\[
\ldots \ldots (12.5)
\]

and the quadratic term is \(115 \times 10^6\), therefore:

\[
0.83 N(k_{40} - k_{50}) = 2\pi \times 115 \times 10^6 = 0.723 \times 10^9
\]

\[
\ldots \ldots (12.6)
\]

To proceed, further assumptions are necessary. Tuesday and Boudart assumed \(k_{20} = k_{50}\), saying the reactions:

\[
H_2O^* + O_2 \leftrightarrow O_2 + H_2O
\]

and \(O_2^* + H_2O \leftrightarrow O_2 + H_2O\)

are superficially similar. This leads, from equation (12.5) to:

\[
Nk_{50} = Nk_{20} = \frac{1.25}{1.83} \times 10^6 = 6.8 \times 10^5
\]

\[
\ldots \ldots (12.7)
\]

Equation (12.5) then gives:

\[
Nk_{40} = 8.7 \times 10^8
\]

\[
\ldots \ldots (12.8)
\]
Henderson, Clark and Lintz (1965) are critical of this assumption and see no evidence for it. In their work they neglected $k_{50}$ in comparison to $k_{40}$ and obtained $Nk_{40} = 10^9$. Tuesday and Boudart obtain $Nk_{40} = 8.5 \times 10^8$. The values of $Nk_{40}$ are therefore of the same order. Experimental results for pure water vapour from Huber and Kantrovitz (1947) give relaxation times of $3.7 \times 10^{-8}$ sec. at $213^\circ$C falling to $2.1 \times 10^{-8}$ sec. at $433^\circ$C. Fugii, Lindsay and Urushihara (1963) find the relaxation time $= 1.5 \times 10^{-8}$ sec. in the temperature range $40 - 180^\circ$C.

The results of Henderson et al., Tuesday and Boudart, and the present work give relaxation values for pure water (taken as $= \frac{1}{Nk_{40}}$), equal to $10^{-9}$ sec., $1.18 \times 10^{-9}$ sec., and $1.15 \times 10^{-9}$ sec. respectively. Thus there is disagreement of about a factor of 10 in the results from a direct measurement on the pure substance, and the indirectly inferred values from the impurity work.

By using the present experimental results from which the relevant $f_o = a_0 + a_1h + a_2h^2$ equations were calculated, $Nk_{10}$ and $Nk_{40}$ can be calculated over the range $298 - 408K$. $Nk_{50}$ and $Nk_{20}$ can be found using Tuesday and Boudart's assumption of equality as is done for the present results, but the uncertainty of their assumption must be remembered.

The results are shown in Table 12.1, together with the relaxation times of the particular transfer processes.

The present measurements do not allow a direct calculation of $k_{30}$. If one uses the results of Harris (1963) on air-water vapour mixtures one can find a value for $k_{30}$, as was done by Henderson and Herzfeld (1965). Harris found $(\frac{f_p}{\rho})_{\text{max}} = 135 + 697h + 423h^2$ (for Air-H$_2$O)
<table>
<thead>
<tr>
<th>Temperature K</th>
<th>$\frac{k_{30}}{k_{03}}$</th>
<th>$N_{k_{10}}$</th>
<th>$\tau(0_{2}-0_{2})$</th>
<th>$N_{k_{50}}=N_{k_{20}}$</th>
<th>$\frac{\tau(H_{2}O-0_{2})}{\tau(0_{2}-H_{2}O)}$</th>
<th>$N_{k_{40}}$</th>
<th>$\tau(H_{2}O^{*}-H_{2}O)$ (Sec.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.830</td>
<td>57</td>
<td>0.018</td>
<td>6.8x10^5</td>
<td>1.47x10^-6</td>
<td>8.7x10^8</td>
<td>1.15x10^-9</td>
</tr>
<tr>
<td>323</td>
<td>0.840</td>
<td>75</td>
<td>0.013</td>
<td>8.0x10^5</td>
<td>1.25x10^-6</td>
<td>8.7x10^8</td>
<td>1.15x10^-9</td>
</tr>
<tr>
<td>343</td>
<td>0.850</td>
<td>88</td>
<td>0.011</td>
<td>8.9x10^5</td>
<td>1.12x10^-6</td>
<td>7.9x10^8</td>
<td>1.27x10^-9</td>
</tr>
<tr>
<td>363</td>
<td>0.860</td>
<td>94</td>
<td>0.011</td>
<td>9.1x10^5</td>
<td>1.10x10^-6</td>
<td>7.8x10^8</td>
<td>1.28x10^-9</td>
</tr>
<tr>
<td>383</td>
<td>0.865</td>
<td>107</td>
<td>0.0093</td>
<td>9.5x10^5</td>
<td>1.05x10^-6</td>
<td>7.6x10^8</td>
<td>1.32x10^-9</td>
</tr>
<tr>
<td>408</td>
<td>0.870</td>
<td>132</td>
<td>0.0076</td>
<td>10.9x10^5</td>
<td>0.92x10^-6</td>
<td>6.9x10^8</td>
<td>1.45x10^-9</td>
</tr>
</tbody>
</table>

The $N_k$'s are the reaction rates and $\tau$ is calculated from $\frac{1}{\tau} = N_{k_{ox}} + N_{k_{xo}}$ in any particular reaction. Also $k_{ox}/k_{xo} = \exp \left( -\frac{T^*}{T} \right)$ where $T^*$ is the characteristic temperature of the excited state in question (or the difference between two such temperatures, as in the resonant exchange). In most cases $N_{k_{ox}} \ll N_{k_{xo}}$ and $\frac{1}{\tau} \approx N_{k_{xo}}$. 
from which, introducing the additional reactions involving nitrogen, Henderson and Herzfeld find $N_{k_0} = 1.6 \times 10^7$ and $N_{k_{03}} = 1.9 \times 10^7$. Henderson et al (1965) also measured the attenuation in mixtures of heavy water and oxygen and by analysing the results in a similar way to that of the oxygen and light water case, they found $k_{03}$ and $k_{30}$ reduced by a factor of over ten, since the exchange is now no longer nearly resonant, and $k_{20}$ and $k_{50}$ are reduced slightly due to the larger mass of the heavy water.

One striking feature of the work of Henderson et al was with mixtures of small amounts of light water with $D_2O$ which produced a vapour (mainly HDO and $D_2O$) which was found to be even more effective in shifting the frequency of maximum absorption than $H_2O$ itself.

In all the preceding work, no account has been made of the possibility of rotational-vibrational energy exchange for the oxygen water vapour mixtures. In all the reliable experimental work performed water has been found to be more efficient in deactivating vibrationally excited oxygen than the more slowly rotating $D_2O$. However, since in the $O_2$-$H_2O$ mixtures vibrational-vibrational resonant exchange processes occur, it is difficult to say what part, if any, rotational-vibrational effects play. However, the work of Henderson who found HDO to be more effective than $H_2O$ in deactivating oxygen suggests that rotational effects could be present. There is thus an obvious need for a theoretical study of vibrational-rotational energy transfer processes for the above named mixtures.
Suggestions for further work

As well as a theoretical study of the vibrational-rotational effects just mentioned, further general theoretical work is needed on the oxygen-water vapour mixtures. The present theories are in terms of rate constants and the processes involved are still far from fully understood on a molecular level. In the light of the present experimental work there lies the need for a theoretical model to account for the effects found.

As regards further experimental work, it would be very interesting to extend the temperature range of the present work both to higher and lower temperatures. A further investigation in the range around 400K and above would be very valuable because of the apparent change in slope of $\ln T$ against $T^{-\frac{3}{2}}$ found in this region.

Further experimental work is needed on pure non-relaxing gases enclosed in tubes, especially over a range of temperatures. Also more theoretical studies would be useful since the present technique used to find the tube absorption is far from satisfactory, and no real reason has been found for the wide spread of differences between the theoretical values calculated using the Helmholtz-Kirchhoff equations and those found in practice. A theoretical study which took account of the presence of standing waves would be particularly useful for future experimental work of this type.

Although these suggestions are by no means complete, they show that the subject is still far from understood and a great deal more work, especially theoretical, has still to be done.
Appendix I

Detailed Breakdown of the Results

Included here is a detailed analysis of the present results in terms of the most common quantities used to describe collision processes.

The collision number $Z$, defined as the average number of collisions for energy transfer, is calculated from equation (2.27). The average time between collisions, $t_c$, is calculated from the viscosity from the equation $\eta = 1.271 \ p t_c$ where $p$ is the gas pressure in dyne cm$^{-2}$, $\eta$ the viscosity in poise. (Herzfeld and Litovitz 1959). For the mixtures the relative collision times, i.e. $(t_c)_{AA}$ are calculated from equation (2.30) and the relative collision efficiency for $O_2$-He mixtures calculated from equation (2.29). The basic data required for the calculations and the results are shown in the Table I.1.
### Table I.1

<table>
<thead>
<tr>
<th>Basic data</th>
<th>( \text{O}_2 )</th>
<th>( \text{He} )</th>
<th>( \text{H}_2\text{O} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sutherland's Constant ( C )</td>
<td>138</td>
<td>76</td>
<td>659</td>
</tr>
<tr>
<td>Molecular weight ( M )</td>
<td>32</td>
<td>4</td>
<td>18</td>
</tr>
</tbody>
</table>

(a) Pure Oxygen

<table>
<thead>
<tr>
<th>Temperature ( K )</th>
<th>( \tau ) (sec)</th>
<th>( \text{tc (O}_2-\text{O}_2) (sec)</th>
<th>( Z )</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>1.59x10^-2</td>
<td>1.58x10^-10</td>
<td>1.01x10^8</td>
</tr>
<tr>
<td>323</td>
<td>1.38x10^-2</td>
<td>1.69x10^-10</td>
<td>0.82x10^8</td>
</tr>
<tr>
<td>343</td>
<td>1.17x10^-2</td>
<td>1.77x10^-10</td>
<td>0.66x10^8</td>
</tr>
<tr>
<td>363</td>
<td>1.04x10^-2</td>
<td>1.85x10^-10</td>
<td>0.56x10^8</td>
</tr>
<tr>
<td>383</td>
<td>0.94x10^-2</td>
<td>1.93x10^-10</td>
<td>0.49x10^8</td>
</tr>
<tr>
<td>408</td>
<td>0.78x10^-2</td>
<td>2.00x10^-10</td>
<td>0.39x10^8</td>
</tr>
</tbody>
</table>

(b) \( \text{O}_2-\text{H}_2\text{O} \) for \( 1 \times 10^{-3} \) molar fraction of water

<table>
<thead>
<tr>
<th>Temperature ( K )</th>
<th>( \tau ) Mixture (sec)</th>
<th>( Z ) Mixture</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>4.93x10^-4</td>
<td>3.13x10^6</td>
</tr>
<tr>
<td>323</td>
<td>4.40x10^-4</td>
<td>2.60x10^6</td>
</tr>
<tr>
<td>343</td>
<td>4.18x10^-4</td>
<td>2.36x10^6</td>
</tr>
<tr>
<td>363</td>
<td>4.15x10^-4</td>
<td>2.24x10^6</td>
</tr>
<tr>
<td>383</td>
<td>3.94x10^-4</td>
<td>2.04x10^6</td>
</tr>
<tr>
<td>408</td>
<td>3.61x10^-4</td>
<td>1.81x10^6</td>
</tr>
</tbody>
</table>
### (c) Temperature

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>tc(0₂-H₂O)</th>
<th>tc(0₂-H₂O)</th>
<th>τ(0₂-H₂O)</th>
<th>Z(0₂-H₂O)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.741</td>
<td>1.17x10⁻⁶</td>
<td>1.47x10⁻⁶</td>
<td>1.26x10⁴</td>
</tr>
<tr>
<td>323</td>
<td>0.752</td>
<td>1.27x10⁻⁶</td>
<td>1.25x10⁻⁶</td>
<td>9.80x10³</td>
</tr>
<tr>
<td>343</td>
<td>0.759</td>
<td>1.34x10⁻⁶</td>
<td>1.12x10⁻⁶</td>
<td>8.36x10³</td>
</tr>
<tr>
<td>363</td>
<td>0.767</td>
<td>1.42x10⁻⁶</td>
<td>1.10x10⁻⁶</td>
<td>7.75x10³</td>
</tr>
<tr>
<td>383</td>
<td>0.773</td>
<td>1.49x10⁻⁶</td>
<td>1.05x10⁻⁶</td>
<td>7.05x10³</td>
</tr>
<tr>
<td>408</td>
<td>0.783</td>
<td>1.57x10⁻⁶</td>
<td>0.92x10⁻⁶</td>
<td>5.86x10³</td>
</tr>
</tbody>
</table>

### (d) O₂-He

<table>
<thead>
<tr>
<th>Temperature K</th>
<th>tc(0₂-He)</th>
<th>Z(0₂-He)</th>
</tr>
</thead>
<tbody>
<tr>
<td>298</td>
<td>0.754</td>
<td>286</td>
</tr>
</tbody>
</table>

The values of τ(0₂-H₂O) are taken from Table 12.1, Chapter 12.
Appendix II

The High Temperature Cement

The high temperature cement was made by mixing together quantities of soluble sodium silicate (water glass) and powdered magnesium trisilicate. A solution of sodium silicate supplied by I.C.I. Ltd. used for the cement had a pH of 10.7 and specific gravity and viscosity at 20°C of 1.42 and 6 poise respectively. The magnesium trisilicate was used to give 'body' to the water glass making the cement expand on setting. The magnesium trisilicate was added in small amounts to the water glass, until when thoroughly mixed the paste could be made to stand in peaks. The cement was cured by heating to 250°C for twenty-four hours to remove the water. The cement was used for all metal to metal surfaces where the usual vacuum seals were impractical. The bond could be improved by cleaning the metal surfaces with a weak solution of sodium silicate before applying the cement. The coil described in Chapter 3 was made of thin asbestos paper bonded together with some of the cement made into a thin paste. The asbestos enters into chemical union with the sodium silicate giving the coil great rigidity. The cement was also a good electrical insulator, which thus gave a greater insulation between the turns of the coil. After treating the cemented joints with lacquer they proved to be reliably vacuum tight over the range of temperatures used in the present work.
Appendix III

Suggestions for Future Design and Improvements

A short account is given here as to possible improvements in the apparatus design in the advent of further work of this kind being undertaken. The experience gained from the present work suggests several possible modifications.

The use of a complete stainless steel system, for both tube and end flanges, would produce a cleaner system and give a much higher upper limit to the temperature range.

The major problem in the present work was due to the seal between the flanges C and B on the loudspeaker assembly (see Fig. 4.9). This was a constant source of small leaks. Unfortunately the design of the diaphragm clamping system was such that if the seal was further compressed the diaphragm clamping was also affected, which was likely to upset its vibration. If a similar clamping system is to be used again it would be very advisable to make it independent of the clamping of any vacuum seals. A better approach for further work would be the construction of a vacuum test rig to enable each completed end assembly to be tested before being mounted on to the resonance tube. For example, the loudspeaker section could be placed open face downwards and sealed by means of an 'o' ring located in a recess made in the face of the flange A, onto a flat metal base. A similar arrangement for the reflector assembly could be used. The seals could then be tested and adjusted if necessary to produce a vacuum tight system before being fitted to the resonance tube.

The present system of sealing each complete end assembly on to the resonance tube with high temperature cement could be improved, if higher temperatures are required. Cements are never particularly reliable for vacuum work and a better system
would be to have two steel flanges brazed at each end of the tube near its end such that the two end assemblies could be bolted on to this via a vacuum seal.

A means of enabling the system to be flushed without the need of the movable plunger at the loudspeaker end would simplify the design. A diaphragm with a series of small holes in its face, positioned to lie in the area between the end of the tube and the clamping gasket, would allow the passage of gas through the system. However, preliminary work would be necessary as to the behaviour of a diaphragm of this kind.

As regards the preparation of the oxygen-water vapour mixtures, a system more on the lines of that employed by Harris and Tempest (1964) where the oxygen was circulated through a saturator maintained at a constant temperature, would remove the need for keeping the system under vacuum for a long period. This would be especially preferable at high temperatures where the outgassing rate would be greater.

The optical system used in the present work was very satisfactory, but better lenses may improve even further on the contrast between the fringes.

A more important improvement would be some electronic scanning device to determine the point at which the first critical amplitude is reached. The saving in eye-strain of the observer would be very welcome and it would probably produce a greater reliability.

These recommendations I hope will serve as a guide to someone continuing work of this type.
Acknowledgements

I would like to express my thanks to the Vice-Chancellor and Governing Body of the University of Surrey for allowing me the opportunity to carry out the research, and the Science Research Council for supplying the grant.

I wish also to thank my supervisor, Dr. R. G. Harlow, for suggesting the problem and his help and advice throughout the period of the research.

To the technical staff, especially to Mr. F. Bristow and Mr. P. Moden, I would like to express my sincere thanks for their help and advice. Lastly, I would like to thank all the members of the Physics Department for helping to make my stay there such an enjoyable and rewarding one.
<table>
<thead>
<tr>
<th>Author</th>
<th>Journal/Book Title</th>
<th>Volume/Issue/Year</th>
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