

RELAXATION TIMES OF HIGHER
ENERGY VIBRATIONAL MODES

by

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CHAPTER 1

INTRODUCTION

Vibrational energy in a gas of polyatomic molecules can be transferred either collisionally or radiatively. The rate of a collisional energy transfer process is characterised by a relaxation time γ . This quantity is defined by the relation

$$d(\Delta T)/dt = -\Delta T/\gamma \dots\dots\dots (1.1)$$

which describes how rapidly a particular degree of freedom reverts to its equilibrium temperature after being perturbed by an amount ΔT . Radiative lifetimes of vibrationally excited states are, on a gas kinetic scale, long; even the shortest being of the order of tens of milliseconds. A molecule must therefore remain vibrationally excited for many collisions before it can fluoresce back to the ground state. Consequently, collisional relaxation usually dominates over radiative relaxation. The collisional process is characterised not only by being inefficient but by showing a vast range in inefficiency. Relaxation times at 1 atm. from 10^{-9} sec. up to 5 sec. provide a challenge for both experimentalist and theoretician (1),(2),(3).

It has been well established, even at high densities, that only isolated binary collisions are involved in the degradation of vibrational energy. Hence the measured

'relaxation time' is inversely proportional to the gas pressure and must be quoted at specified pressure and temperature. By invoking some model to define a collision (4) the observable relaxation time can be reduced to a molecular parameter, such as the probability per collision for a certain transition. Here we have the necessary link between the results of theoretical and experimental investigations:

One of the ultimate aims of chemistry must be the interpretation of chemical reaction at a molecular level. Accumulation and interpretation of knowledge about vibrational energy transfer should help us towards this end. As in chemical reaction the energy transfer process involves an intramolecular change caused by an intermolecular event. However, the changes being only small, a quite detailed specification of the system is possible on a molecular scale. We can then severely test our grasp of molecular interactions in attempting to explain the wide range of observed results. Molecules, in order to decompose, must become highly excited vibrationally or, if newly formed, must rapidly lose vibrational energy to achieve stability. Transfer of vibrational energy is, therefore, an important aspect of the current theoretical approach (5) to the prediction of absolute rates for unimolecular decomposition and atom recombination.

Many gas laser systems, especially those operating in the infra-red e.g. CO₂-N₂ laser (6), depend for their design and operation upon an appreciation of vibrational relaxation processes.

More generally, vibrational relaxation means that the thermodynamic properties of gases are time-dependent. By observing some suitable bulk property of a gas in a system incorporating a built-in time scale relaxation times can therefore be measured. The classical techniques in the field, the dispersion and absorption of ultrasonic waves, measure the time-dependence of the heat capacity against the frequency of the ultrasound. Until recently most of our knowledge about energy transfer came from ultrasonic measurements (1). Acoustical methods are, however, fundamentally limited in scope since the energy which probes the translational-vibrational coupling is supplied to the translational mode. Very high, experimentally inaccessible temperatures are required before the populations of the higher energy modes in a molecule contribute sufficiently to the heat capacity to make them 'visible'. This upper energy limit to ultrasonic investigation ($\sim 1,500 \text{ cm}^{-1}$) is used to define, rather arbitrarily, what we mean by a "Higher energy vibrational mode". Furthermore, after the translational temperature is perturbed the energy relaxes up into all the accessible vibrational modes and the observed relaxation time cannot refer to any one in particular. The technique is non-specific. By postulating a model (1), ultrasonic workers endeavour to improve their measurement (γ) by conversion into a reduced relaxation time (β) which is taken to refer to the lowest vibrational mode in the molecule. Development (1), (8) from the basic theory of Zener (9) has produced, on the whole, good agreement between

calculation and experiment for the relaxation times of the low energy modes of simple molecules.

The theory of energy transfer from the higher modes is not well developed (10), (11), reliable experimental results being scarce. In addition to simple collisions transferring vibrational energy directly to translation ($V \longleftrightarrow T$ process), the possibility of 'complex collisions' must be considered. These involve an exchange of vibrational energy between the internal modes of collision partners ($V \longleftrightarrow V$ process). A simple example easily demonstrates the great importance 'complex collisions' can have in removing energy from the higher modes in a polyatomic molecule. Consider the ν_3 -mode in carbon dioxide (2349 cm^{-1}). Direct de-excitation by simple collision would have a relaxation time of many seconds. (c.f. $\text{CO}_2 \nu_2 = 2143 \text{ cm}^{-1}$, $\tau = 4 \text{ sec}$ (12)) Transfer by a $V \longleftrightarrow V$ process to the third harmonic of the ν_2 bending mode, then a rapid 'cascade' down to the fundamental ν_2 which relaxes with a τ of $6.5 \text{ } \mu\text{sec}$ (1) might show an overall relaxation time of $7 \text{ } \mu\text{sec}$. The possibility of complex collision has improved the efficiency of the energy transfer by a factor of a million.

Much more information is required about the relaxation times of higher energy vibrational modes and this research has been concerned with the further (13) development of a technique for their measurement. During the construction of apparatus an ultrasonic method for studying non-ideality in polar gases was developed. This work is reported at the end of the thesis.

CHAPTER 2

METHODS FOR HIGHER ENERGY VIBRATIONAL MODES.

What are the problems facing the experimentalist who wishes to study the relaxation of specific higher energy modes? After finding some means of exciting the vibration he must be able to measure how swiftly the energy returns to its equilibrium value. Such a system will measure a "relaxation time" as defined by (1.1). It is also possible to learn about energy transfer by introducing the perturbation at one level, say vibration, and watching the energy reappearing, after a time lag, at another level, say translation, c.f. the 'spectrophone'. However, without being aware of the degradation mechanism one isn't fully justified in equating this time lag with the "relaxation time" of the specific mode initially excited (see p.65).

Absorption of suitably energetic radiation makes the specific excitation of an infra-red active mode easy. Otherwise, generation of a high translational temperature in the gas, as in a shock-tube, can be used to non-specifically excite all the modes in the molecules. Furthermore, some vibrationally excited species e.g. $N_2(V=1)$ (14) are extremely stable to both collisional and radiative degradation. A high concentration of these, allowed to mix with a gas of polyatomic molecules, will increase the vibrational temperature of the most nearly resonant mode (15), (16). For small energy differences this $V \leftrightarrow V$ transfer may be very rapid

e.g. $\text{N}_2(2,331 \text{ cm}^{-1})$ and $\text{CO}_2(2,349 \text{ cm}^{-1})$ (6) or N_2 and $\text{CO}(2143 \text{ cm}^{-1})(17)$. On the other hand, a considerable mismatch may provide an opportunity for measuring a slow $V \leftrightarrow V$ process e.g. CO^* and $\text{CH}_4, \Delta \sim 617 \text{ cm}^{-1}$ (18). Lastly, when the heat of a reaction appears largely as the vibrational energy of the product, chemically activated molecules (19), excited to very high vibrational levels, are made available.

How have these sources of vibrationally excited molecules been exploited in the current techniques for relaxation measurement?

THE SPECTROPHONE: Having excited a particular vibrational mode by irradiating the gas at the appropriate wavelength, the energy is collisionally degraded to translation. If the radiation is modulated at sonic frequencies, then there will be a corresponding oscillation in the translational temperature, which, in a constant volume system, will generate a sound wave. Because of relaxation this sound wave will lag behind the modulated radiation input. In principle, measurement of the phase lag provides an ideal method for preferentially studying energy transfer from specific vibrational levels. Since the object of this research has been the design and operation of a 'reliable' spectrophone, further comment on the topic will be reserved for the next chapter.

THE SHOCK TUBE: High translational temperatures are rapidly, uniformly and homogeneously generated in a gas by the sharp

adiabatic compression associated with the passage of a shock wave. Gas at ambient temperature ahead of the shock must pass through a region of change, the "shock front", before returning to equilibrium at the much higher temperature of the 'shocked' sample. Within some ten collisions of the incident shock the molecular motion has been randomised to a new translational temperature. For all but monatomic gases the ensuing redistribution of energy among the translational, vibrational and rotational modes extends the shock front. Investigation of shock front structures has therefore been widely used (3) for studying the mechanics of energy transfer at high temperatures (800 - 5,000°K).

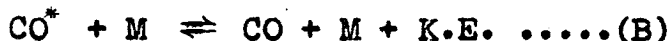
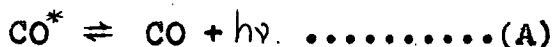
Because of fluid dynamic constraints, the vibrational relaxation region is one of essentially constant pressure. Therefore, as the translational temperature of the gas falls (in order to supply energy to the vibrational modes) there is a corresponding rise in gas density. Various techniques have been developed (1), (3) to study the resultant density profile at the shock front. By following the relaxation of the translational temperature, however, only a general rate constant, describing the flow of energy into all the accessible vibrational modes, is measurable.

There have also been several attempts at defining the vibrational temperature in a shock front. The growth of the infra-red emission from shock-heated gas has been used to

follow the excitation of specific modes. Several molecules, including carbon monoxide (20), (21), carbon dioxide (22) and the hydrogen halides (23) have been studied in this manner. Although still a matter of debate (3) alkali metal atoms in a shock front are thought to follow the vibrational rather than the translational temperature of the gas, allowing measurement of vibrational excitation by the sodium line reversal techniques (24). Obviously the shock tube's future in this field will depend upon the discovery of observables sensitive to specific vibrational temperatures. Several ideas of less general application than those described above already seem promising. The method of Richards and Sigafos (25) for methane serves to illustrate the type: since only vibrationally excited methane molecules can absorb the $1470\overset{\circ}{\text{A}}$ Xenon resonance radiation, the continuum of the first electronic level starting from $\lambda \leq 1455\overset{\circ}{\text{A}}$, the observed absorption coefficient is a function of the vibrational temperature.

QUENCHING OF VIBRATIONAL FLUORESCENCE: It has already been stated (p. 1) that collisional relaxation usually dominates over radiative relaxation. If, however, the relaxation time and the radiative lifetime are of the same order of magnitude the two processes will compete. Under these circumstances, for an optically thin gas (no self-absorption), the 'radiative lifetime', being independent of both pressure and temperature, can be used to gauge the rate of collisional degradation. Applying these ideas Millikan has developed a quenching experiment to study

relaxation in carbon monoxide mixtures (26), (27), (28).

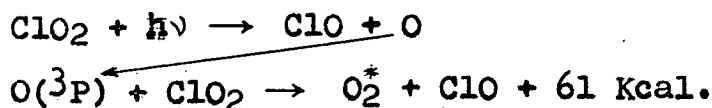


The radiative lifetime corresponding to (A) is 0.033 sec., while the relaxation time (B) at 300°K and 1 atm. pressure is >1 sec. if M is CO or Ar. Under strict experimental conditions the carbon monoxide, raised by irradiation to a vibrational temperature of 1,000°K, returns all the energy as resonance fluorescence. If the chance of collisional degradation is now increased by introducing, in known amounts, some more efficient collision partner M (e.g. H₂, CH₄) the intensity of the observed fluorescence is decreased. At 'half-quenching' the rates of the radiative and collisional processes have been equalised.

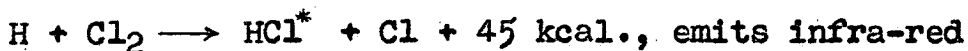
Another consequence of competition between radiative and collisional energy transfer has been exploited at Edinburgh, where a spectrophone experiment (see p. 6) has been used to measure the relaxation times of pure carbon monoxide (12) and the hydrogen halides (7). Incident energy absorbed by the gas but lost in fluorescence cannot contribute to the collisionally generated optic-acoustic signal. Comparison, therefore, of the signal level in the pure gas with that developed after fluorescence has been fully quenched by some efficient collision partner e.g. H₂, leads to a value for the pure gas relaxation time.

SPECTROSCOPIC METHODS: Both absorption and emission spectroscopy have been used to follow directly the redistribution of energy among the vibrational levels of highly excited molecules.

Excited species formed in flash photolysis experiments (29) e.g.



have been studied by recording the ultra-violet absorption spectra at progressively longer delay times after the flash. Hydrogen chloride, chemically activated during its formation in the reaction



chemiluminescence used by Charters and Polanyi (30) to determine the populations in the various vibrational and rotational levels. Such techniques have been usefully applied to a number of simple systems.

CONCLUSION: Of the two problems posed to the experimentalist at the outset of this discussion it has been the second, the measurement of specific vibrational temperatures, which has proved more difficult. No generally applicable method has evolved. A suggestion by Gauthier and Marcoux (31) might give a lead to future developments. Since the intensity of a mode's infra-red absorption depends upon the rate of change of dipole moment during vibration, the first excited level should absorb more strongly than the ground state. They applied this idea to the ν_3 -mode of nitrous oxide. Now, if tunable I.R. lasers

become available their highly monochromatic output will permit a much sharper distinction between the ground and excited states to be exploited. By tuning the laser radiation to a unique rotational line in an upper level the observed absorption coefficient will give a specific and instantaneous (rotational relaxation being very rapid) measure of the vibrational temperature of the mode.

THE OPTIC ACOUSTIC EFFECT AND ENERGY TRANSFER.

That certain gases, when subjected to modulated irradiation, emit sound was discovered independently by three workers as early as 1881 (32), (33), (34). One of these, Tyndall, established that the pressure rise was caused by absorption of energy near the red end of the visible spectrum, now known to be the infra-red region, but the lack of a convenient sound detector halted further progress. Not until 1938 was interest in the 'optic-acoustic effect' revived. Aided by a deeper understanding of the interactions between molecules and radiation and by the availability of developed microphonic and electronic technique several workers constructed optic-acoustic gas analysers (35), (36), (37). By incorporating a monochromator into his equipment Veingerov (38), using the strength of the optic acoustic signal as a measure of the gas's intensity of absorption, recorded infra-red spectra of good resolution. This device was called a "Spectrophone".

To date, all attempts to measure relaxation times with the Spectrophone have been based on Gorelik's original suggestion (39). He pointed out that if there is a time lag between the absorption of a vibrational quantum and its degradation to thermal energy, then it should determine a phase difference between the modulation of the incident radiation and the emitted sound wave (c.f.p.6) Although, according to an analysis by Cottrell (40), the frequency dependence of the mean translational temperature is also

determined by the translational-vibrational relaxation time, the effect was later (1) shown to be probably very small (1 in 10^4 - 10^5). Delaney (41) confirmed this estimate, being unable to experimentally detect any change.

Theoretically, the optic-acoustic effect has been treated in two ways. Both, the kinetic-molecular treatment used by Delaney (41) and Kaiser (42) and the thermodynamic treatment started by Gorelik (39) and developed by Cottrell and McCoubrey (1), predict the same frequency dependences (13) for the phase and the amplitude of the sound wave. The treatment due to Cottrell and McCoubrey will be followed.

We consider a volume of gas whose linear dimensions are small compared with the length of the sound wave which corresponds to the frequency of modulation of the infra-red radiation. For an average gas at a frequency of a few hundred cycles per second the wavelength of sound is between 10 and 100 cm., thus this condition is easily fulfilled. The state of the gas is characterised by two temperatures, T_{tr} and T_{vib} . These are the translational (and rotational) and vibrational temperatures and it is assumed that they are not in equilibrium with each other. $W_{tr}dt$ and $W_{vib}dt$ are the energies received from outside during time dt by each of these groups and C_{tr} and C_{vib} are their respective heat capacities. The energy transmitted in time dt from the group at T_{tr} to the group at T_{vib} is $\propto (T_{tr} - T_{vib}) dt$ and the energies given by each of

these groups to the environment (at temperature T_0) are respectively $\beta_1(T_{tr} - T_0) dt$ and $\beta_2(T_{vib} - T_0) dt$. The principle of conservation of energy gives the equations:

$$C_{tr} \frac{dT_{tr}}{dt} + \alpha(T_{tr} - T_{vib}) + \beta_1(T_{tr} - T_0) = W_{tr} \dots\dots (3.1)$$

$$\text{and } C_{vib} \frac{dT_{vib}}{dt} + \alpha(T_{vib} - T_{tr}) + \beta_2(T_{vib} - T_0) = W_{vib} \dots\dots (3.2)$$

$W_{tr} = 0$, since the volume of the system is assumed constant, and $W_{vib} = W_0 + A \exp(i\omega t)$, ω being the angular frequency of modulation of the radiation and W_0 , A being constants. The temperature of the gas may be expressed as ..

$$T_{tr} = \bar{T}_{tr} + \theta_{tr} \exp(i\omega t) \dots\dots\dots (3.3)$$

$$T_{vib} = \bar{T}_{vib} + \theta_{vib} \exp(i\omega t) \dots\dots\dots (3.4)$$

θ_{tr} is the oscillatory part of the translational temperature which, for a constant volume system, is proportional to the oscillatory part of the pressure. We therefore require to calculate θ_{tr} as a function of the oscillatory part of the energy input. Inserting these expressions for the temperature, considering only the oscillatory part of the equations, we have

$$\theta_{tr} = \frac{\alpha A}{\Delta} \dots\dots\dots (3.5)$$

where: $\Delta = \alpha(\beta_1 + \beta_2) + \beta_1 \beta_2 + i\omega(\alpha C + \beta_2 C_{tr} + \beta_1 C_{vib}) - \beta_1 \beta_2 C_{tr} C_{vib}$

$$\text{and } C = C_{tr} + C_{vib}$$

The assumption is now made that energy transfer from vibration to translation is much quicker than energy transfer from the apparatus to the environment.

Thus $\alpha \gg \beta_1, \beta_2$

and
$$\theta_{tr} = \frac{\alpha A}{i\omega C - \omega^2 C_{tr} C_{vib}}$$

which leads to

$$|\theta_{tr}| = \frac{A}{\omega C \left(1 + \frac{\omega^2 C_{tr} C_{vib}}{\alpha^2 C^2} \right)^{\frac{1}{2}}} \dots\dots\dots(3.6)$$

If ϕ is the phase angle between θ_{tr} and A,

$$\tan \phi = \frac{\alpha C}{\omega C_{tr} C_{vib}} \dots\dots\dots(3.7)$$

We now require a molecular interpretation for α .

The energy transmitted in time dt from the group of molecules at T_{tr} to the group at T_{vib} is

$$dE = \alpha (T_{tr} - T_{vib}) dt$$

$$\therefore \frac{dE}{dt} = \alpha \Delta T \text{ where } \Delta T = T_{tr} - T_{vib} \dots\dots(3.8)$$

But
$$\frac{dE}{dt} = -C_{vib} \frac{d\Delta T}{dt} \dots\dots\dots(3.9)$$

Therefore, from (3.8) and (3.9)

$$\frac{-d\Delta T}{dt} = \frac{\alpha}{C_{vib}} \Delta T$$

and comparing this with (1.1) we see that

$$\frac{\alpha}{C_{vib}} = \frac{1}{\tau} \dots\dots\dots(3.10)$$

For a two state gas (vibrational levels 0 and 1)

$$\frac{1}{\gamma} = f_{10} + f_{01} \dots \dots \dots (3.11)$$

where f_{10} and f_{01} are transition probabilities per molecule per second for the $1 \rightarrow 0$ and $0 \rightarrow 1$ processes.

Now:- $f_{01} = f_{10} \exp(-h\nu/kT) \dots \dots \dots (3.12)$

where ν is the vibration frequency.

For $\exp(-h\nu/kT) \ll 1$, (3.11) becomes:-

$$1/\gamma = f_{10}$$

and hence $\alpha = C_{vib} f_{10} \dots \dots \dots (3.13)$

With the more usual energy transfer notation where $C_{tr} + C_{vib} = C_o$

and $C_{tr} = C_o$, (3.7) may be written as

$$\tan \phi = \frac{f_{10}}{\omega} \frac{C_o}{C_o}$$

or as $\tan \left(\frac{\pi}{2} - \phi \right) = \frac{\omega}{f_{10}} \frac{C_o}{C_o} \dots \dots \dots (3.14)$

defines the phase (ϕ) of the oscillatory component of the translational temperature relative to the modulated light input and, substituting for α in (3.6):-

$$|\theta_{tr}| = \frac{A}{\omega C_o \left(1 + \frac{\omega^2}{f_{10}^2} \left\{ \frac{C_o}{C_o} \right\}^2 \right)^{1/2}} \dots \dots \dots (3.15)$$

gives the amplitude of the

fluctuations. Consider two cases; for modulation frequencies low compared with f_{10} , then:-

- $\omega \ll f_{10}$ (1) sound wave is 90° out of phase with vibrational energy input i.e. $(\pi/2 - \phi) \sim 0$ (Eq. 3.14), and;
- (2) amplitude is inversely proportional to the frequency i.e. $|\Theta_{tr}| \sim A/\omega C_0$ (Eq. 3.15),

but as ω becomes comparable with f_{10} , then:-

- $\omega \gg f_{10}$ (1) a phase lag develops, defined by $\phi = \tan^{-1} \gamma$ (3.14); $C_0 \sim C_\omega$, especially for γ large), and:-
- (2) amplitude becomes inversely proportional to the second power of the frequency.

The full relationships are plotted, in Fig. 1 for the phase change and in Fig. 2 for the amplitude. The frequency dependence, therefore, of either the phase or the amplitude of the optic-acoustic signal should give information about gaseous relaxation times.

Of the several assumptions required by this analysis of Gorelik's model only one seems capable of deviating sufficiently from reality, under practical conditions, to invalidate the theory: that $\alpha \gg \beta_1, \beta_2$. Here, it has been assumed that the transfer of heat from the gas to the environment occurs at a rate negligible in comparison with that of the relaxation mechanism. Refining the basic equations to take account of the heat conduction effect Dehany (41) defined a parameter μ which must be $\ll \omega$ for wall effects to be negligible.

$$\mu = \frac{K_0 \pi^2}{\rho \cdot C_m a^2} \dots \dots \dots (3.16)$$

where: K is the thermal conductivity of the gas, ρ is its density,

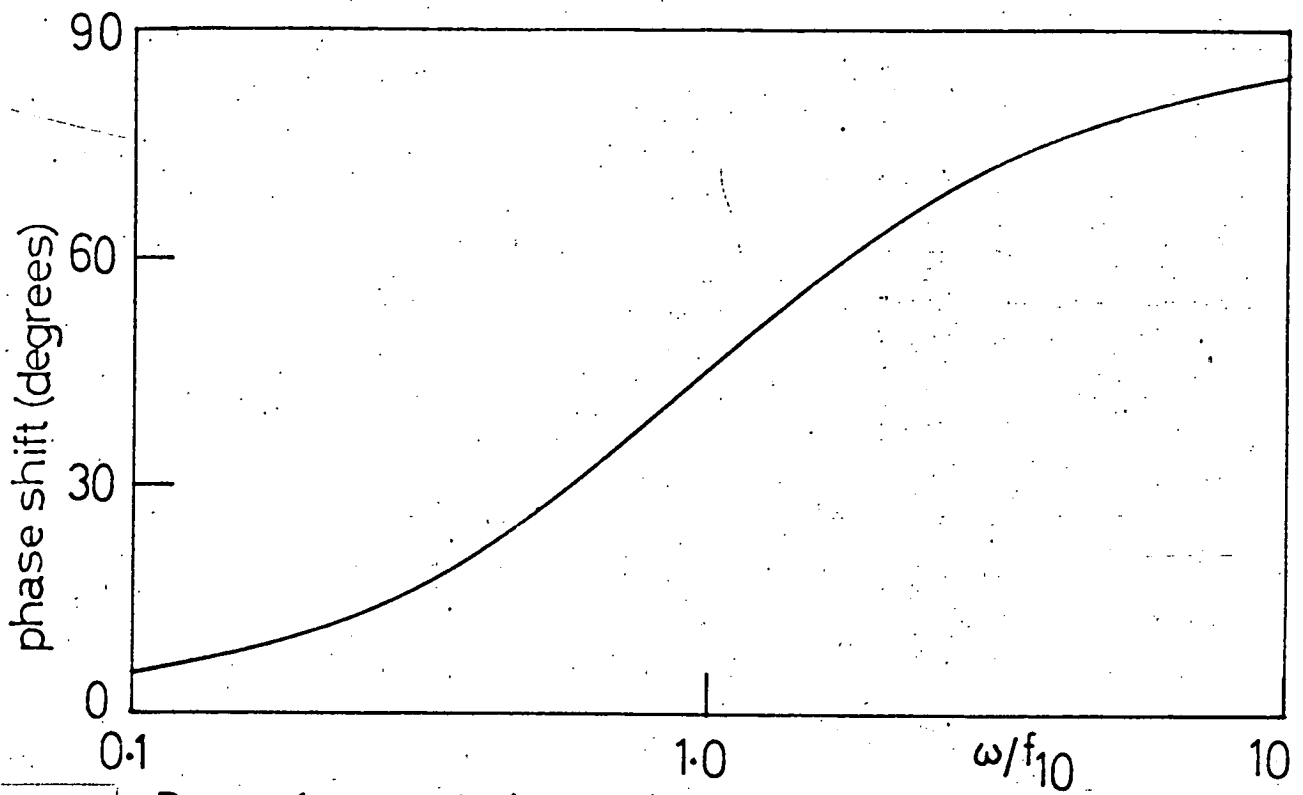


FIG.1 : Dependence of phase shift upon ω/f_{10}

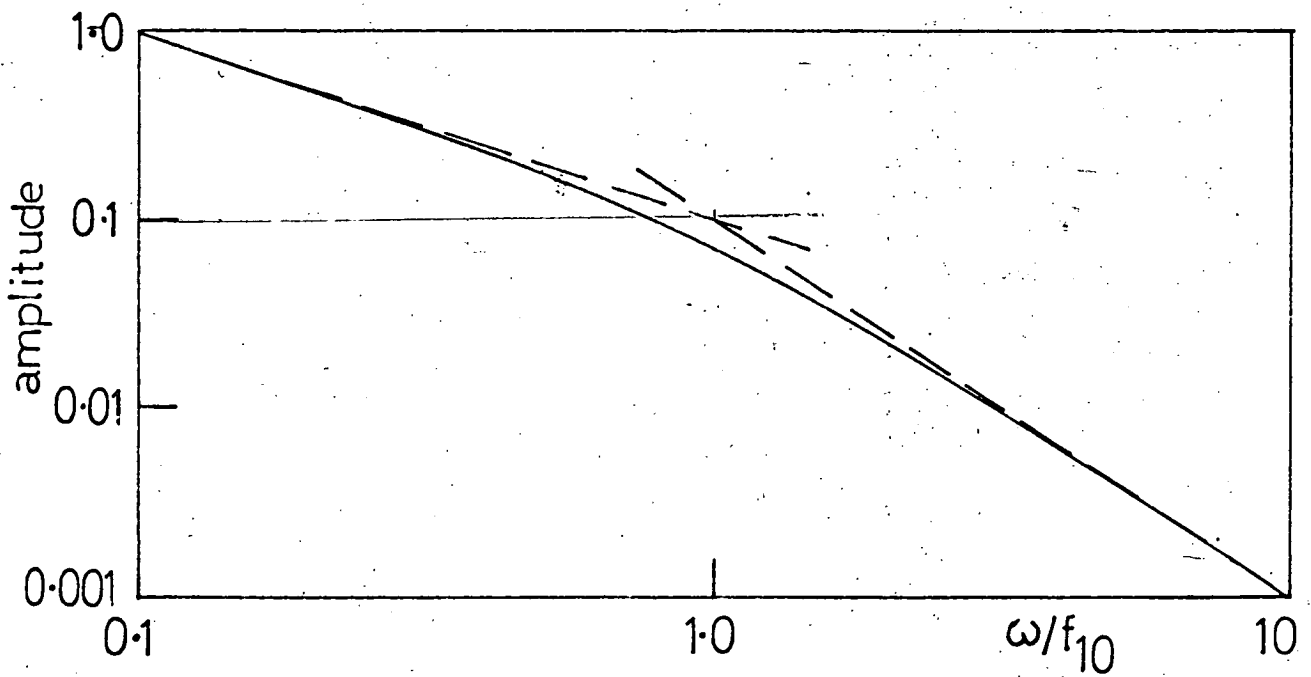


FIG.2 : Dependence of amplitude upon ω/f_{10}

C_m the specific heat per unit mass and 'a', the radius of the vessel (considered spherical). The relevant gas property, termed the "thermal diffusivity" $\Delta = K/\rho C_m$, should give an idea of when and how the simple Gorelik model might be expected to break down. Introducing a frequency dependent phase lead and decreasing the amplitude of the acoustic pressure, thermal diffusivity can interfere with both the observables suitable for relaxation studies. For an average gas e.g. carbon dioxide at S.T.P. $\Delta \sim 10^{-1} \text{cm}^2 \text{sec}^{-1}$, giving $\mu \sim 1 \text{sec}^{-1}$ for a vessel of radius 1 cm. However, for a light gas, e.g. methane at 0.01 atm. pressure $\mu \sim 300 \text{sec}^{-1}$, and a high modulation frequency would be required to damp the effect, the calculated phase lead at $\omega^{250}/\text{c}/\text{sec}$ (1571rad.sec^{-1}) being $\sim 10^\circ$. Furthermore, the efficiency of the relaxation process is also important for the continuing satisfaction of the inequality $\alpha \gg \beta_1 \beta_2$. If, in addition to β_1 and β_2 increasing α undergoes a large and simultaneous reduction e.g. CO_2/N_2 mixtures (see Chapt.7) then this crucial condition and hence the validity of the Gorelik treatment may be easily broken. Experimentally, however, it is possible to focus attention on the relaxation phenomenon by raising the modulation frequency (ω) to a sufficiently high level.

Elsewhere it was assumed that $\exp(-h\nu/kT) \ll 1$ and that the gas had a uniform temperature. For a gas at 300°K , and with a vibration frequency of $1,000 \text{cm}^{-1}$ $\exp(-h\nu/kT) = 8 \times 10^{-3}$. The latter, however, is not strictly true, but, Delaney (41), on

calculating the temperature distribution and hence the average temperature for spherical and cylindrical vessels, obtained results agreeing with those of the simple theory. Delaney, in his extensive study of the optic-acoustic effect (41),(43), has also experimentally confirmed the predictions of the simple model within its range of applicability.

In addition to the phenomena due to these two fundamental processes, relaxation and heat conduction, further frequency-dependent effects can arise from the properties of the apparatus. Indeed, recognition and elimination of spurious phase and amplitude changes, defines essentially the problem of 'spectrophony'. There have been two lines of attack. The first, pioneered by Slobodskaya in Russia (44), sets out to measure phase lags while the second, pursued by Decius in the U.S.A.(45), uses the frequency-dependence of the signal amplitude.

EXPERIMENTAL DEVELOPMENT: Although there have been important developments in the technique of spectrophony over the past fifteen years, the basic experiment has remained the same (Fig.3) A beam of infra-red radiation, condensed and filtered through an optical system, is modulated by a motor-driven chopping disc and focussed into a spectrophone cell filled with the absorbing gas. The optic-acoustic signal generated is detected by a sensitive microphone whose output can be compared with a

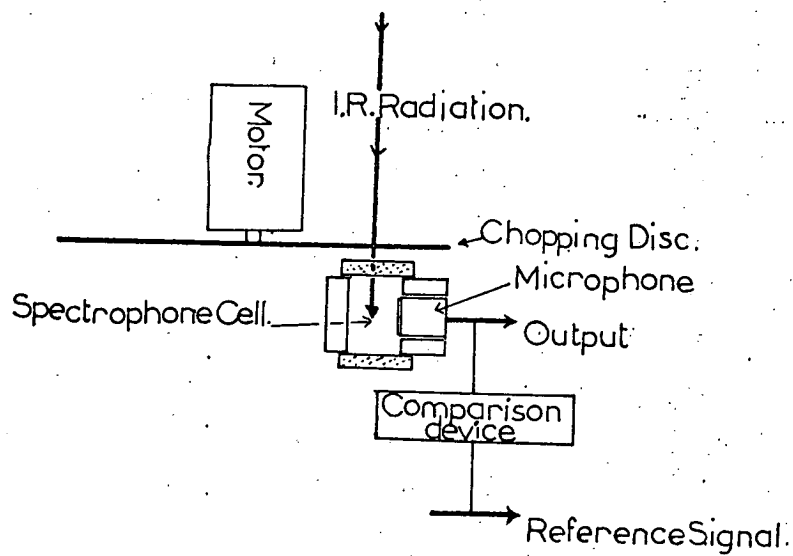


FIG 3: SPECTROPHONE Experiment.

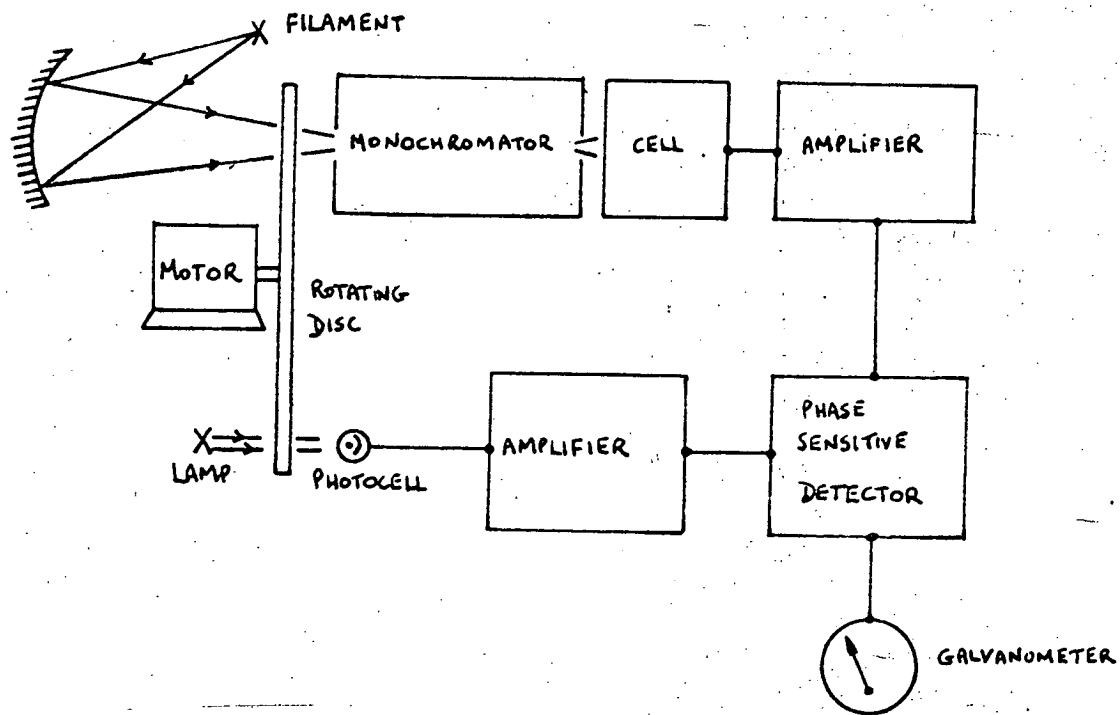


FIG. 4. Diagram of Slobodskaya & Gasilevich apparatus.

reference for either phase or amplitude properties. Since the bulk of gas in the cell and the microphone diaphragm are in oscillation, gross interference from resonances is possible and can modify both phase and amplitude readings.

Phase changes, experimentally determined, can be split into four components:

$$\phi_{Exp} = \phi_{Relax} + \phi_{Dia} + \phi_{Elec.} + \phi_{gas} ; \dots (3.17)$$

where:

ϕ_{Relax} is the required phase lag

$\phi_{Dia.}$ is the phase shift due to diaphragm properties

$\phi_{Elec.}$ is the phase shift caused by the Electronics of the detection system

$\phi_{Gas.}$ is the phase shift caused by variations in gas properties e.g. thermal diffusivity, sound velocity.

Slobodskaya's exploratory work (44), although not very productive in terms of relaxation measurements, established an approach which formed the basis for a study on carbon dioxide-nitrogen mixtures by Slobodskaya and Gasilevich (46). Their spectrophone system (Fig.4) provided a reference signal of adjustable and measurable phase from a photocell and lamp for an electronic null-comparison with the microphone output. Phase lags were measured for a series of mixture compositions at a number of modulation frequencies but at constant gas pressure. Since nitrogen is very inefficient in de-exciting carbon dioxide, the relaxation lags, very large at low CO₂ concentrations, decrease with the proportion of nitrogen until, at high CO₂ concentrations

they fall below the detection level of the system. Therefore, by assuming the apparatus phase shift ($\phi_{\text{Dia}} + \phi_{\text{Elec}} + \phi_{\text{Gas}}$) to be independent of mixture composition its value is determined by the asymptote of the phase characteristic. That the lags measured relative to this level for the 4.3μ band described relaxation times (τ) self-consistent for the various modulation frequencies, was taken as proof of the method's validity. No direct confirmation about the behaviour of the apparatus phase shift was, however, attempted and the phase characteristic associated with the 2.7μ mode was anomalous, passing through a maximum. Although the results do not follow the simple relationship $1/\tau \propto (\text{CO}_2)$ an extrapolation based on its applicability has been forced (41) to give a relaxation time of $12 \mu\text{sec}$ for the 4.3μ band in carbon dioxide.

Thus, essentially Slobodskaya's approach requires the relaxing gas to be mixed with an inefficient diluent which lengthens the relaxation time of the mixture. By measuring phase changes as a function of mixture composition an estimate of the apparatus phase shift, assumed constant for constant gas pressure is given at the fast-relaxing end of the scale and is used to correct the observations made at the slow-relaxing end. Now, if the possibility is accepted of controlling the apparatus phase shift, even under conditions of changing pressure, a much more flexible experiment is conceivable. Lowering the gas pressure reduces the collision frequency and hence lengthens the relaxation time. Both single gases and

mixtures can, therefore, be studied by the pressure-dependence of their phase shifts and the non-participation of the apparatus can be checked with fast relaxing gases in which τ_{Relax} is Zero.

A first attempt at the pressure-dependent method was reported by Jacox and Bauer (47) who observed the phase shifts in a number of gases at a high modulation frequency (2.550 kc/sec). However, gross deviations from the theoretical lines, thought to have been due to the inertial phase lag of the microphone (τ_{Dia}), completely obscured any connection the results may have had with relaxation processes.

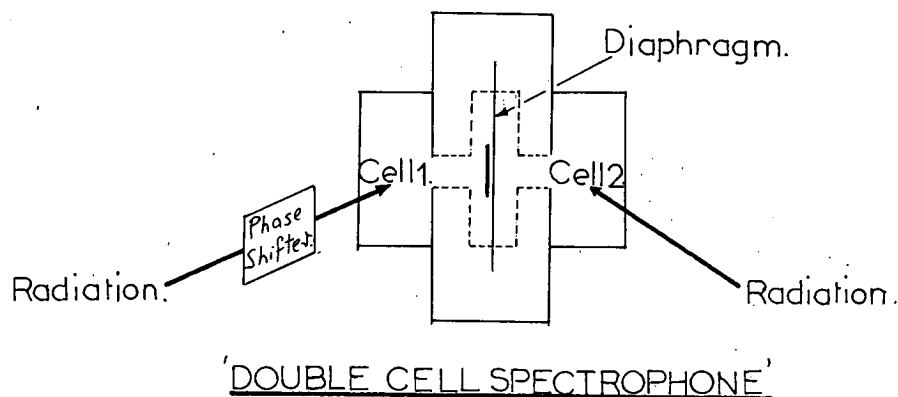
Delaney (41), measuring phase lags electronically and determining the inherent microphone phase shift (τ_{Dia}) by a reciprocity technique before each measurement, studied (at 520 c/sec) carbon monoxide and carbon dioxide by both the Slobodskaya-type and the pressure-dependent methods. Although the performance of the apparatus seems to have been faultless the gas purities were suspect; the carbon monoxide result at 13 μsec being too short by five orders of magnitude (12). When examined over a pressure range, the 4.3 μ band in carbon dioxide was found to relax in 2.3 μsec , but when a series of CO_2/N_2 mixtures was analysed in terms of a linear relation between $1/\tau$ and (CO_2) , the relaxation time was estimated at 11 μsec . Delaney suggests that the 2.3 μsec value has been lowered by impurities.

Recently, the frequency response of an I.R. gas analyser has been expressed in terms of thermal effects,

influence of capillary passages and the relaxation time of the gas (48). An electrostatic compensation technique was used to trace the frequency-dependence of the signal phase in carbon monoxide-nitrogen mixtures between 2 and 100 c/sec. By fitting the results to the theoretical expression a value of 300 μ sec emerges for the relaxation time of carbon monoxide: very short. The author invokes impurity effects, but attempting to separate several closely involved phenomena in the analysis of results must always be inferior to experimentally limiting attention to one. This approach can have little future, therefore, in energy transfer studies.

Turning now to the work involving the frequency-dependence of signal amplitude, Woodmansee and Decius (45) have reported a study on carbon monoxide in which they find $\tau \sim 2$ msec. Once more the fact that the gas produced any optic-acoustic signal at all proved its impurity (p. 9). It is unfortunate that carbon monoxide attracted the attention of spectrophone workers during the development of their equipment because its very long relaxation time is exceedingly sensitive to impurities and in a static metal system adequate purity control is impossible. However, Decius's measurements were also hampered by resonances in the cell. Although these were thought to be standing waves made possible by the compliance of the microphone diaphragm, Helmholtz resonances set up by the shape of the cell cavity are much more likely. Redesign of the system has cured the resonance problem and the ν_3 mode in methane is being studied

at modulation frequencies up to 1,600 c/sec.(49). A novel spectrophone system for unambiguously isolating relaxation phase lags from other gas and apparatus effects was suggested by Cottrell (50) and investigated by Read (13).

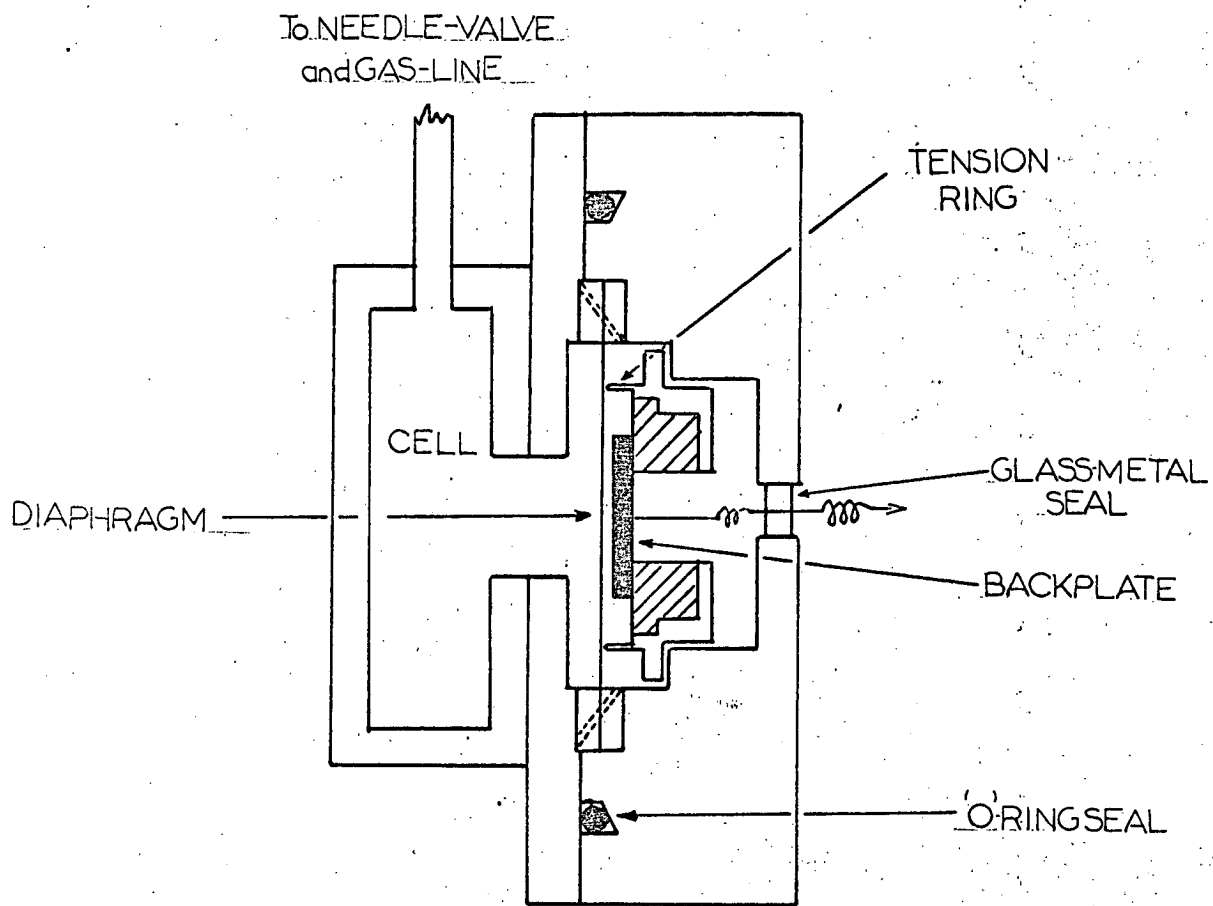


Optic-acoustic signals of equal amplitude generated in two volumes (1 and 2) of gas separated by a microphone diaphragm will be in phase with one another when the microphone diaphragm remains stationary ($\therefore \phi_{Dia} = 0$) and no signal is detected ($\therefore \phi_{E1} \cong 0$). By matching gas properties ($\therefore \phi_{Gas} = 0$), the phase lag which has to be introduced into the beam illuminating a fast-relaxing gas in cell 1 is a direct measure of the relaxation lag characteristic of the gas in cell 2. Unfortunately, while the diaphragm had to be stiff to separate the gases, the detection of the low signals near to balance demanded great flexibility. These two requirements were incompatible.

Some of the advantages of this conceptually elegant device were salvaged in a two-cell spectrophone system which Read (13) then developed. Instead of generating a reference

signal for phase comparisons with a photocell it was supplied by a second spectrophone filled with a fast relaxing gas. By matching cell sensitivities and gas properties it was hoped to eliminate most of the apparatus phaseshift ($\phi_{\text{Dia}} + \phi_{\text{Gas}} + \phi_{\text{El}}$). Several gases (CO_2 , N_2O , CH_4) were briefly studied at one modulation frequency (189 c/sec) and a relaxation time of 100 μsec for the ν_3 mode of methane was reported (51).

The initial promise of the two-cell approach encouraged further work to confirm its preliminary results and to establish the technique more solidly. These aims motivated the research currently being reported.



0 1 2cm.

FIG 5: A SPECTROPHONE CELL

CHAPTER 4

"THE TWO-CELL SPECTROPHONE EXPERIMENT".

As the two-cell spectrophone experiment had seemed to offer a superior method for studying relaxation processes involving higher energy modes it was decided firstly to consolidate on Read's results (13); then to establish the experiment on an absolute basis by measuring an ultrasonically determined mode e.g. ν_4 in methane.

In this system phase comparison of signals from two spectrophone cells is used. A fast-relaxing gas generates a reference signal in one cell with which the lagging output from a gas with a long relaxation time is compared. It should be possible, therefore, to compensate to some extent for non-relaxion phase shifts.

SPECTROPHONES: The brass spectrophone cells (Fig.5) have condenser microphone diaphragms made from metallized 'Melinex' polyester film (35 gauge) stretched on an adjustable tensioning ring. The position of the condenser back-plate is also adjustable. A 2 cm. absorption path is bounded by polished sodium chloride windows. The cells are connected to a conventional high-vacuum system by needle valves, and external vibration is minimised by fixing the spectrophone to a rubber-mounted steel plate supported from a main wall of the building.

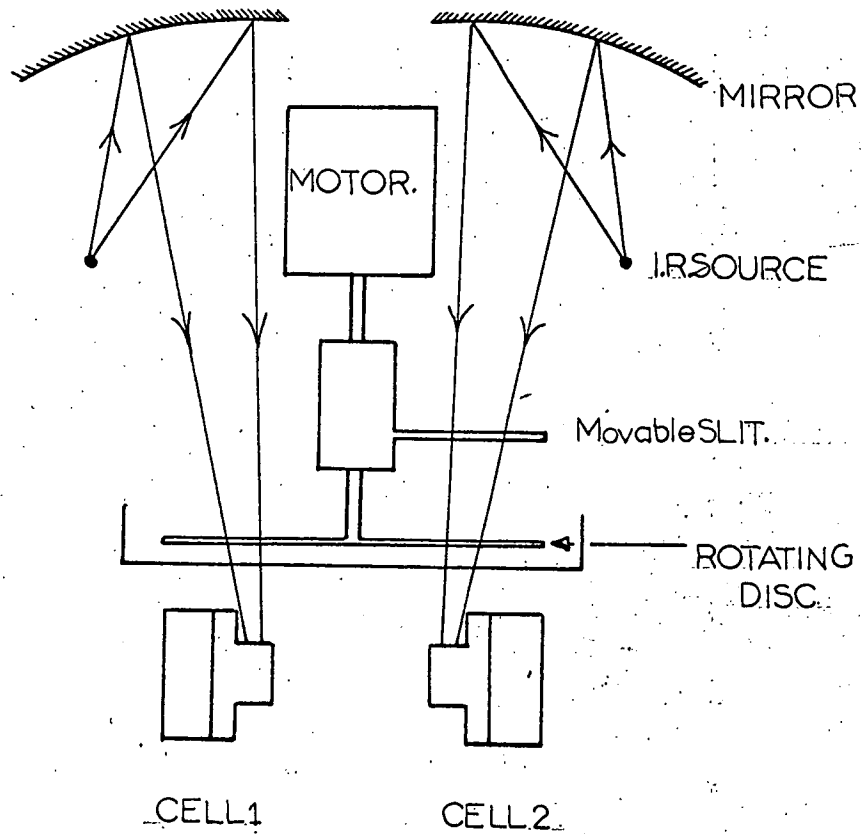


FIG. 6: OPTICAL SYSTEM

OPTICAL SYSTEM: (Fig.6): Infra-red energy from two electrically (13 v, 120 amp) heated nichrome rods (7 cm. long, 0.3 cm. dia.) is focussed by 23 cm. dia. front-silvered mirrors. The radiation is modulated by a chopping disc, driven by a Synchronous motor. The phase of one of the beams is controlled by a movable slit which can be rotated about the same axis as the rotating disc. Angular movement of the slit shifts the path of the light beam round the arc of the chopping disc, hence altering its phase of modulation with respect to the other beam. When necessary, low energy radiation ($< 1,700 \text{ cm}^{-1}$) is eliminated by an optical filter (Barr & Stround calcium aluminate glass type BS.39B).

ELECTRONICS: Each spectrophone has a detecting channel, one of which is shown as a block diagram in Fig.7. The diaphragm acts as the tuning capacitor of a solid state Franklin oscillator and produces a 10.7 Mc/s carrier wave whose deviation is proportional to pressure fluctuations. Conventional frequency modulation and detection techniques, followed by selective amplification of the audio output, allow the two signals to be displayed on an oscilloscope for phase comparison. Basic signal output is monitored by a long-time-constant millivoltmeter and a meter indication is given of carrier frequency.

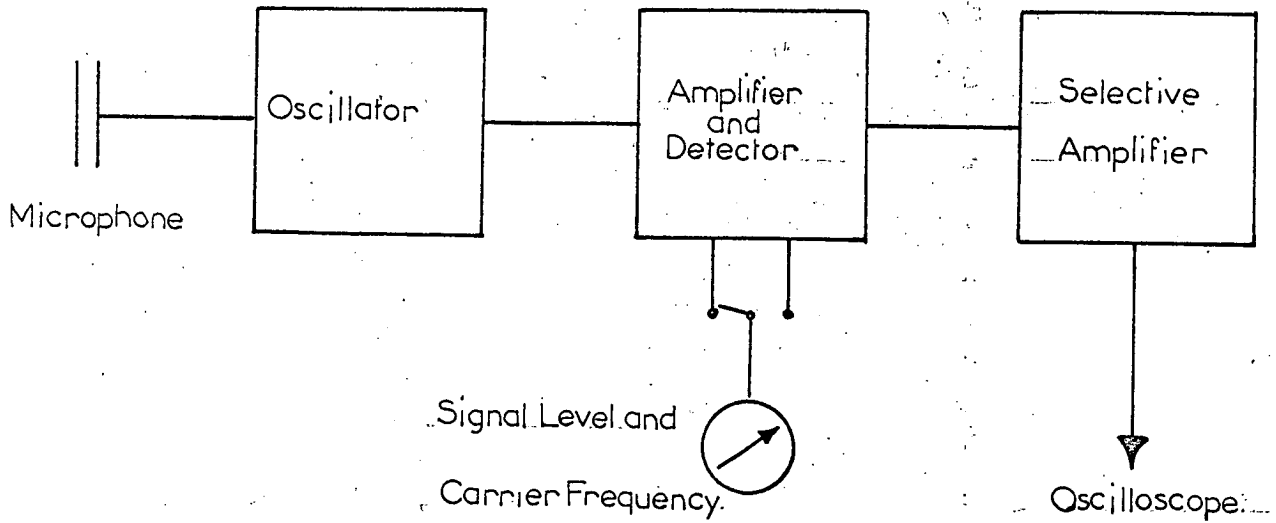


FIG.7: BLOCK DIAGRAM OF ELECTRONICS

EXPERIMENTAL PROCEDURE: The sensitivities of the microphones in the two cells were matched as closely as possible, using a loudspeaker driven at the chopping frequency to provide the input. Complete matching of the cells was never achieved.

In fact microphone sensitivity was not a constant, the diaphragms appearing to "mature" for several days after fitting until the sensitivity reached a relatively constant value which drifted with changing environment e.g. temperature. The "maturing" was thought to be due to the natural 'relaxation' of the plastic material at points of strain on the tensioning ring. After assembly and pumping, the spectrophones were filled with gas and the optic acoustic signals, observed on the oscilloscope, brought into coincidence by manipulation of the phase-shifting mechanism, a precision of about $\pm 1^\circ$ being obtained.

The experimental phase lags were plotted against the reciprocal of gas pressure and compared with the curves defined by (3.14)

$$\tan \phi = \frac{\omega \gamma}{p}$$

where ϕ is the phase lag, ω is the modulation frequency in radians/sec., γ is the relaxation time at 1 atm., and p is the pressure in atmospheres.

MATERIALS: Infra-red analysis was used as the criterion of purity for all the gases used.

CHLOROTRIFLUOROMETHANE: (I.C.I. 'Arcton 13') was chosen as the reference gas. A strong infra-red band around 1150 cm^{-1} absorbs energy which is expected to relax rapidly by complex collisions into the lowest vibrational level which has a very short relaxation time.(52). Cylinder 'Arcton 13' was purified by low-temperature distillation.

Carbon Dioxide was prepared by heating sodium bicarbonate, dried over magnesium perchlorate and phosphoric oxide, and stored over phosphoric oxide for several weeks.

Methane from a cylinder was purified by low-temperature distillation, and dried over phosphoric oxide. The vapour pressure was 8.3 cm. at -183.1°C .

Nitrous oxide was the middle fraction from a low-temperature distillation of a cylinder sample, dried over phosphoric oxide.

RESULTS: Signal phase was independent of amplitude over the accessible range. This was determined with CClF_3 in both cells, controlling signal amplitude by varying source intensity.

Initially a relaxation phase lag for carbon dioxide was sought by noting the phase differences between a series of pressures of CO_2 in cell 1 and a fixed pressure of CClF_3 in cell 2. However, as the pressure of CO_2 was reduced, the phase of the signal from cell 1 was found to advance with respect to that from cell 2: the opposite direction from a relaxation effect. This was due to varying gas density influencing the phase, confirmed by observing a similar, though

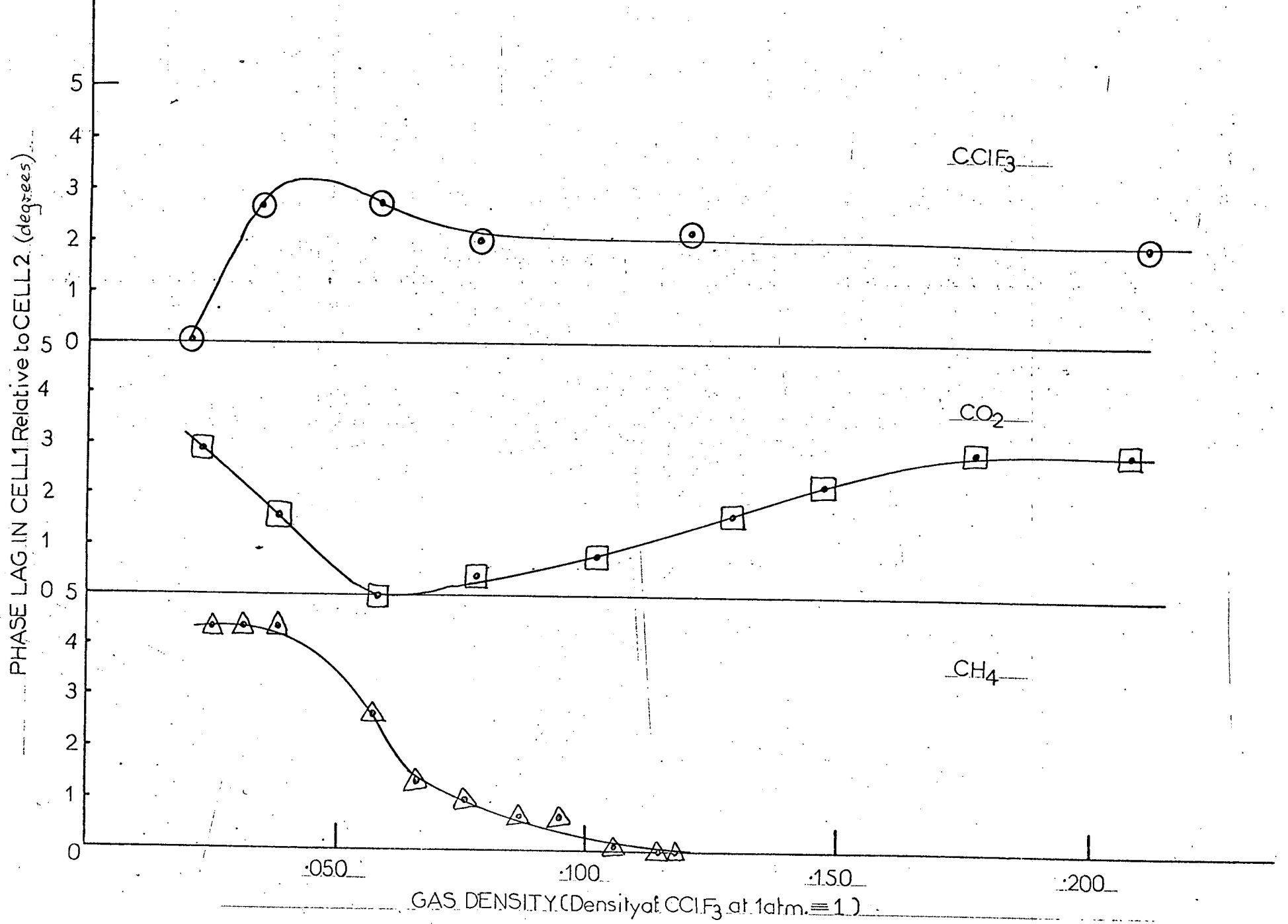


FIG.8 : CELL MISMATCH CURVES

greater, effect between a varying and a fixed pressure of CClF_3 .

Another series of experiments showed that if both cells were filled to the same pressure with the same gas, a pressure-dependent phase change was observed, although ideally there should be no such change under these conditions, since any phase changes in one cell should be cancelled by equivalent phase changes in the other. Several of these phase characteristics are shown in Fig. 8. The degree of mismatch between the cells appeared to be the crucial factor in determining the size of the effect which could become large.

Before making relaxation measurements, correction procedures to deal with these phase changes had to be devised. The first was compensated for by generating the reference signal in a pressure of CClF_3 which matched the density of the slowly relaxing gas. Correcting for the cell mismatch by applying the data in Fig. 8, however, involved some uncertainty, there being two equally applicable but different mismatch curves for each pair of gases. It was therefore essential to minimise the mismatch.

Phase lags, measured in a number of gases at two modulation frequencies (189 c/sec. and 283.5 c/sec.), were analysed by Read's (13) correction technique and interpreted as relaxation phenomena. Only high energy modes being examinable through the radiation filters currently available it was not possible, at this stage, to establish the validity of the interpretation by studying an ultrasonically determined

FIG. 9: PHASE LAG PLOTS : 189 c/sec modulation

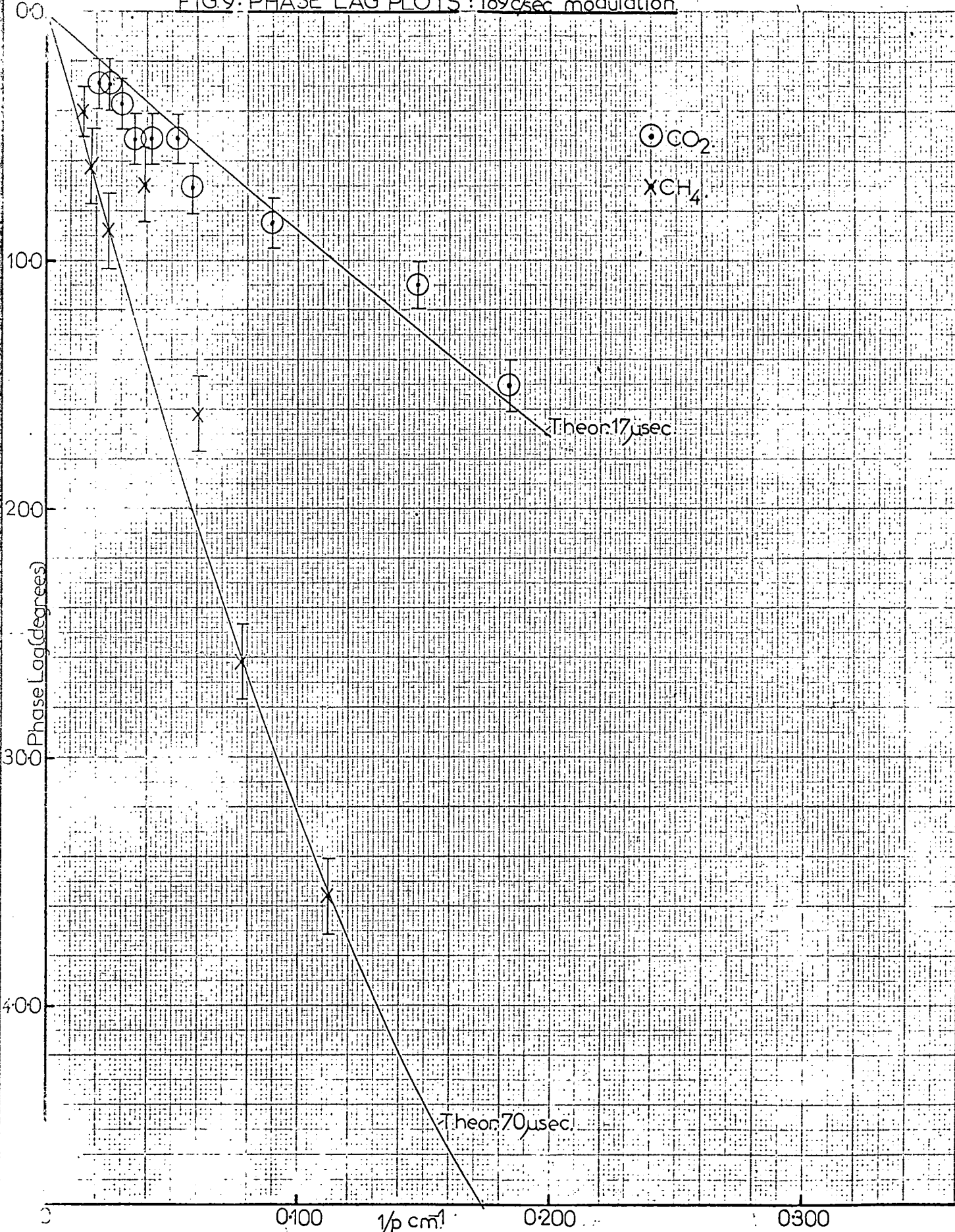
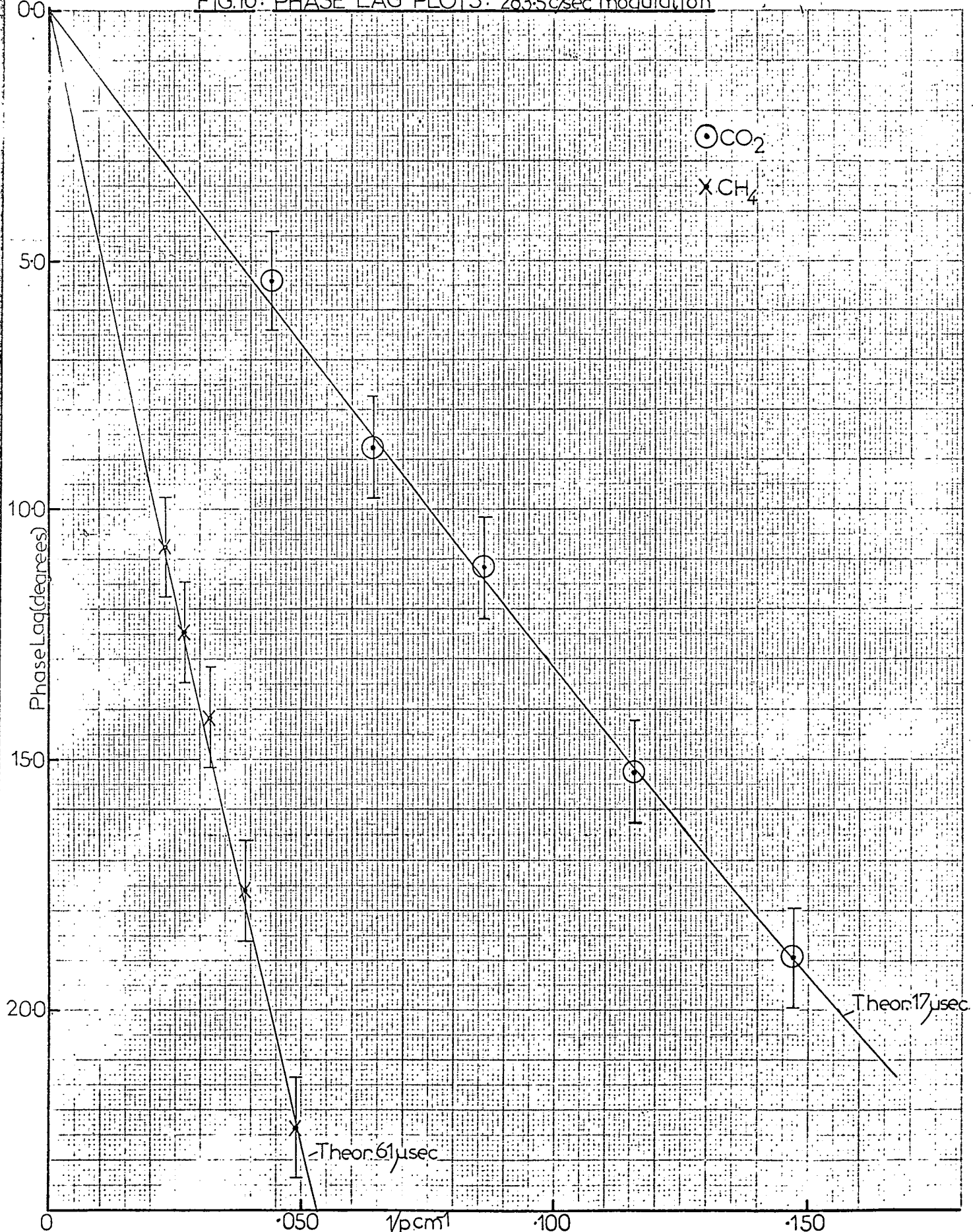


FIG.10: PHASE LAG PLOTS: 283.5c/sec modulation



○ CO₂
× CH₄

Theor: 61 usec

Theor: 17 usec

mode. However, the good agreement of the results, which were self-consistent for the two modulation frequencies, with Read's original work, even after a complete apparatus rebuild, suggested that it was a fundamental and not an apparatus effect which was being observed. The sets of phase measurements agreed closely with the shape of theoretical relaxation curves (see Figs. 9 & 10) and the accumulated results are compared with Read's values in

Table 1: TWO-CELL SPECTROPHONE EXPERIMENT: APPARENT RELAXATION TIMES.

GAS	Mode Excited.	At 189 c/sec.	At 2835 c/sec.	At 189 c sec. READ's results(13)
CH ₄	$\nu_3, 3020 \text{ cm}^{-1}$	$70 \pm 15 \text{ } \mu\text{sec.}$	$61 \pm 10 \text{ } \mu\text{sec.}$	$100 \pm 30 \text{ } \mu\text{sec (51)}$
CO ₂	$\nu_3, 2349 \text{ cm}^{-1}$	$17 \pm 3 \text{ "}$	$17 \pm 3 \text{ "}$	$17 \pm 6 \text{ "}$
N ₂ O	$\nu_3, 2223.5 \text{ cm}^{-1}$	$13 \pm 6 \text{ "}$	—	$13 \pm 6 \text{ "}$

Although at this stage in the work the interpretation of the experimental results still depended on the assumptions that the observed phenomena were due to relaxation and that Arcton relaxed very rapidly, it was obvious that the spectrophone would have to be established absolutely. Due to the fundamental restrictions on conventional experimental techniques, relaxation times at normal temperatures were only available for the lowest modes in molecules. Generation of a usable optic-acoustic signal through these low-energy modes raised two problems. Once an efficient means of filtering the high-energy component from the incident radiation was achieved, enough power had to be made available at the long wavelengths transmitted to produce a useful pressure signal in the gas. This

second problem, on account of the spectral distribution of the source emission, later proved to be the controlling factor in most experiments.

During the course of this work a 'Peekel Phase Meter' (Type FB.120) was incorporated into the system to supersede the mechanical "null method" of phase measurement. An unforeseen discrepancy between the theoretical and actual phase shift (ϕ actual = $0.76 \times \phi$ theoretical) produced by the rotating vane was revealed and subsequently shown to be due to the 4.5 cm. gap between the vane and the chopping wheel (see Fig.6). Since the energy emitted from the filament was condensed by a spherical mirror the incident angle of the radiation on the vane changed with the vane's position, hence introducing an unwanted phase change. The elimination of this discrepancy by constructing a vane almost in contact with the chopping wheel confirmed the explanation. This discovery made it necessary to revise the 'relaxation times' quoted in Table 1 to the following values:-

At 189 c/sec. modulation, $2349 \text{ cm}^{-1} \text{CO}_2 = (12 \pm 2) \times 10^{-6} \text{ sec.}$

$3020 \text{ cm}^{-1} \text{CH}_4 = (50 \pm 4) \times 10^{-6} \text{ sec.}$

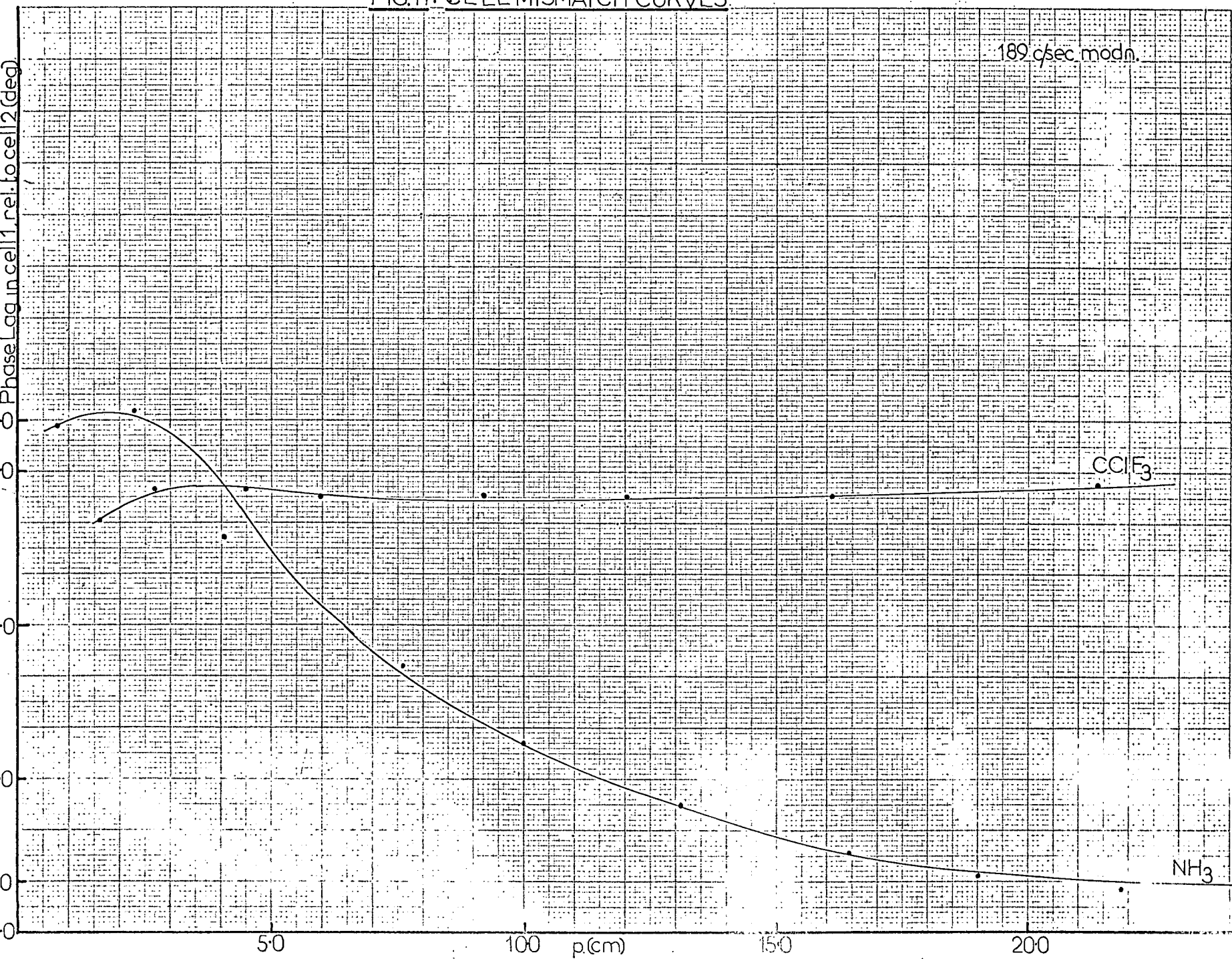
At 283.5 c/sec Modulation, $2349 \text{ cm}^{-1} \text{CO}_2 = (13 \pm 2) \times 10^{-6} \text{ sec.}$

$3020 \text{ cm}^{-1} \text{CH}_4 = (46 \pm 4) \times 10^{-6} \text{ sec.}$

AMMONIA AS AN ABSOLUTE REFERENCE:

By virtue of its very short relaxation time ($\tau < 0.15 \times 10^{-8} \text{ sec}$) (53) and not too low energy ($931.58 - 968.08 \text{ cm}^{-1}$) the ν_2 mode in ammonia

FIG.11: CELL MISMATCH CURVES



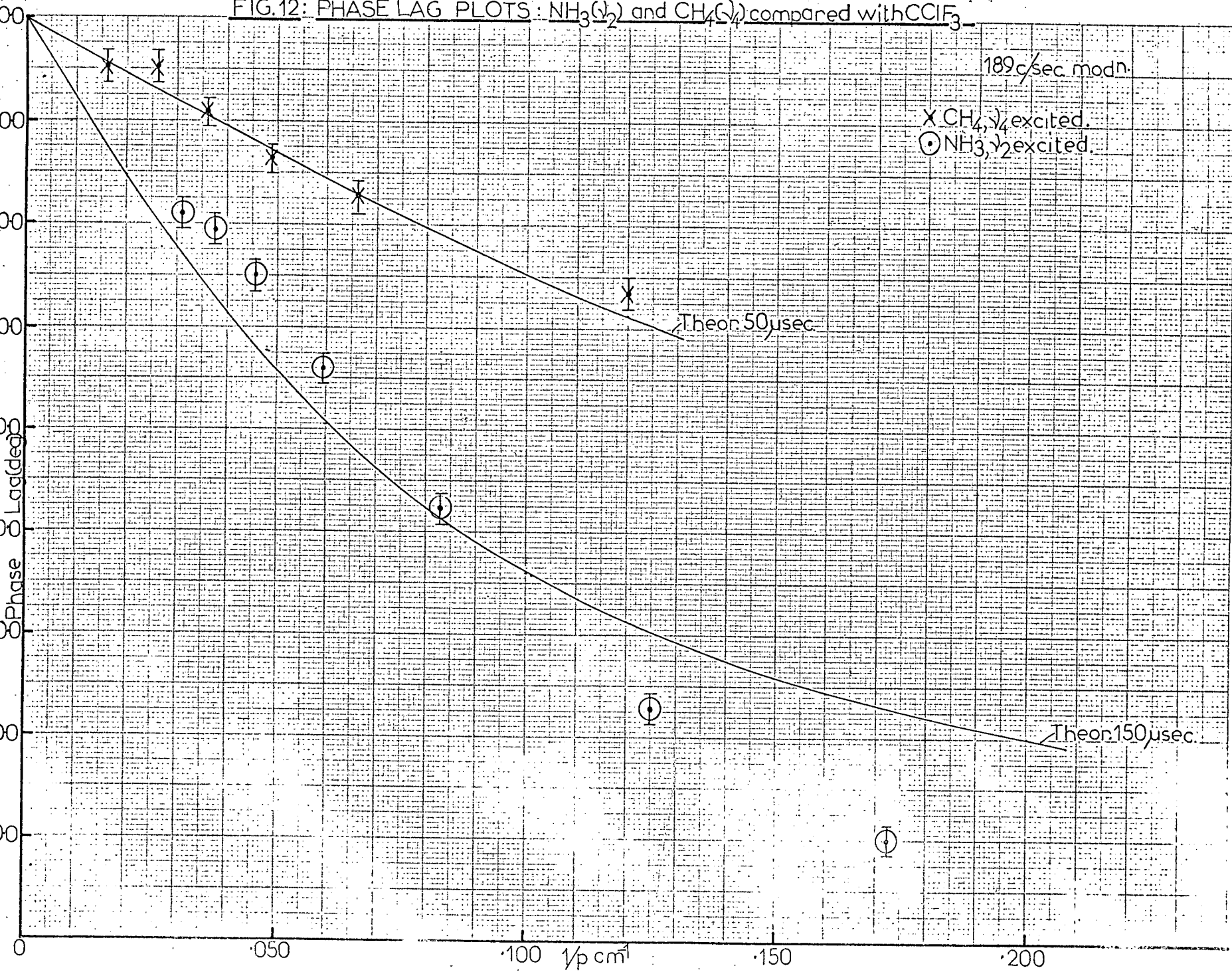
seemed to offer a reasonable path towards establishing the spectrophone on an absolute basis. At this time radiation filtering was by some 'chemical filter' capable of removing the frequencies corresponding to the ν_1, ν_3 and ν_4 modes whilst remaining tolerably transparent in the $900 - 1,000 \text{ cm}^{-1}$ region. Eventually formamide was found to answer these requirements and a critical assessment of source emission, absorption intensities, filter transmission and observed signal strengths established the belief that it was efficient in permitting the excitation of only the ν_2 -mode.

Construction of the "correction curves", by measuring the phase shifts with equal pressures of the same gas in both cells, in preparation for the $\text{NH}_3(\nu_2) / \text{Arcton}$ experiment gave the first hint of anomaly; the ammonia run producing a large phase change i.e.

Arcton/Arcton, total $\Delta \phi \approx 3^\circ$ } Fig.11)
but, Ammonia/Ammonia, total $\Delta \phi \approx 41^\circ$ } (c.f. Fig.8)

Balancing the densities of ammonia and Arcton and exciting only the ν_2 -mode in ammonia was expected to generate signals showing little pressure-dependent phase change (once corrected). Since relaxation of $\text{NH}_3-\nu_2$ is effectively instantaneous and that of Arcton is conceivably longish, a slight lagging of the Arcton signal with decreasing pressure would not have been surprising. The large phase lag observed was certainly not anticipated; the ammonia lagged behind the Arcton. Application of the correction factor was of little significance since the plot of phase lag against reciprocal gas pressure extrapolated to infinity. However,

FIG.12: PHASE LAG PLOTS : $\text{NH}_3(\nu_2)$ and $\text{CH}_4(\nu_4)$ compared with CClF_3



another ammonia/Arcton run with the gases in the opposite cells to the first experiment gave a more manageable set of phase values which were processed to give an indifferent fit to the theoretical line for a 150 μ sec relaxation time (Fig.12)

An explanation based on the modification of the physical properties of the Melinex polyester diaphragm by its absorbing large amounts of the compact, polar ammonia molecules seemed feasible. Support for this idea came from several sources. On observing the capacitance of the microphone in an atmosphere of ammonia, it was found to increase with the pressure of the gas and the time of treatment up to a maximum of +13% its original value, whilst an ordinary parallel plate condenser was unaffected. Melinex film left in an ammonia atmosphere showed a 1% weight increase and literature from I.C.I. described its embrittlement and reduction in mechanical strength. Although subsequent 'correction curves' for Arcton, CO₂ etc. showed some aggravation the physical nature of the absorption was established when the diaphragms regained their original properties after several days pumping.

Hence, a progressive accumulation of ammonia within the polymer matrix increasing the diaphragm's inertia and affecting its rigidity seemed the only solution. Without doubt these factors must have played their role in ammonia's anomalous behaviour, but the root of the problem, not reached until the analysis of the methane experiments, was much more general.

METHANE as an ABSOLUTE REFERENCE:

Sound velocity and absorption studies in methane have determined the relaxation time of the ν_4 -mode to be $2.0 \mu\text{sec}$ ($\beta = 1.5 \mu\text{sec}$) (54). Very close to the practical limits of interferometry the relatively high energy (1306 cm^{-1}) of this mode made it probably the most suitable reference on which to establish the spectrophone. A long wavelength path interference filter acquired from Perkin Elmer cut on sharply at 4.8μ and gave a 70% transmission level at the desired wavelength. In addition to calibrating Arcton, methane provided an opportunity of comparing different modes within the same molecule i.e. measuring the ν_3 -mode ($5.0 \mu\text{sec}$?) against the established ν_4 -mode.

These two crucial experiments altogether invalidated our previous interpretation of the spectrophone results. No phase lag was detected between the ν_3 (3020 cm^{-1}) and the ν_4 (1306 cm^{-1}) modes in methane, and the ν_4 -methane/Arcton run found the methane lagging behind the Arcton with decreasing gas pressure, to yield an apparent relaxation time of $50 \mu\text{sec}$ (Fig.12).

After some speculation about the possibility of the molecules initially going through a relatively stable electronically excited state before transferring the energy to vibration by an inefficient collisional process, it seemed most probable that the measured phase lags had, in fact, no connection with relaxation processes. Having reached this unwelcome conclusion the correct source of these phase lags had to be traced.

PHASE LAG HYPOTHESIS:

A good mathematical model for the critical processes occurring within a spectrophone cell was found in Heading (p.469) (55).

Consider a particle of unit mass (i.e. the diaphragm) moving along the axis OX under the action of the following forces:-

(1) An applied force $a\cos wt$ (a and w being constants), which approximates to the pressure wave generated optic-acoustically from the trapezoidally-modulated infra-red beam.

(2) A restoring force, proportional to its distance from 0, $-n^2x$. This is the critical factor in the analysis, n being the natural frequency of the system: when $w = n$ the system comes into resonance. Apart from the mechanical properties of the diaphragm, the influence of the gas surrounding it must also be considered. Obviously the gas pressure behind the diaphragm reinforces the restoring influence of the material's tension and hence raises the natural frequency of the system. However, during compression the inertia of the gas has to be overcome and hence it must be added to the inertia of the diaphragm i.e.

$$n^2 = \frac{C}{M} = \frac{\text{tension of diaphragm} + \text{pressure of gas}}{\text{mass of diaphragm} + \text{mass of gas}}$$

$$\underline{n^2 = \frac{A + B.p}{M_d + M_g} \dots\dots\dots (4.1)}$$

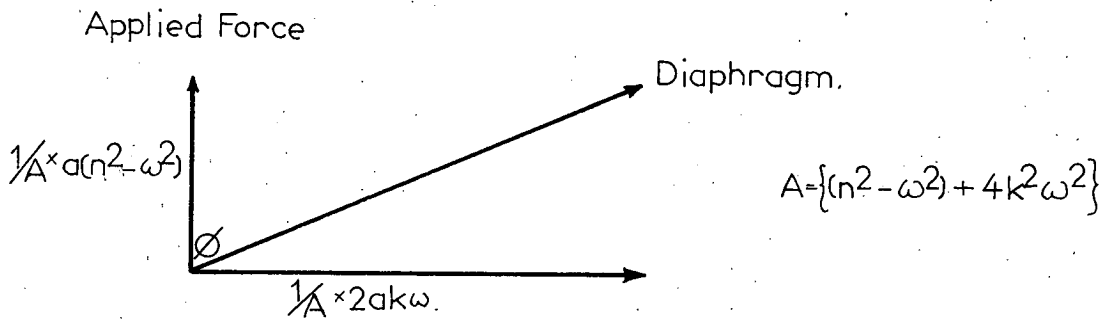
(3) A resistive force proportional to velocity, $-2kx$, is exerted as a result of the viscosity of the gas when it is forced out on compression, between the diaphragm and the back-plate. At normal pressures viscosity is independent of pressure, but under conditions when the molecular mean free path is of the same order as the dimensions of the system, then viscous drag is proportional to

density. Arcton at the lowest pressures used (0.50 cm.Hg) has a mean free path of about 0.6 μ . Assuming the spectrophone to be comparable with the B. & K. microphone, which has a 22 μ gap between the diaphragm and back-plate, the pressure-independent situation should still apply to these low pressure measurements.

Solution of the relevant differential equation for this problem gives the diaphragm's equation of motion:-

$$X = \frac{a(n^2 - \omega^2) \cos \omega t + 2a.k.\omega \sin \omega t}{(n^2 - \omega^2)^2 + 4k^2\omega^2} \dots\dots (4.2)$$

and by considering the vector diagram,

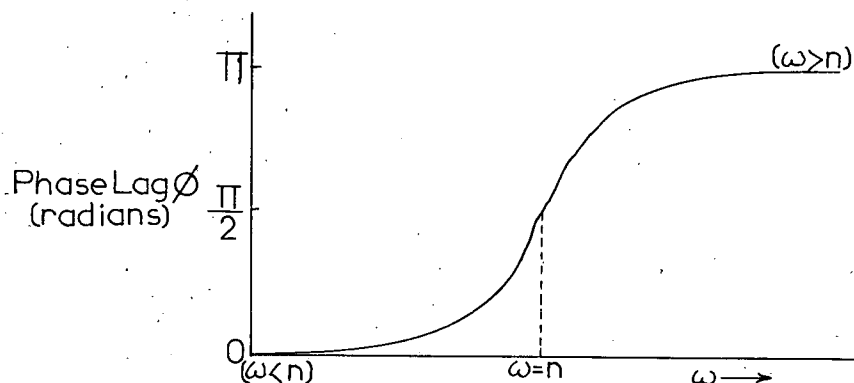


the phase lag of the diaphragm behind the applied pressure wave (ϕ) is given by:-

$$\tan \phi = \frac{2k\omega}{(n^2 - \omega^2)}, \text{ and inserting the expression for } n^2 \text{ (4.1)}$$

$$\tan \phi = \left\{ \frac{A + B\omega}{M_d + M_g} - \omega^2 \right\} \dots\dots\dots (4.3)$$

If $n^2 \gg w^2$, then $\tan \phi, \phi \rightarrow 0$ and none of these factors can introduce any pressure-dependent phase shifts. However, if $n^2 \sim w^2$ then enormous pressure-dependent phase shifts are easily induced. Graphically, the situation near resonance can be represented by:-



Now, the two properties of a gas critical to the positioning of the resonance frequency for the system are its pressure and its density, but these act in the opposite sense to one another i.e.

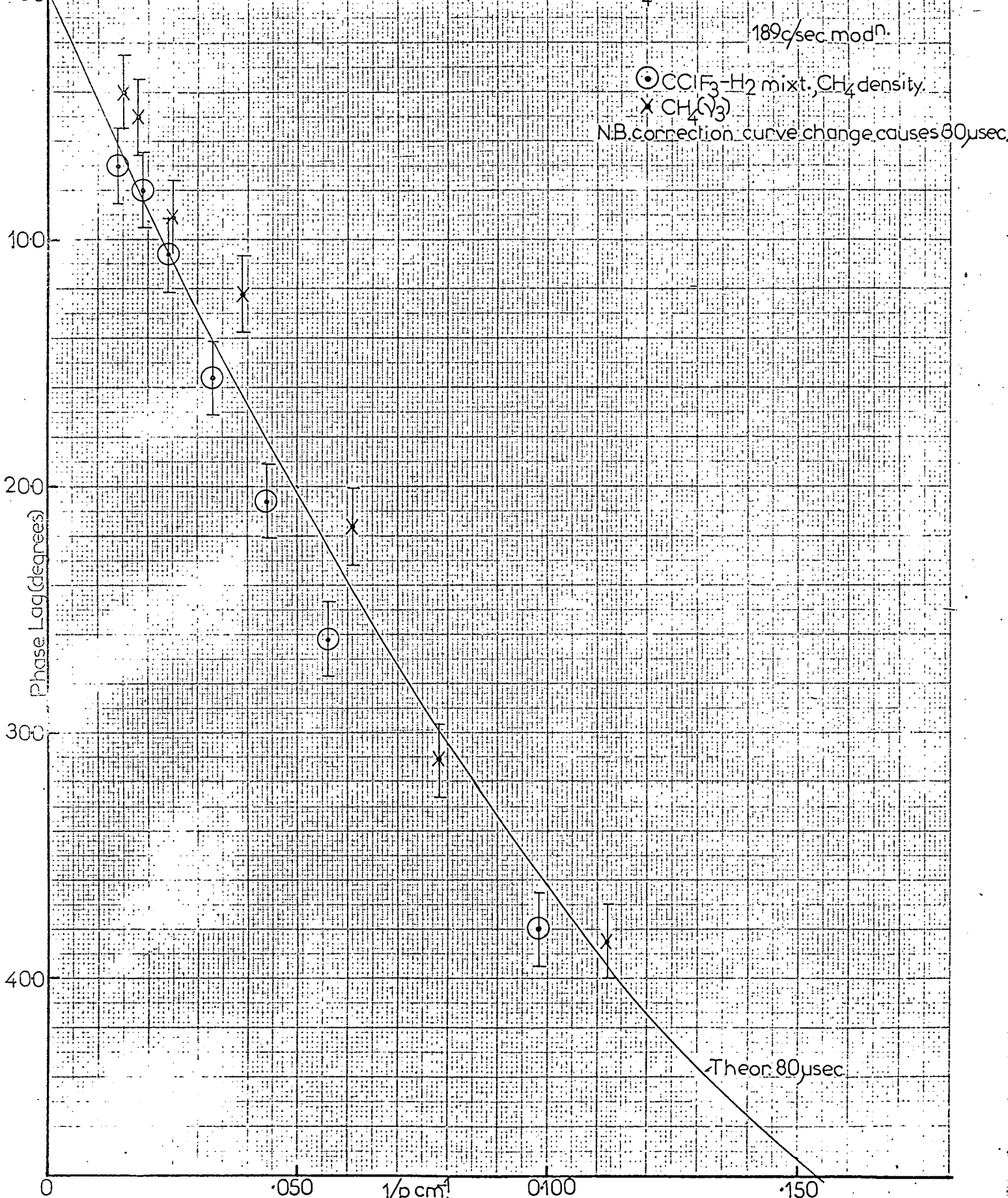
(1) An increase in pressure raises the natural frequency of the diaphragm (B.p. term in (4.3)) and produces a phase lead.

(2) An increase in density raises the inertia term (Mg in (4.3)), hence lowering the resonance frequency and introducing a phase lag.

While both effects operate simultaneously, for the light gases e.g. CH_4 , NH_3 the "pressure effect" will predominate and for the heavy gases e.g. Arcton, CO_2 , the 'density effect' will be dominant.

An easy explanation is now available for all the anomalous phase changes which have appeared experimentally. The phase lead observed when a decreasing pressure of Arcton or carbon dioxide was compared with a fixed pressure of Arcton was the 'density effect'

FIG.13: PHASE LAG PLOTS: (CCl₃-H₂)mixture (d_{CH₄}) and CH₄(v₃)



whilst the corresponding experiment with a fixed and variable pressure of methane gave a lag because of the 'pressure effect'. By matching the densities of the gases in the two cells the chance of a phase lead with decreasing pressure was eliminated, but the measured phase lags merely reflected the difference between the actual densities through the different pressures e.g. in a typical CH₄/Arcton experiment.

$$\Delta p \text{ CH}_4 : 18.0 \text{ cm Hg} \rightarrow 43.5 \text{ cm.Hg}$$

$$\Delta p \text{ Arcton: } 2.73 \text{ cm Hg} \rightarrow 6.67 \text{ cm Hg.}$$

Only in the comparison of different modes within the same molecule can the perfect matching of gas properties necessary for relaxation measurements be approached e.g. $\nu_3(\text{CH}_4)/\nu_4(\text{CH}_4)$ experiment.

Although this hypothesis explained the existing situation clearly, its ultimate validity had to be judged on the basis of its predictions. If in fact the methane phase lags arose not from molecular relaxation but as a result of the gas's low density, then a mixture of Arcton and hydrogen of methane density should produce the same apparent relaxation time. It did. (Fig.13).

The successful theory then suggested that the simultaneous matching of both pressure and density in the sample and the reference, by diluting the Arcton with hydrogen, should permit a rough examination of relaxation phenomena in the spectrophone. On this assumption, the 2349 cm^{-1} band in CO₂ was compared with the necessary mixture and gave phase lags corresponding to a

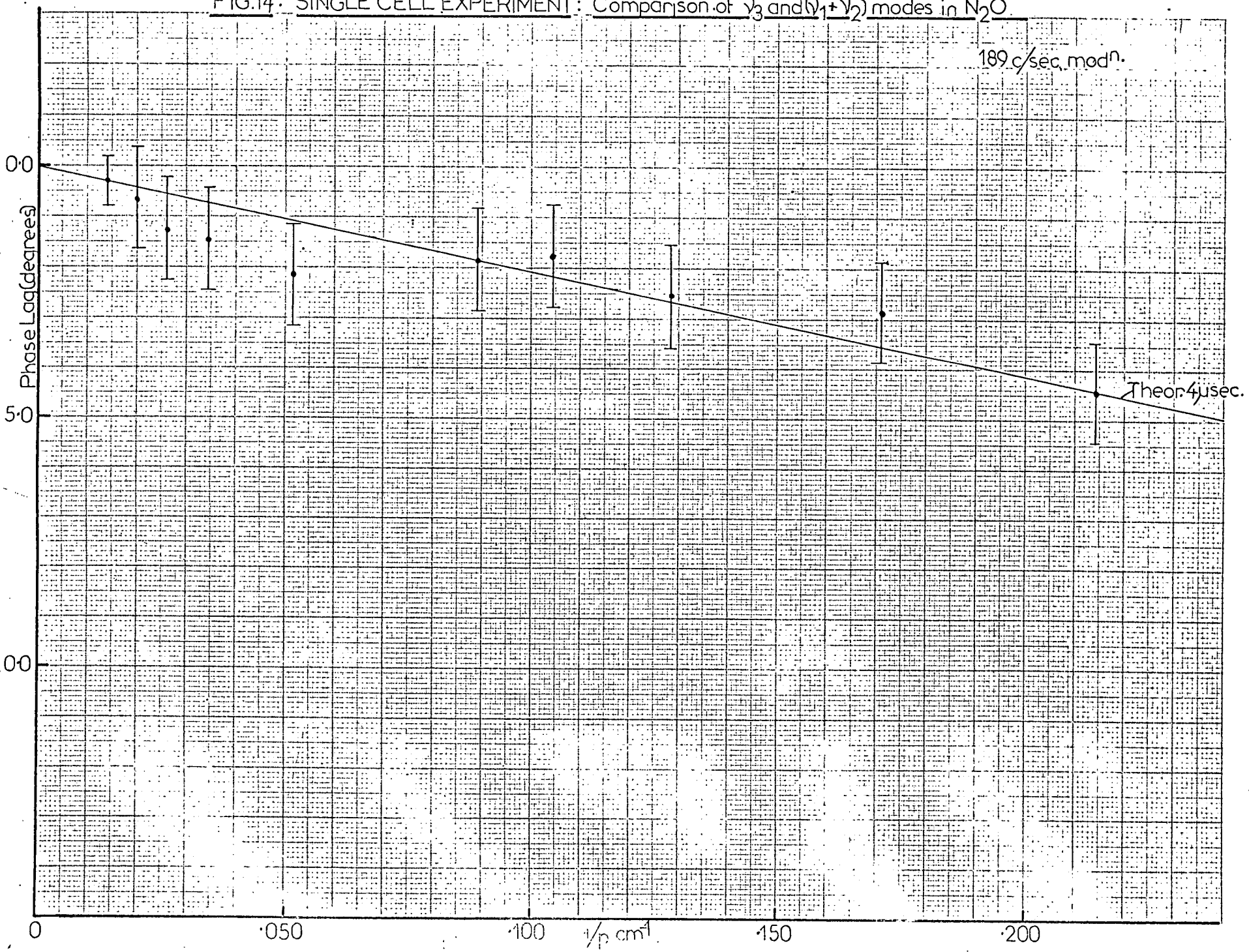
(4.0 ± 1.0) $\mu\text{sec.}$ relaxation time. Rather shorter than expected (667 cm^{-1} mode in CO_2 has $\tau = 6.8 \mu\text{sec.}$)(56), the points nevertheless shewed little deviation from the theoretical line over a long pressure range.

Several experiments comparing modes within molecules were not very encouraging in that they indicated very short relaxation times for the higher energy modes, certainly beyond the capabilities of the spectrophone in its current state of development e.g.

<u>GAS DETAILS</u>		<u>APPARENT RELAXATION TIME</u>
(ν_3)3020 cm^{-1} CH ₄	against (ν_4)1306 cm^{-1} CH ₄	0 \pm 2 $\mu\text{sec.}$
(ν_3)2,349 cm^{-1} CO ₂	" (ν_2) 667 cm^{-1} CO ₂	0 \pm 4 $\mu\text{sec.}$
(ν_3)2,223.5 cm^{-1} N ₂ O	" (ν_1)1,285 cm^{-1} N ₂ O	1.75 \pm 1 $\mu\text{sec.}$
(ν_3)3,287 cm^{-1} C ₂ H ₂	" (1328.1 + 729.1 cm^{-1} C ₂ H ₂	0 \pm 1 $\mu\text{sec.}$

The hypothesis was further strengthened by a series of 'Third reference channel' experiments in which a fixed 'base-line' was provided for phase measurements by a photocell signal. Previously, without a stable reference for guidance, one could not distinguish experimentally between a phase lag on one channel and a lead on the other. These experiments showed all the measured phase lags to be differences between two much larger individual channel variations. In the case of the 'correction curves' where signals from the same pressures of the same gas in both cells were compared, the differences in individual response which produced the phase changes were merely a reflection of slightly different diaphragm resonances. This later received direct experimental confirmation.

FIG.14: SINGLE CELL EXPERIMENT: Comparison of ν_3 and $(\nu_1 + \nu_2)$ modes in N_2O .



For the heavy gases e.g. Arcton, carbon dioxide the correction factors were small because the density and pressure effects worked in opposition, whereas in the case of the light gases e.g. methane, ammonia large phase changes arose from big pressure fluctuations nearly uncompensated by the density effect.

Carbon dioxide and nitrous oxide having the same molecular weight, it was argued that their relaxation properties could be safely compared in the spectrophone. This experiment between the ν_3 -mode of CO_2 and the ν_3 -mode of N_2O , when previously done by Read (13), had given a difference in relaxation times of 4.6 μsec . Since these results showed some scatter the experiment was repeated giving a value of 3.3 μsec . for $\Delta\gamma$.

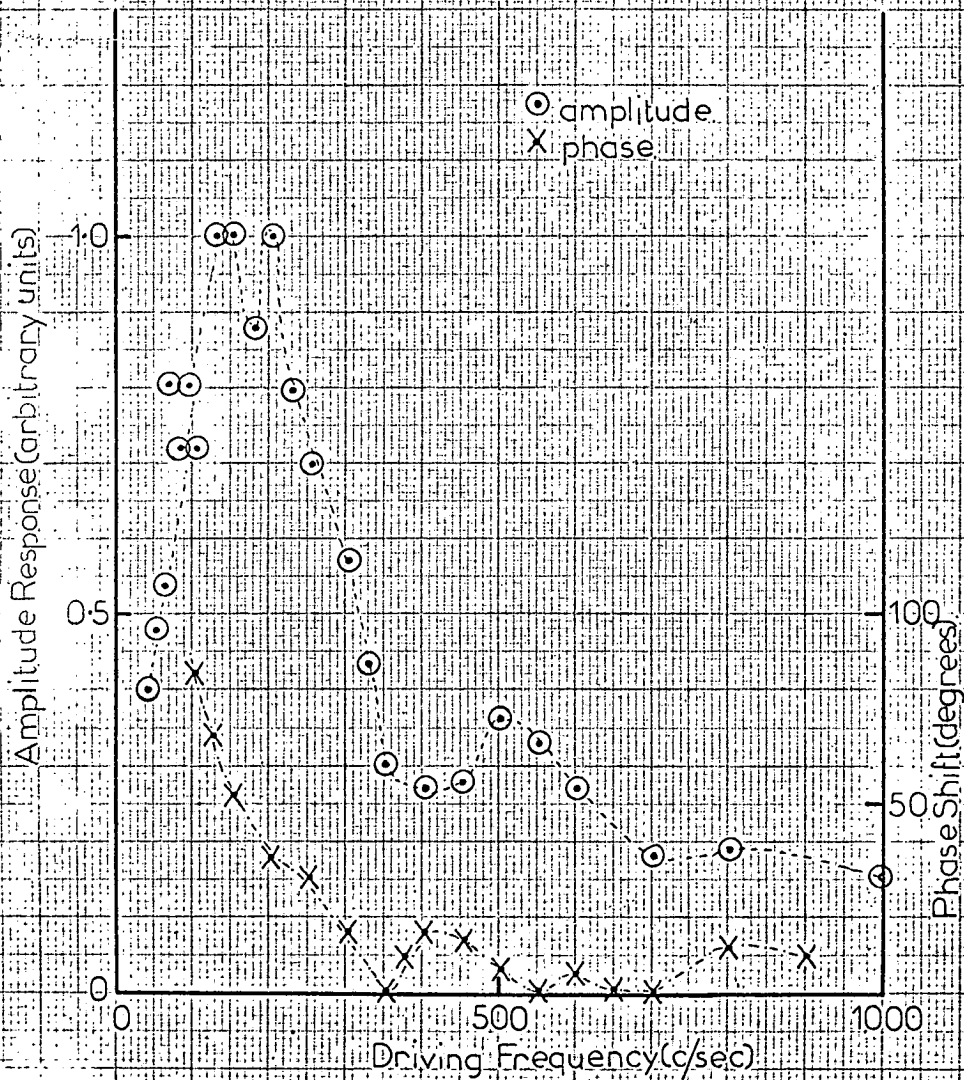
Finally, nitrous oxide was studied in what had been shown to be the only reliable system possible with this spectrophone; the single cell system. Using only one cell the outputs generated by successive excitation of the ν_3 and the ν_1 modes, equalised in intensity by adjustment of the I.R. sources, were compared at each pressure with the phase of the fixed standard from the photocell. Thus, the cell characteristics could only have exerted a minor influence on any phase shifts measured. Three runs, two in the green and one in the red cell showed, with excellent agreement, the higher mode lagging behind the lower to give a difference in relaxation times of:-

both green cell runs gave $\Delta\gamma = (4.0 \pm 2.0 \mu\text{sec.})$ (Fig.14)

the red cell run gave $\Delta\gamma = (4.5 \pm 2.0 \mu\text{sec.})$

Despite the complete experimental fulfilment of its predictions,

FIG.15: AMPLITUDE and PHASE Characteristics of SPECTROPHONE CELL



the hypothesis still required the diaphragms to have an extremely low resonance frequency. Whereas most microphone systems resonate at ~ 10 kc/sec, the spectrophone cells would have to resonate at several hundred cycles. A Bruel and Kjaer (Type 4132) condenser microphone, taken as a standard of flat amplitude and phase response, was used to calibrate the cells' loudspeaker test rig (see p.28) and their amplitude and phase characteristics were measured directly. Fig.15 shows the results for one of the cells. That the cell diaphragm resonance lies in the range 100 c/sec. \rightarrow 200 c/sec. fully substantiates the hypothesis evolved to explain the large pressure dependent phase changes found in the apparatus.

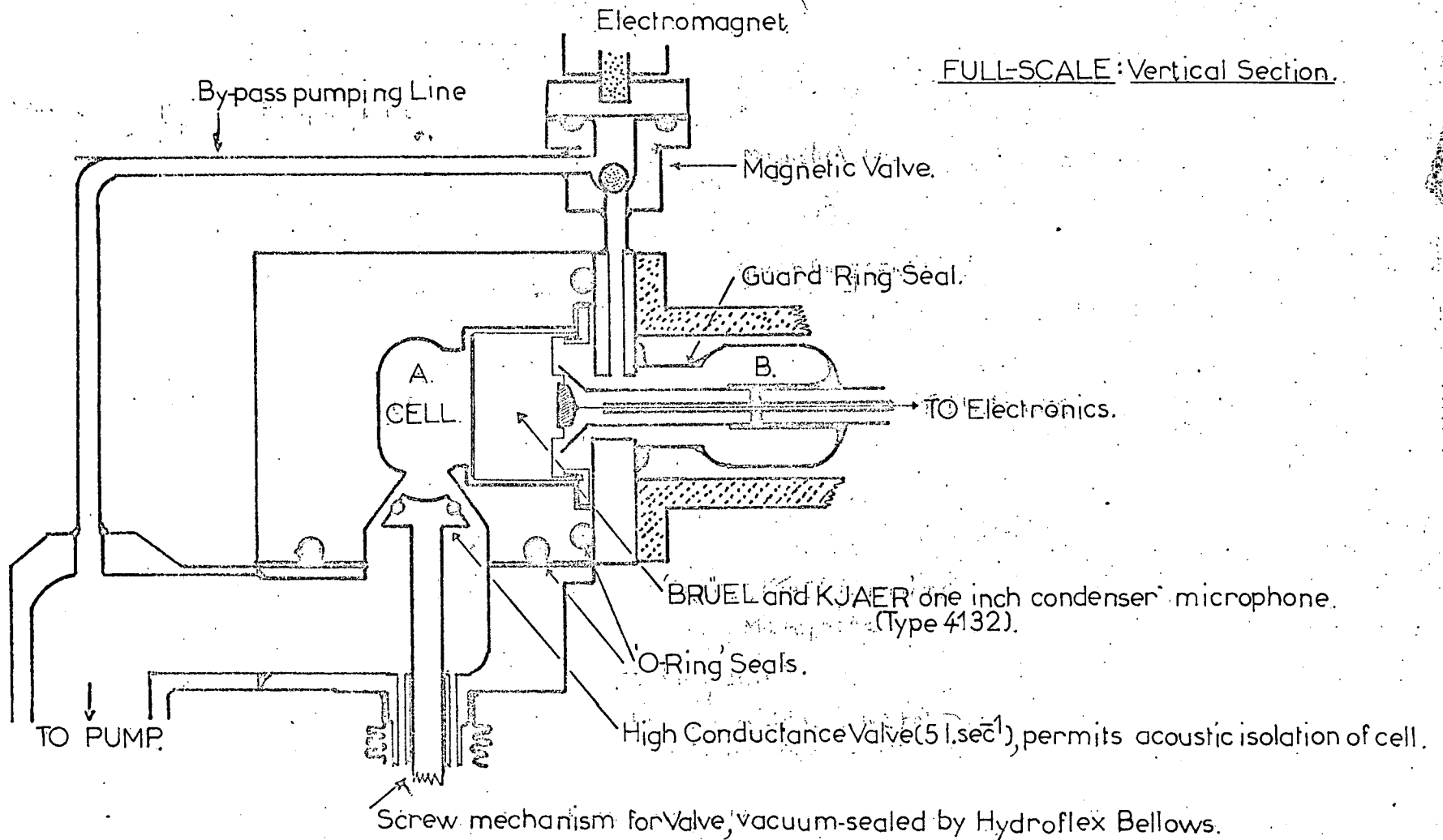
Why the resonance frequency was so seriously underestimated during the design of this spectrophone (13) may be due, in part, to the choice of Melinex as a diaphragm material. During the "maturing period" described earlier (p.28) the plastic may flow from the region strained by the tensioning ring to leave a relatively thick, heavy, central portion supported by a thin annulus of material. Such a system would resonate at a lower frequency than the original uniform diaphragm.

Jacox and Bauer (47), as reported previously (p.22), found inexplicable pressure-dependent phase changes confusing their spectrophone measurements. Although these workers used a commercial condenser microphone (CAPPS CM-2003X) which should have had a resonance in the 10 kc/sec region, they modulated the infra-red energy at 2.550 kc/sec. Now, the B.&K. one inch condenser

microphone No.4132, being a high quality commercial product, should have a comparable phase angle characteristic to the Capps. At 2.5 kc/sec there is a 35° lag. A similar situation, therefore, seems to have prevailed in the Jacox and Bauer experiments in which their meaningless (relaxation-wise) phase measurements were due to a pressure-dependent microphone-resonance.

Using the experience gained in operating and investigating the "Two-Cell Spectrophone Experiment" a new system was designed round Brueland Kjaer condenser microphones: the "B. and K. Spectrophone Experiment."

FIG. 16: THE B. and K. SPECTROPHONE CELL



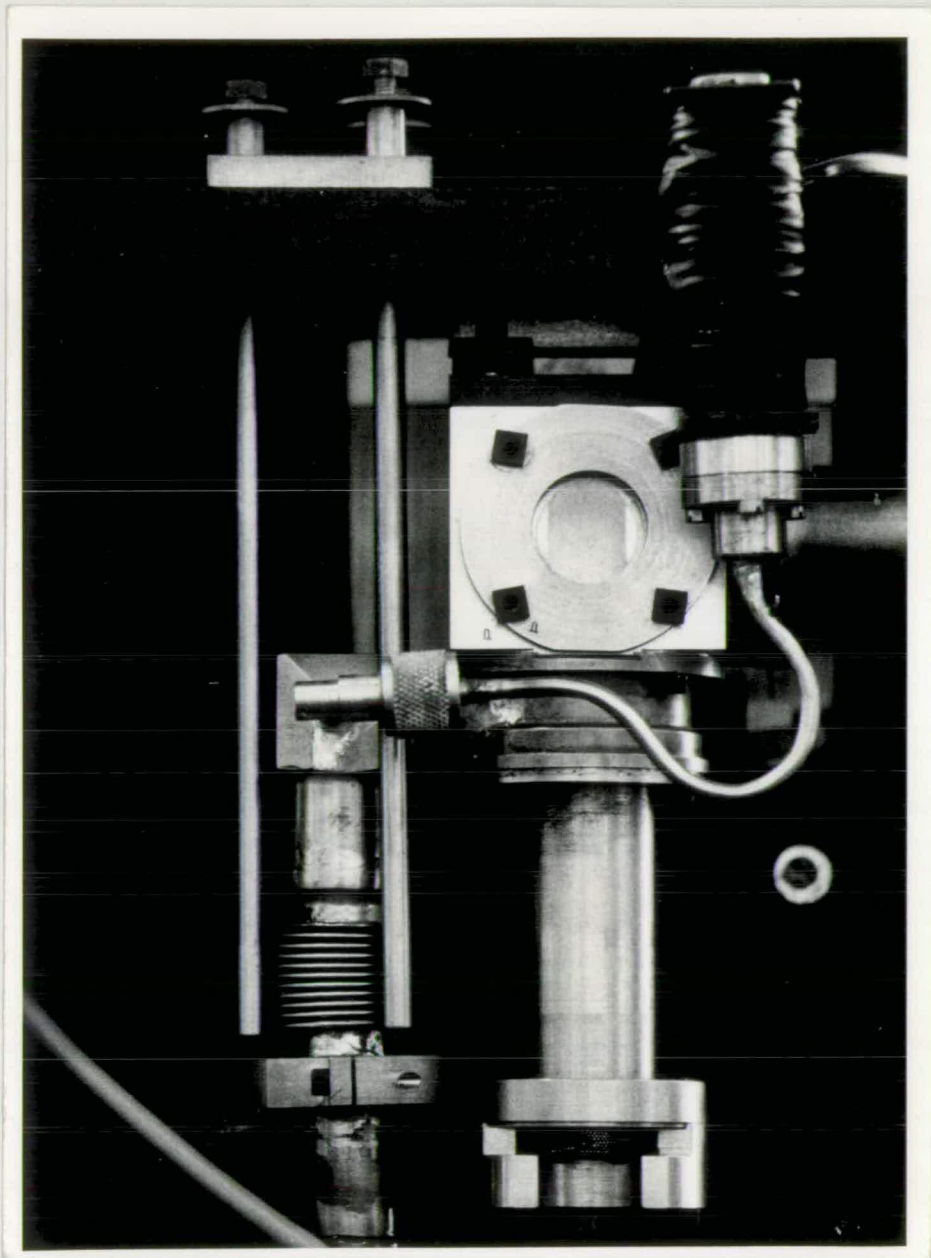
(The by-pass and magnetically operated valve were added after the first experiments, see text).

CHAPTER 5.

'THE B. and K. SPECTROPHONE EXPERIMENT: DESIGN AND DEVELOPMENT'.

From the previous experiment, practicable matching of either gas or apparatus properties being inadequate, it was learnt that the balancing of spurious phase lags in a spectrophone was no substitute for their absolute elimination. Only by using the one spectrophone cell to successively examine different modes within the same molecule could the matching necessary to ensure reliable relaxation comparisons be achieved. The current experiment, based on the flat audio-frequency response and low inherent noise of a highly developed condenser microphone, (Bruel and Kjaer Type 4132) should permit sensitive yet faithful detection of optic-acoustic signals over a wide pressure-range. Although designed as a single-cell system with a photocell signal, as in the classical experiments, providing the phase reference, two spectrophones were initially incorporated to accelerate the development stage. Subsequently only one of these was taken up to the final specification.

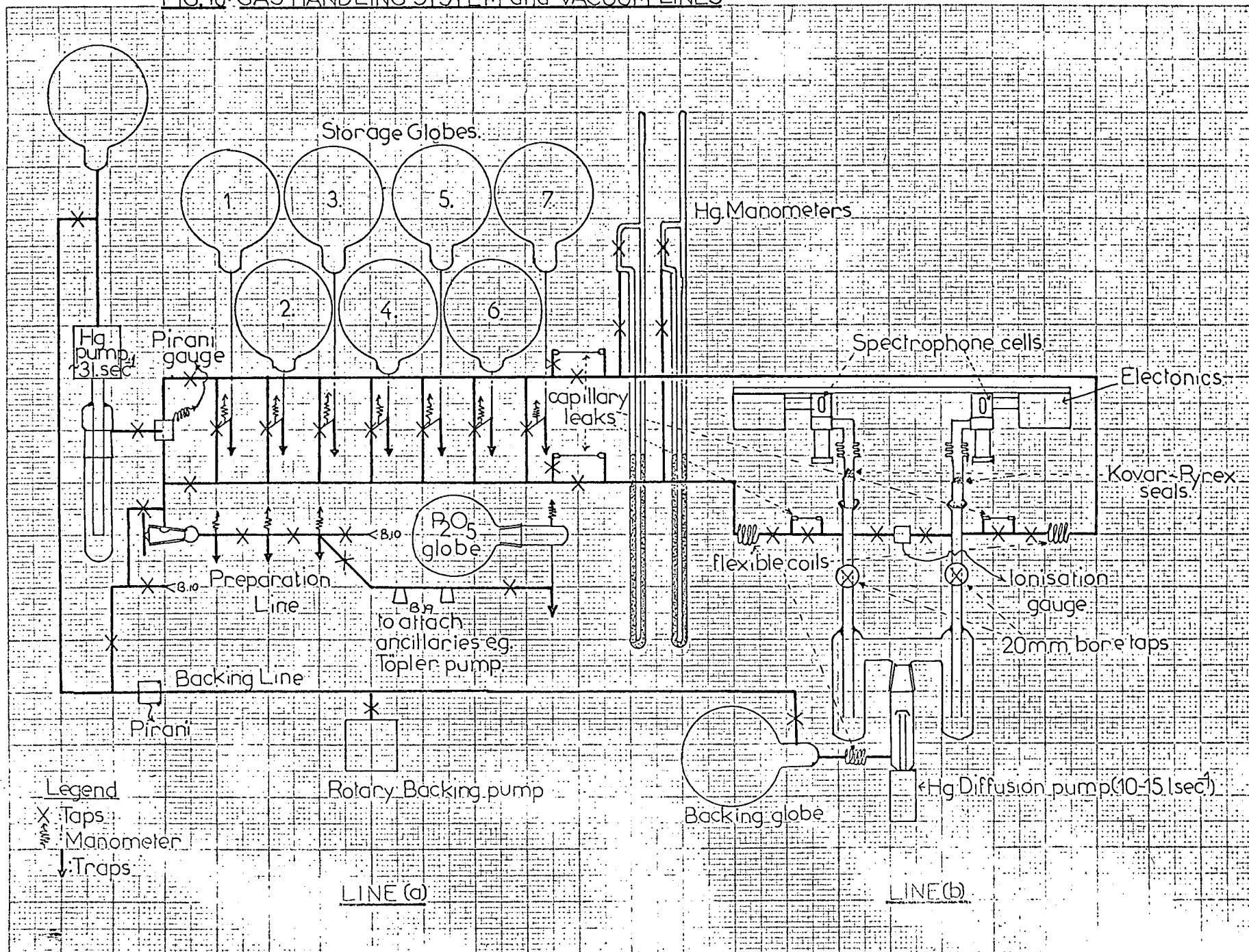
SPECTROPHONE CELL: The stainless steel spectrophone cell is shown in Figs. 16 and 17. One wall of the cell chamber is formed by the diaphragm ~~of the diaphragm~~ of the Bruel and Kjaer (Type 4132) one inch condenser microphone which feeds out through a guard-ring seal (Kodial glass, Nilo-K) into its cathode-follower via a $3\frac{1}{2}$ inch long connecting system. Separation of the electronics from the



· FIG 17 : 'B. and K. SPECTROPHONE' : Modified (see text). ·

cell allows the latter to be baked if required. Up to frequencies of 1 kc/sec. the diaphragm of this microphone remains in phase with the driving force to within 1° . Radiation traverses a 3 cm. absorption path parallel to the diaphragm and bounded by polished sodium chloride windows. All the detachable components, including the windows, are vacuum-sealed to the cell-body by Viton O-rings set in trapezoidal grooves. To efficiently evacuate the chamber, gas purity being crucial to the successful study of long-relaxing species, while retaining the ability to isolate it acoustically from the pumping system during phase measurements required the design of a special 'bakeable' valve. By compressing the 'Hydroflex' bellows (see Fig.16) a plunger completely fills the high conductance (5 l. sec^{-1}) pathway provided by the chamber entrance, sealing it with an O-ring. This valve links the cell through a flexible coupling to the main glass pumping system. The collar (seen in Fig.17) below the flexible coupling is located in space by three steel rods and prevents the tension produced by the atmospheric pressure acting on the evacuated bellows from straining the fragile and immediately adjacent Kovar-Pyrex seal. During assembly all joints were tested to the satisfaction of a Centronic mass spectrometer leak detector. (leak rate $< 10^{-9} \text{ l. } \mu\text{s}^{-1}$). The cells are suspended from an insulated bar which, along with their main pumping line, is supported by a light Dexion frame. Normally firmly secured to the optical bench, the frame can easily be freed during phase measurements to float on a set of foam rubber pads minimising

FIG.18: GAS HANDLING SYSTEM and VACUUM LINES



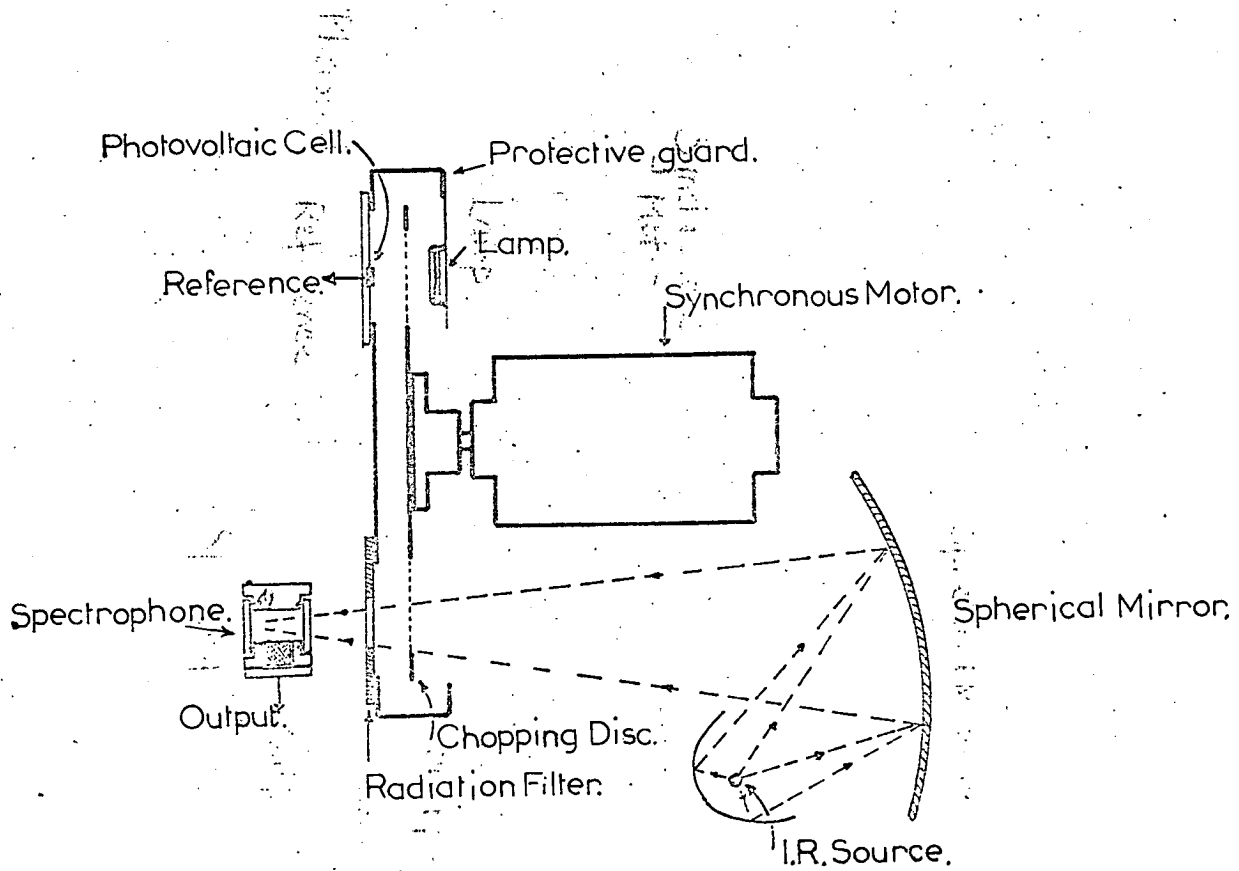
interference due to external vibration.

VACUUM SYSTEM: (fig.18): A two-stage rotary pump backs two separate conventional high-vacuum systems.

(a) A Pyrex gas-handling system is evacuated by a small mercury diffusion pump (speed $\sim 3 \text{lsec}^{-1}$). Pressure monitoring in both this and the backing line is by Pirani gauge, registering to 10^{-3} torr. Two lines linked into the storage globes via T-taps allow both spectrophone cells to be simultaneously supplied through the capillary leaks with any of the gases available.

(b) A fast pumping system, based on a Speedivac G.M.2 mercury diffusion pump (speed $\sim 10-15 \text{lsec}^{-1}$), to allow efficient evacuation of the spectrophones is built into the light Dexion frame supporting the cells. By optimising the bores of the tubing, taps and traps (57) and minimising the distance between the pump and the cell, the maximum available pumping speed is developed at the chamber. Without baking the metalwork a pressure of 5×10^{-7} torr. is possible under ~~unfavourable~~ ^{favourable} conditions, but the working range, swiftly and reliably reached is $(8 - 10) \times 10^{-7}$ torr. Pressure measurement is by ionisation gauge. Although facilities for bakeout are available they have yet to be found necessary. Gases are admitted from system (a) through a series of capillary leaks and flexible glass coils; the latter permitting the framework to float freely during relaxation measurements.

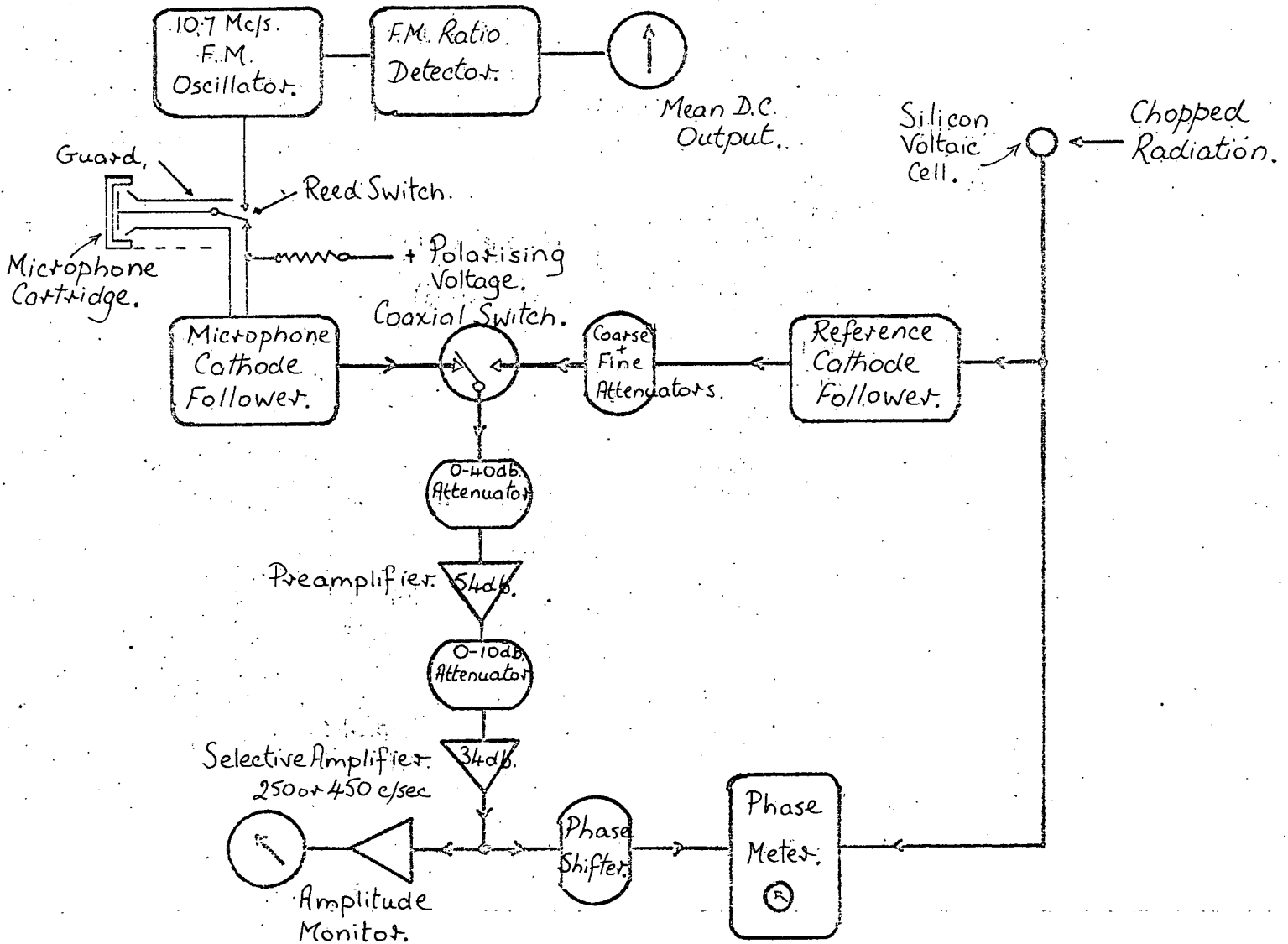
FIG.19 : OPTICAL SYSTEM.



OPTICAL SYSTEM: (Fig.19): Infra-red energy from an electrically heated nichrome rod (7 cm. long, 0.3 cm. diameter) is focussed by front silvered mirrors. When necessary filters are used to eliminate either high energy radiation ($>2100 \text{ cm}^{-1}$, Perkin-Elmer interference filter) or low energy radiation ($<1700 \text{ cm}^{-1}$, Bart and Stroud, calcium aluminate glass Type BS39B). A 3,000 r.p.m. synchronous motor drives the 12" diameter chopping discs. Unless the radiation holes in the chopper guard are kept blocked, for example with the filters, they generate a 'siren effect' with the aid of the holes in the revolving disc. The resultant noise is a serious problem for, being at the chosen modulation frequency, it cannot be removed electronically.

ELECTRONICS: (Fig.20) The condenser microphone is used with a D.C. polarizing voltage of 200v. when it has a capacity of 57 pf. and a sensitivity of 4.0 mv/ μ bar. In order to avoid damaging the 4 μ thick diaphragm it is essential to monitor its position during the evacuation or filling of the cell. A reed switch, therefore, is incorporated in the connection between the microphone and its cathode-follower within the guard tube which provides input capacitance degeneration. By operating the switch the unpolarized microphone may be made to form the capacitor in the tuned circuit of a 10.7 Mc/sec. Franklin-type transistor oscillator whose output, monitored with a conventional frequency-modulated ratio detector, gives a sensitive indication of diaphragm position.

FIG. 20: BLOCK DIAGRAM OF ELECTRONICS.

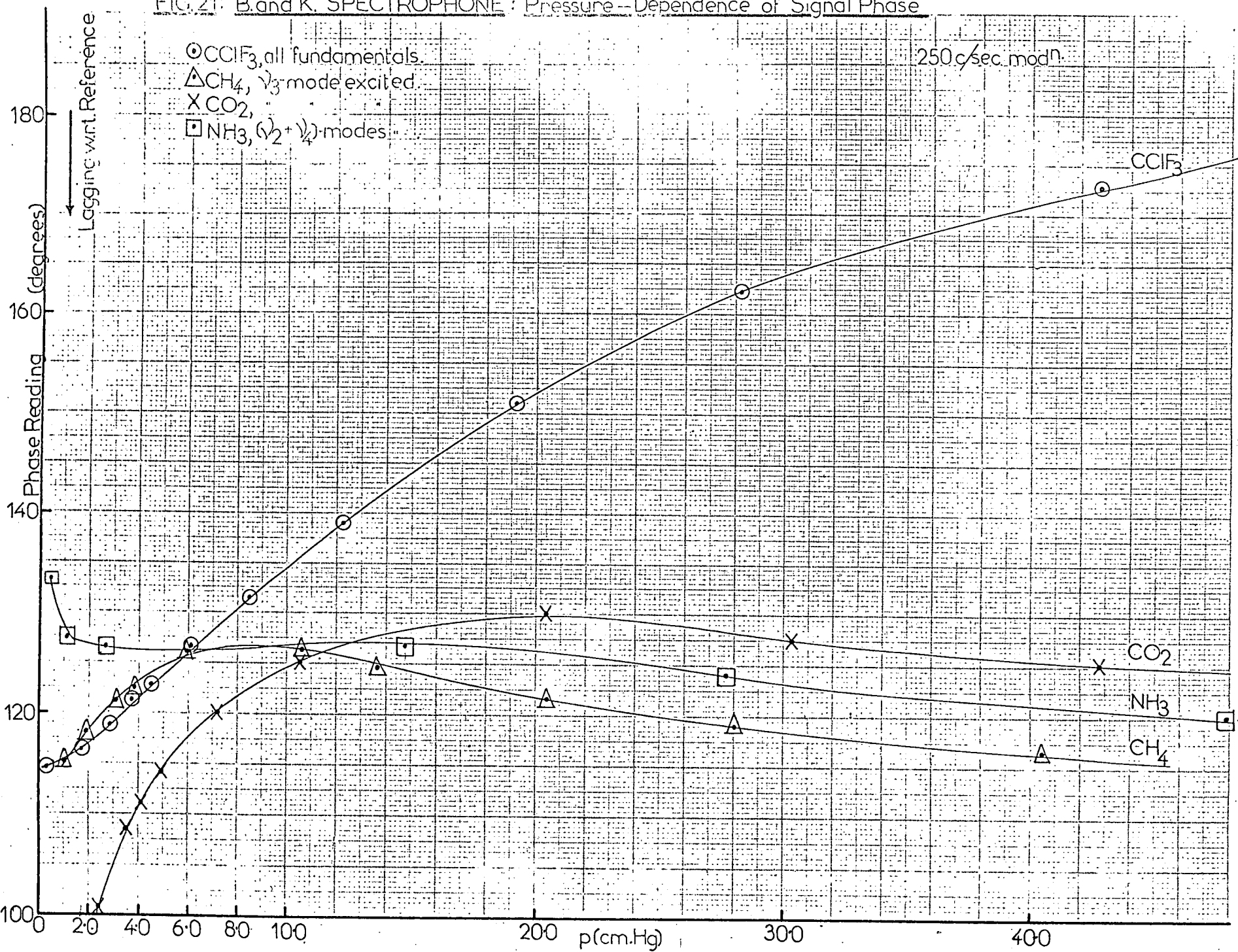


The output from the high input impedance, zero phase shift, cathode follower undergoes preamplification, then selective amplification at a bandwidth which is typically 10 db. down at 50 c/sec. either side of signal frequency. Maximum gain through the system is about 90 db. A phase meter (Peekel Type FB.120) is used to compare this signal with a reference supplied by a lamp and photovoltaic cell operating on the chopping disc. The reference signal, by means of a coaxial switch and a phase shifter, can also be used to set a zero phase shift condition between the channels, eliminating before a measurement is made, the slight phase shifts due to motor speed variations and drift in the selective amplifier. Extensive testing of the electronics showed that phase shifts due to operation of attenuators etc. were less than 0.5° .

EXPERIMENTAL PERFORMANCE:

After the cell's evacuation to an acceptable level ($\leq 1 \times 10^{-6}$ torr.) the spectrophone pump was shut off at the large taps and gas slowly admitted through the capillary leaks at a rate set by the diaphragm position monitor until the required pressure, read on the manometer in the gas-handling line, was developed in the cell. In the first experiments a five sector chopping disc modulated the incident radiation at 250 c/sec. Having firmly closed the acoustic valve the spectrophone frame was released and allowed to float freely on its rubber supports: the conditions for phase measurement. When the degree of amplification required by a

FIG. 21: B. and K. SPECTROPHONE : Pressure -- Dependence of Signal Phase



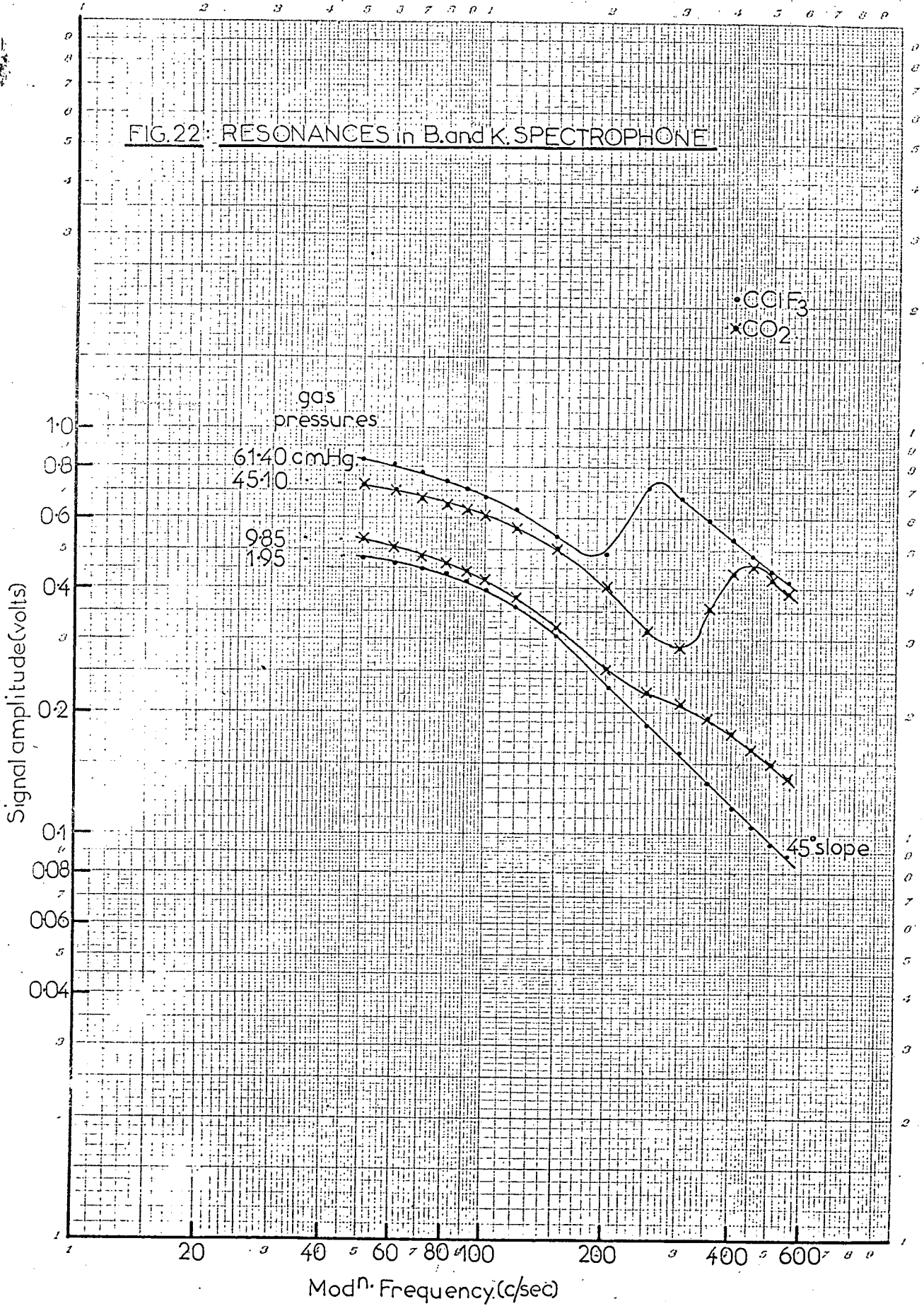
particular signal was set, the photocell reference was commoned (see p.48) through both channels and the electronics adjusted to read an arbitrary zero phase shift. Immediately, the channels were separated and the phase difference between the two signals read from the phase meter.

At the outset, before attempting relaxation measurements, criteria for the spectrophone's required performance had to be set and satisfied. The pressure-independence of signal phase in fast relaxing gases of high molecular weight offered testing of least ambiguity, deviations due to thermal diffusivity (p.18) being possible in light gases e.g. NH_3 . It was demanded, therefore, that the spectrophone signal remain constant in phase over the accessible pressure range in Arcton 13 (CClF_3) (cf.p.29)

A RESONANCE PROBLEM: The criterion was not satisfied (Fig.21). The Arcton signal, far from being pressure-independent, developed a phase lead of 65° between the pressures of 1cm.Hg and 55 cm.Hg. On extending the investigation to a range of gases, a confusion of effects emerged. While at the lower pressures (2→ 10cmHg) some gases (e.g. CO_2 , N_2O , CH_4) lagged increasingly with decreasing pressure in a manner suggestive of relaxation their higher pressures showed anomalous phase leads. Another heavy molecule, SF_6 , behaved (35° lead) similarly to Arcton but at the lowest pressures ($< 2\text{cmHg}$) the phases of all the gases started to lead with further pressure lowering.

In order to gain greater insight into these phenomena the

FIG. 22: RESONANCES in B. and K. SPECTROPHONE



frequency-dependence of the signal amplitude was studied. The variable frequency motor used to drive the chopping disc allowed scanning of the range between 50 c/sec. and 550 c/sec.

According to the predictions of Gorelik's model (eq.3.15) the amplitude of the optic-acoustic signal is inversely proportional to a modulation frequency (ω) small compared with the collision efficiency (f_{co}) in the gas. Delany (41) has experimentally confirmed this down to the modulation frequencies ($\lesssim 50$ c/sec.) where heat conduction effects lower the intensity of the acoustic signal. A double logarithmic plot of signal amplitude against modulation frequency should, therefore, be a straight line of gradient minus one.

Instead of a straight line the Arcton signal described a strong resonance peak centred at a modulation frequency of ~ 255 c/sec. (Fig.22). Likewise,

SF₆ resonated at ~ 215 c/sec. modulation,

CO₂ " " ~ 430 c/sec. " (Fig.22)

and CH₄ " " > 550 c/sec. " ; the positions

of the resonance peaks being in direct proportion to the sound velocities in the various gases. Although their characteristic frequencies were pressure-independent, the resonances did not appear until a certain critical pressure (~ 10 cmHg. in all cases) had been exceeded; thereafter their intensity developing with its continuing increase. Even at the higher pressures all the gases showed a low-frequency ($\omega < 100$ c/sec.) deviation presumably due to the heat conduction effects.

Similar behaviour was previously noted in a spectrophone experiment by Decius (45). A set of pressure-independent resonances was found at modulation frequencies between 400 and 600 c/sec, the resonance frequency for any gas being directly proportional to the velocity of sound in the gas. Encouraged by the large phase changes associated with this phenomenon to abandon phase measurements in favour of amplitude studies, Decius went no further than to suggest that a critical factor in the development of these resonances might be the compliance of the diaphragm which forms one cell wall.

Diaphragm resonance, as found in the 'Two-cell Experiment', being impossible with the B. and K. microphone and the metre wavelengths, associated in these gases with 250 c/sec sound, being incapable of "seeing" the spectrophone cell, whose characteristic dimensions, with its valve closed, are only 2 cm., the only acoustically feasible explanations remaining had to involve a Helmholtz Resonator. Decius's idea, that the compliance of the diaphragm somehow permits the development of standing waves in the cell, was experimentally disproved by establishing the resonance frequencies' independence of the diaphragm tension. The tension was reduced by changing the microphone polarization voltage from 200v to 137v.

A Helmholtz resonator (59) is a mechanical system analogous to a mass suspended on a spring. Looking at Fig.16, two gas volumes, A and B, are seen to be connected by the annular pumping passage around the microphone cartridge. If



the inertia of the gas in the annular neck plays the part of the mass and the compressibility of the gas in either A or B that of the spring, then the conditions are satisfied for a resonating system with a fundamental frequency given by,

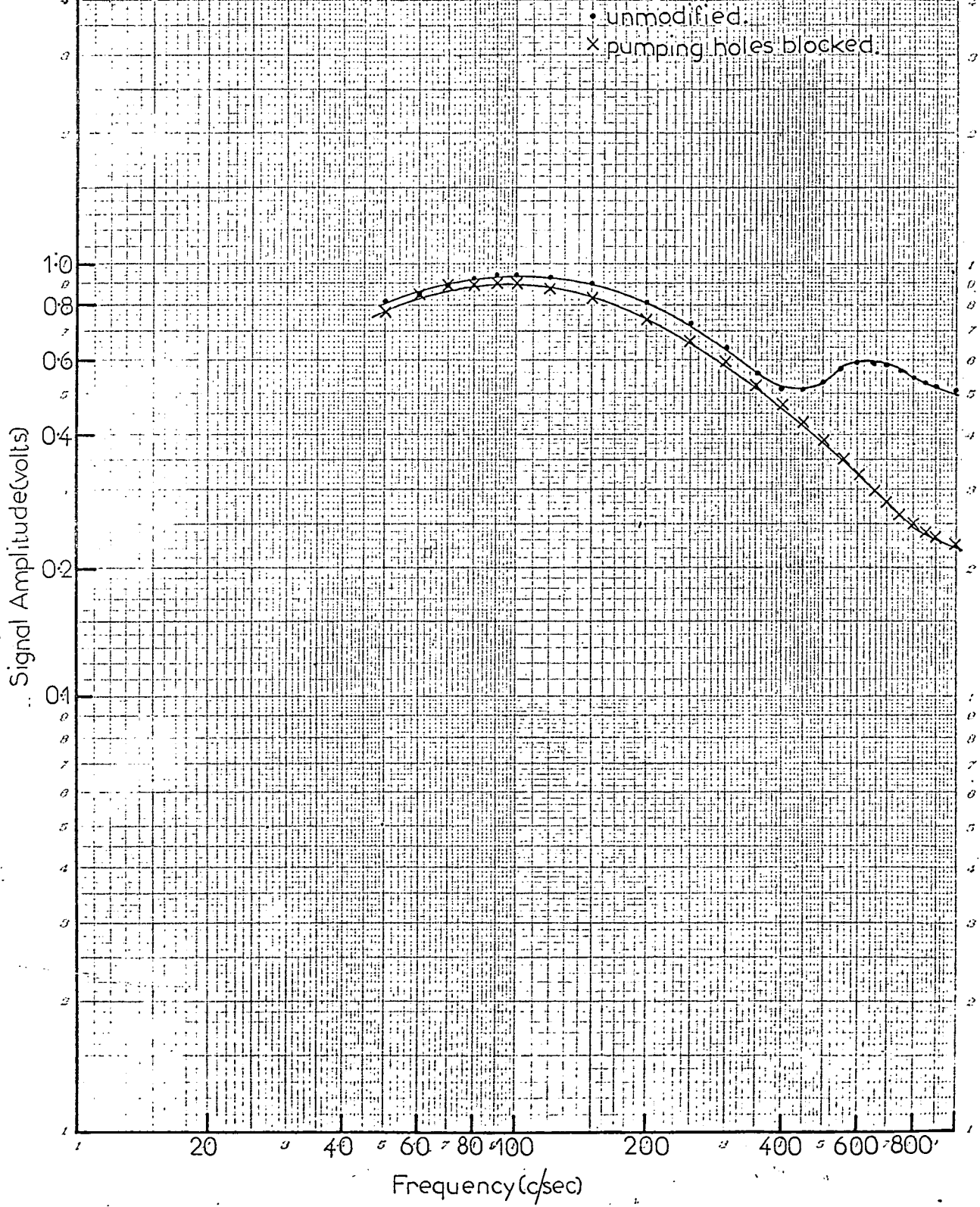
$$f = \frac{S}{2\pi} \sqrt{\frac{C}{l.V}} \dots\dots\dots (5.1)$$

Where S is the velocity of sound, C the cross-sectional area and l the length of the neck, and V the volume of the cavity.

Confirmation of the hypothesis was sought by screwing a collar to the microphone cartridge, reducing the cross-sectional area of the annulus (C). The expected lowering of the resonance frequencies was not, however, observed. Not until later in the investigation did a technique, of sufficient power to confirm the Helmholtz resonance, evolve. During the intervening period several experiments were devised which, although negative in outcome, were interesting in their failure to reveal any further flaws in the system.

At high gas pressures an optic-acoustic signal is formed near the front window of the cell. Propagating back into the chamber the pressure wave sweeps across the face of the diaphragm with the possibility of exciting complex oscillations of unknown properties. A thin stainless steel plate with a 2.5 m.m. hole centrally bored was fixed in front of the diaphragm ensuring that pressure pulses only struck its centre normally. The frequency characteristics were unmodified: the propagation effect is therefore unimportant.

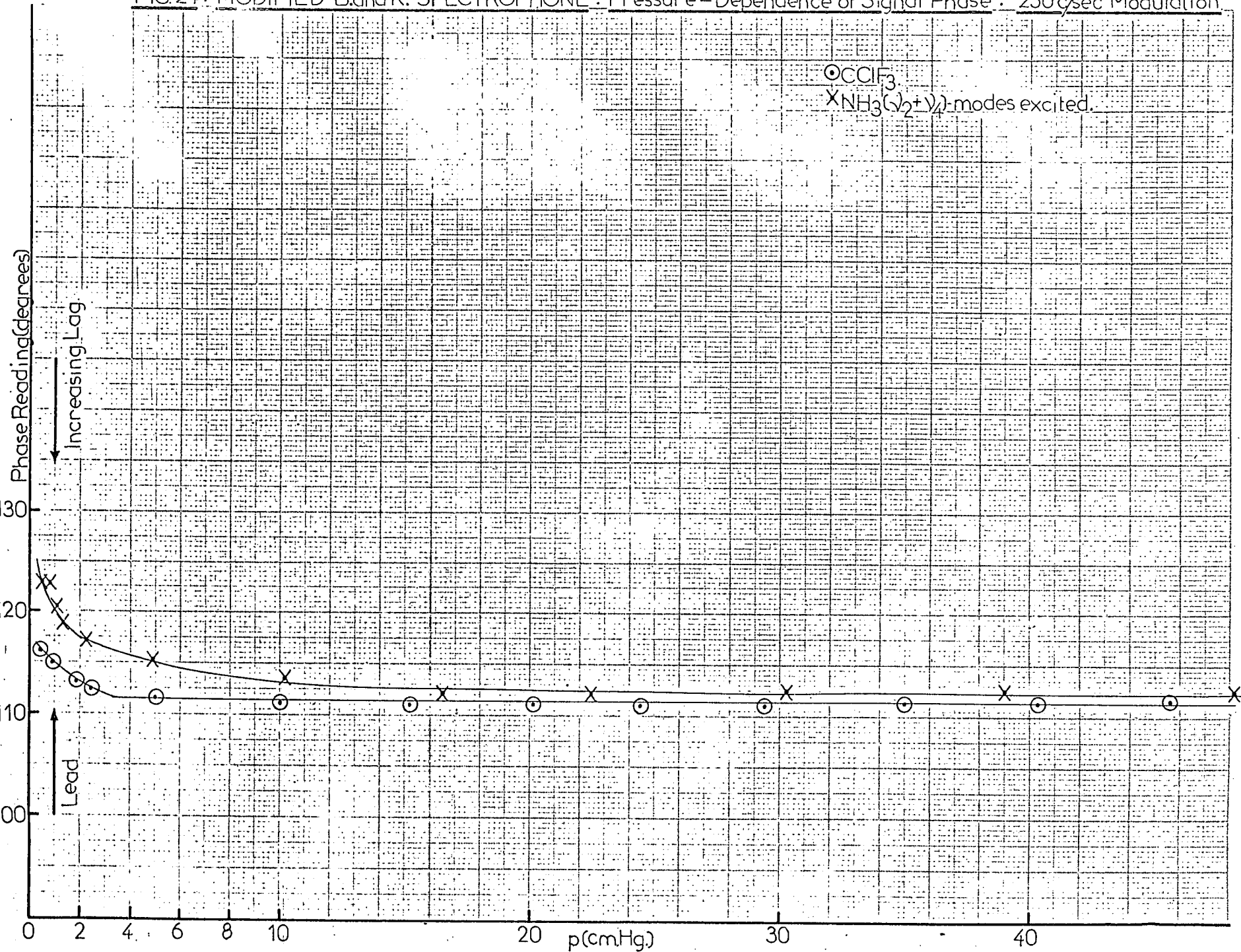
FIG. 23: 'AshidaVox' SOUND SOURCE in SPECTROPHONE



That the resonances were not unique to optic-acoustically generated signals was demonstrated by introducing a sound wave into the spectrophone from a small pressure transducer (Ashida Vox) mounted in a brass plate replacing one of the cell windows. From the previous data the system was expected to resonate at ~ 600 c/sec for laboratory air. A resonance was detected at 610 c/sec. Another transducer, with a quite distinct free space calibration, was fitted and the resonance measured at 620 c/sec. In addition to establishing the resonances' independence of sound source the transducer experiment, by not requiring the cell to be either filled with an infra-red active gas or bathed in radiation, allowed the system to be much more instructively modified. Volume B was separated from both the annular neck and volume A by blocking the three pumping holes in the microphone support flange. The anomaly at 600 c/sec disappeared (Fig.23): the Helmholtz Resonance hypothesis was proved.

Before this proof could be checked with an optic-acoustic signal the spectrophone cell had to be modified to provide a new pumping route for the gas volume behind the microphone. A stainless steel tube, sunk into the back plate (Fig.16) was brought round the front of the cell and fitted into the main pumping line outside the acoustic valve. In order to permit acoustic isolation of the minor volume (B) a simple magnetic valve involving the movement of a ball-bearing was incorporated into the auxiliary line. Only one of the two spectrophone cells

FIG. 24: MODIFIED B. and K. SPECTROPHONE: Pressure-Dependence of Signal Phase: 250 c/sec Modulation

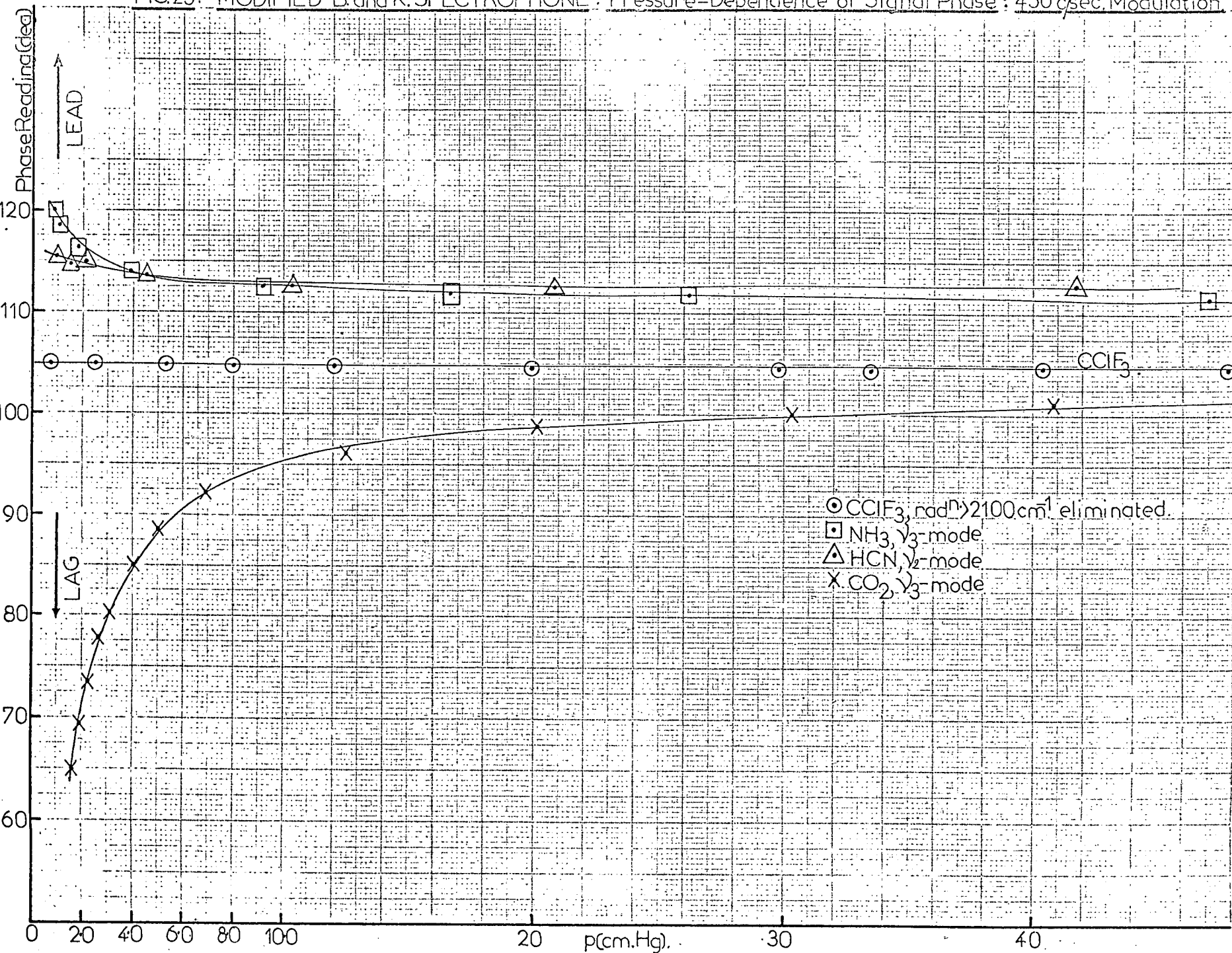


originally built was modified (Fig.17).

HEAT CONDUCTION EFFECTS: Optic-acoustic signals (for $\omega > 100$ c/sec) in all the gases now obeyed the linear relationships required by theory (3.15); no trace of resonance remained; the evidence from the transducer experiment was substantiated. Only at frequencies $\omega < 100$ c/sec did the amplitudes deviate, falling below the ideal line of 45° slope. Although Delany (41) noted the same effect, which is predictable from a consideration of heat conduction to the cell walls (see p.18), at $\omega \approx 50$ c/sec., the dissipation of acoustic energy remained an observable in the 'B. and K.† Spectrophone' at rather higher modulation frequencies. That the cell dimensions are critical to the extent of the deviation has already been shown (3.16); another factor seemed to involve the irradiation of the cell walls by the divergent incident beam. By allowing the beam access to the cell through only a small aperture in the centre of the front window, the direct surface heating of the walls was eliminated. Under these conditions the signal from a sulphur hexafluoride sample followed the theoretical line down to $\omega = 60$ c/sec, to be compared with its normal limit for linearity at $\omega = 120$ c/sec. It was therefore concluded that, on returning to the fixed frequency phase measurements some thermal diffusivity lead was to be expected at the lowest gas pressures.

Down to 2.5 cm.Hg the signal phase in Arcton 13 (Fig.24) was pressure-independent (c.f. Fig.21), but between 2.5 cm.Hg

FIG.25: MODIFIED B. and K. SPECTROPHONE : Pressure-Dependence of Signal Phase : 450 c/sec. Modulation



and 0.5 cm.Hg a phase lead of 40 developed; our criterion was not quite satisfied. Before attempting to reduce the effect by further apparatus modification the origin of the lead was checked by studying ammonia whose light, fast-relaxing (53) molecules would magnify wall-effects without interference from relaxation lags. At the lowest pressure (0.7 cm) the phase lead reached 11° (Fig.24); indeed worse than Arcton.

Solving (41) the equations for heat flowing radially in a spherical container describes the phase and amplitude of an oscillating pressure signal in terms of a summation whose first term is adequate for comparison with experiment. The relevant phase lead is,

$$\phi = \tan^{-1} \mu/w \dots\dots\dots (5.2)$$

where μ was defined in (3.16) and w is the modulation frequency. At 0.5 cm.Hg pressure, spherical radius $a = 1$ cm. and $w = 1571$ rad/sec., the lead predicted for Arcton 13 is $\phi \approx 2.0^\circ$ and for Ammonia is $\phi \approx 9.0^\circ$

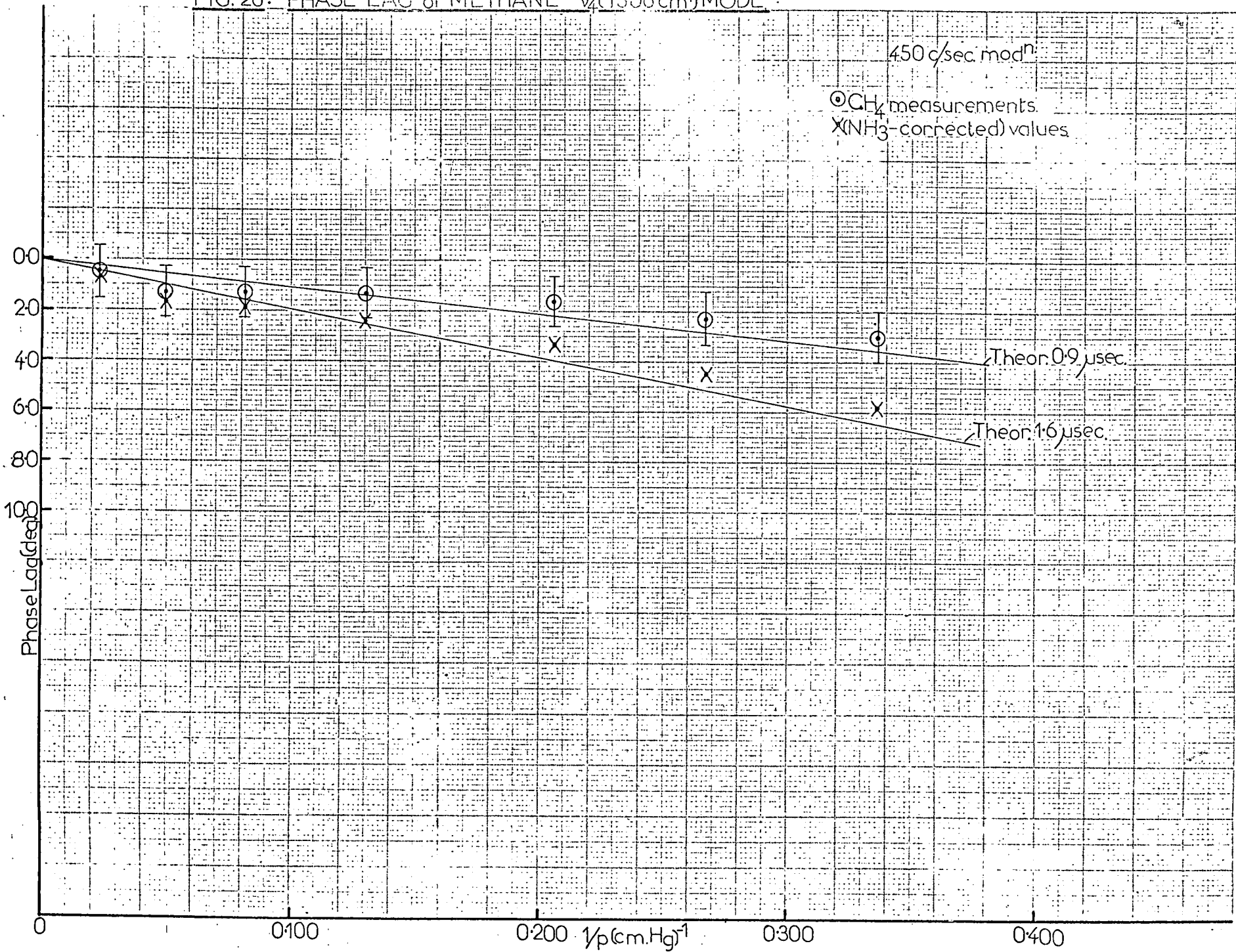
Varying correctly with gas properties and in quantitative agreement with the predictions of the simple heat conduction model, it seemed certain that the small deviations still marring the spectrophone's performance were due to the thermal diffusivity of the gas and as such, could be further reduced by raising the modulation frequency (c.f.p.18) to 450 c/sec.

In the new, higher frequency, experiment the phase of the Arcton signal remained constant over the accessible pressure range (Fig.25): the criterion was satisfied.

Although the set standard had been achieved, relaxation lags at the lowest pressures in light gases were still confused by thermal leads. The effect being small, however, (5° or 6° at most) measurements on fast-relaxing gases were assumed suitable for correcting the phase lags in gases of similar transport properties. Ammonia and hydrogen cyanide are shown in Fig.25. The latter on excitation ($\sqrt{2} + 2\sqrt{2}$ modes) by low energy radiation (Perkin Elmer filter) relaxes rapidly ($\tau < 0.1 \mu\text{sec}$ (60)) and as might be expected from its molecular weight, ($M = 28$) gave phase leads midway between ammonia and Arcton. From the trend it can be seen that the midweight gases e.g. $\text{CO}_2, \text{N}_2\text{O}$ will suffer little interference; a set of carbon dioxide results added to Fig.25 serves as a reminder of the experiment's goal: the study of relaxation phenomena.

MOVING SIGNAL CENTRE EFFECT: At higher pressures in most gases the optic-acoustic signal is formed near the front window of the spectrophone. When the pressure is lowered, especially in weakly absorbing gases, the radiation may have to penetrate significantly further into the cell before all the relevant energies are removed and therefore the origin of the pressure pulse is shifted. In the 'B. and K. Spectrophone', with an absorption path of 3 cm., the signal centre will move 1.5 cm. from the edge to the middle of the cell and in gases with low sound velocities this may produce a few degrees of phase lead with decreasing pressure. Only one weakly absorbing gas studied,

FIG. 26: PHASE LAG of METHANE- $\nu_4(1306\text{ cm}^{-1})$ MODE



sulphur hexafluoride, had a low sound velocity (136 m/sec c.f. $\text{VNH}_3 = 440$ m/sec.) and being fast relaxing ($\beta = 0.2 \mu\text{sec.}$ (61)) could clearly show these small phase leads ($\Delta\phi = 9^\circ$ between $p = 5.0$ and 0.5 cm.Hg), dependent on both pressure and signal intensity. In this system at 250 c/sec. the phase sensitivity calculated as a function of signal position is 1° per 0.14 cm. Restricted in influence, the effect did not interfere with any of the other studies, the gases being either more intensely absorbing or having higher sound velocities.

ESTABLISHING THE EXPERIMENT ABSOLUTELY: So far the spectrophone's performance has only been tested negatively with gases capable, because their relaxation is rapid, of revealing ^{undesirable} ~~undescribable~~ phase effects. Before all measured phase changes can be confidently claimed as relaxation lags a link with classical technique is required; this is possible through the ν_4 -mode (1306 cm^{-1}) in methane (c.f. Chapt. 4 p. 35). Phase measurements made in methane (Perkin Elmer filter) and corrected for thermal diffusivity as described above by phase leads observed in ammonia, an essentially similar molecule from this point of view, are plotted in Fig. 26 and compared with the theoretical relaxation line for $1.6 \mu\text{sec.}$; the ultrasonic β at 25°C is $1.5 \pm 0.2 \mu\text{sec.}$ (54): excellent agreement.

The belief that the 'B. and K. Spectrophone Experiment' is capable of reliably measuring relaxation phase lags in gases seems

therefore to be fully justified. In the next chapter studies on the higher energy modes of a series of simple molecules are described.

CHAPTER 6

THE B. and K. SPECTROPHONE EXPERIMENT: RELAXATION IN SIMPLE GASES.

Assuming pressure-dependent phase lags to be due solely to molecular relaxation processes several simple gases were studied in the 'B. and K. Spectrophone'. Phase changes measured at 450 c/sec. modulation by the technique described in the previous chapter were plotted against the reciprocal of gas pressure and compared with curves defined by (3.14):

$\tan \phi = \frac{\omega \cdot \tau}{p}$ where ϕ is the phase lag, τ the relaxation time at 1 atm., p the pressure in atm. and ω the modulation frequency in radians per second.

The importance of gas purity in relaxation measurements has been repeatedly demonstrated, particularly in studies of the longer relaxation times; water's strong catalytic effect on the degradation of energy from the ν_2 -mode in carbon dioxide (6.5) is a well-known example. Details of the procedures used to purify the gases measured in this work are summarised in Table II.

Restricted to simple molecules, their few fundamental modes normally being of well separated energies, a situation often improved in the infra-red by the non-appearance of Ramanactive vibrations, these experiments allowed adequately specific excitation of modes to be achieved with the two filters described under Optical System (Chapt. 5, p.47). The Barr and Stroud filter eliminates low energy ($< 1,700 \text{ cm}^{-1}$) and the Perkin Elmer

TABLE 2.

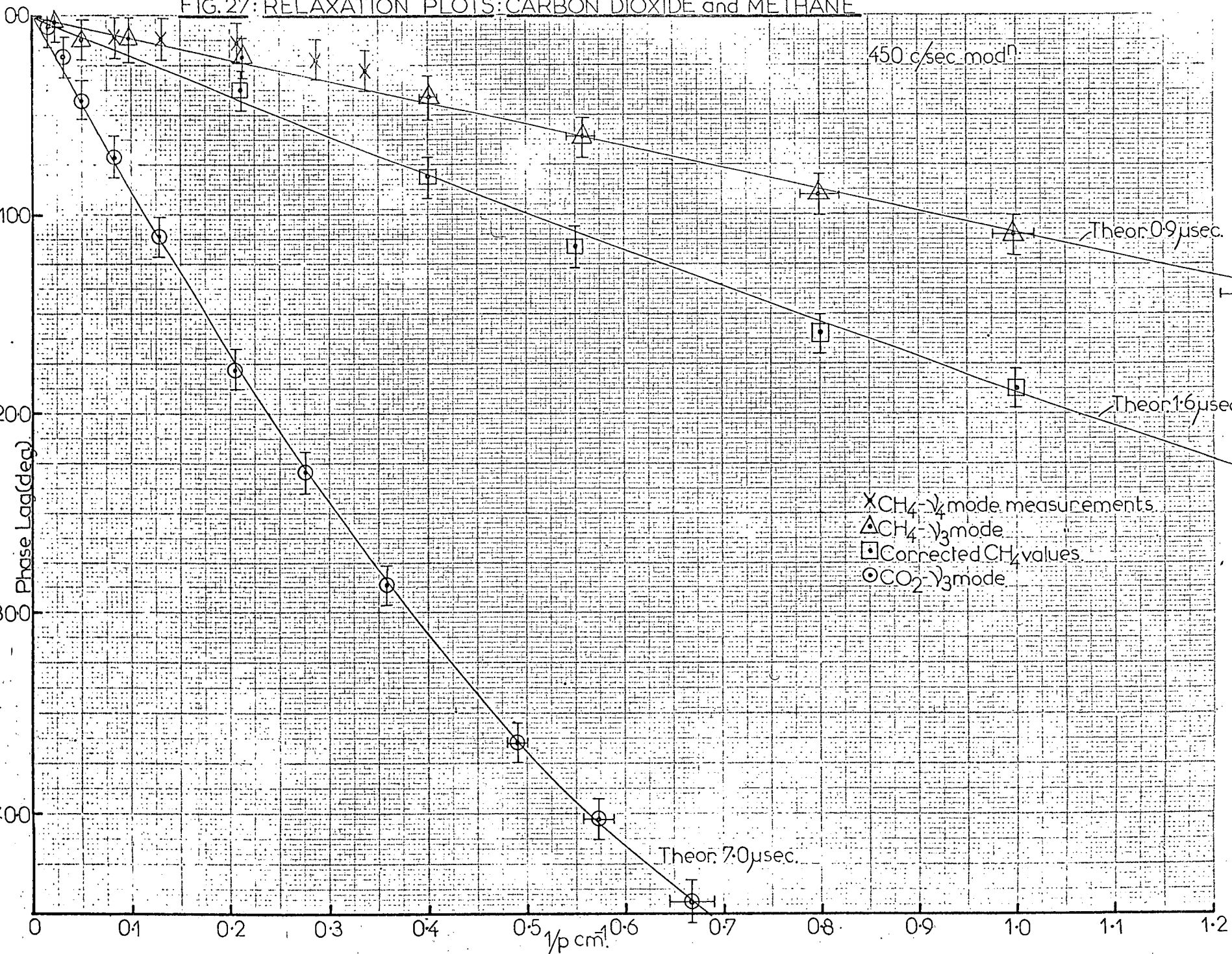
GASES USED IN B. and K. SPECTROPHONE EXPERIMENT.

GAS	ORIGIN	PURIFICATION		CRITERION OF PURITY
		DISTILLATION	DRYING	
Carbon Dioxide	'Analar' NaHCO_3 + heat	By warming from liq N_2	P_2O_5 (3 Days)	Infra-red Analysis.
Nitrous Oxide	Dental Cylinder	From liq N_2	P_2O_5	Infra-red Analysis.
Methane	Cylinder, 97% pure	Clusius - Riccobini (58) (Column reflux- ing under liq O_2)	P_2O_5	Mass spectrometer, traces of $\text{M} = 28$, probably CO (<0.4%).
Chlorotrifluoro- methane (Arcton 13)	I.C.I. Ltd: cylinder	From liq N_2	P_2O_5	Infra-red Analysis.
Sulphur Hexafluoride	I.C.I. Ltd: cylinder	From liq N_2	P_2O_5	Infra-red Analysis.
Ammonia	Cylinder (anhydrous)	From liq N_2	CaO	Infra-red Analysis.
Carbonyl Sulphide	Matheson Co. Inc. (97% pure). lecture bottle	From liq N_2 & equilibrated at -63.5°C .	P_2O_5	Infra-red and mass- spectrometer. 1% CS_2 present.
Nitrogen	B.O.C. Ltd. (O_2 free)	--	P_2O_5	--
Xenon	B.O.C. Ltd	--	--	Quoted 99% Xe, trace Kr.
Neon	B.O.C. Ltd			Quoted 99.9% Ne, 0.1% He. 2 p.p.m O_2 , 1 p.p.m. H_2 .
Hydrogen Cyanide	I.C.I. Ltd: cylinder	from solid CO_2 + acetone then ice + salt mixture.	P_2O_5	Infra-red Analysis.

high energy radiation ($> 2,100 \text{ cm}^{-1}$).

A precision of better than $\pm 1^\circ$ can be quoted for the phase measurements; the reliability of a relaxation time estimate depends, however, on the available signal strength in the gas. If the limiting signal level is reached at 10 cm. pressure then short relaxation times ($< 5 \text{ } \mu\text{sec.}$) can only be quoted to $\pm 1 \text{ } \mu\text{sec}$ whereas the relaxation time of a gas allowing measurements at 1 cm. is determined to within $\pm 0.1 \text{ } \mu\text{sec.}$

FIG. 27: RELAXATION PLOTS: CARBON DIOXIDE and METHANE



RESULTS:

CARBON DIOXIDE, Fig.27: irradiated at

(1) high energies ($> 1,700 \text{ cm}^{-1}$): $\nu_3(2,349.3 \text{ cm}^{-1})$ vibration excited with possible small contributions from overtone and combination bands. The measured phase lags, thermal effects being small for this molecule, are compared with the 7 μsec theoretical relaxation line.

(2) low energies ($< 2,100 \text{ cm}^{-1}$): $\nu_2(667.3 \text{ cm}^{-1})$ vibration excited but, because of the source's spectral distribution, insufficient energy was absorbed to generate a useful signal. No measurements were possible.

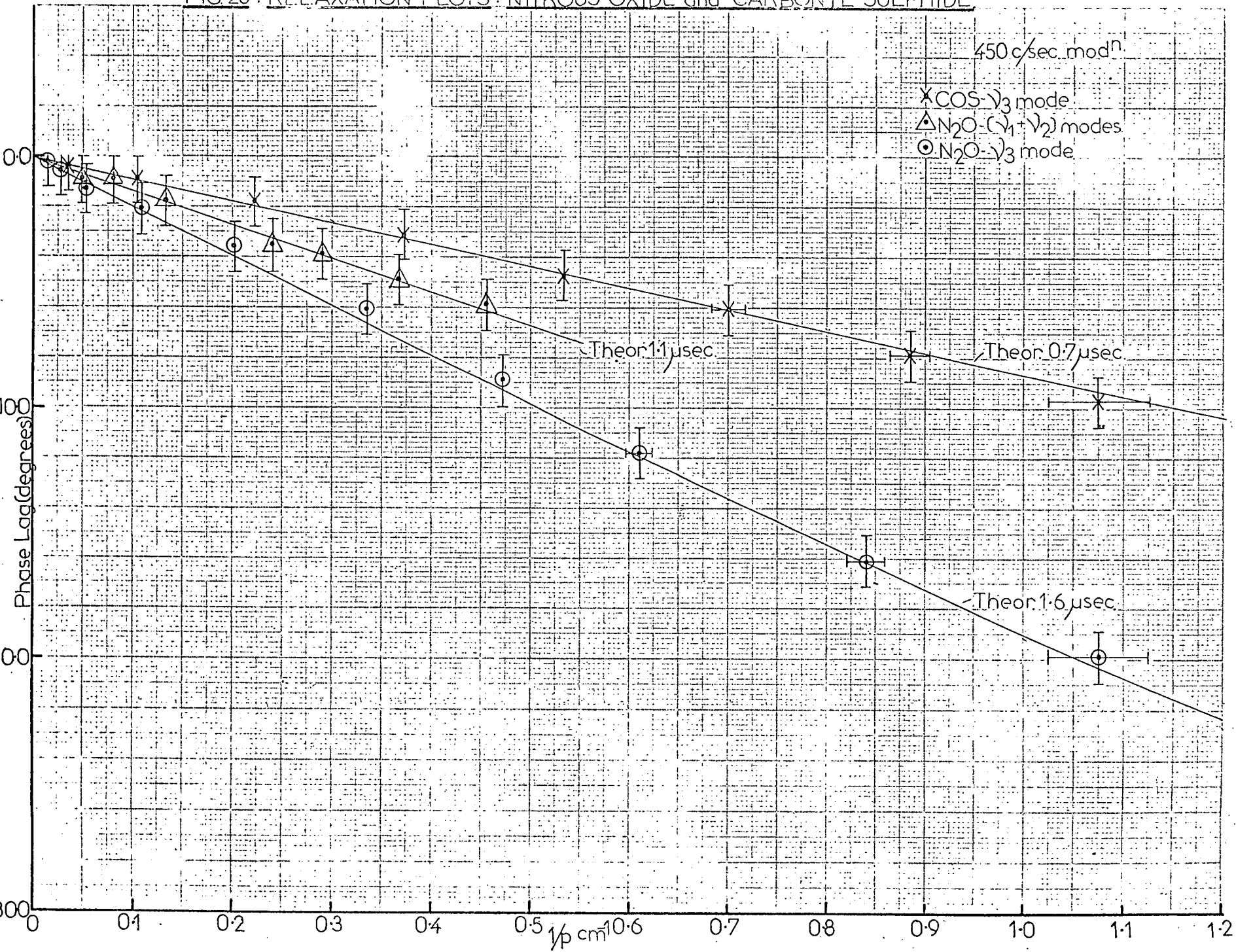
METHANE, Fig. 27: irradiated at

(1) high energies : $\nu_3(3020.3 \text{ cm}^{-1})$ vibrational mode excited; measured phase lags are compared with the 0.9 μsec relaxation line.

(2) low energies: $\nu_4(1306.2 \text{ cm}^{-1})$ vibrational mode excited; phase lags are included with the ν_3 results, but were only measurable down to 3 cm. pressure, the signal level being low.

Thermal effects must be considered for this light molecule and a set of corrected phases, derived by the previously described (p.56) ammonia procedure, are compared with the 1.6 μsec . relaxation line.

FIG 28 : RELAXATION PLOTS : NITROUS OXIDE and CARBONYL SULPHIDE



NITROUS OXIDE, Fig.28: irradiated at

(1) high energies ($>1,700 \text{ cm}^{-1}$): $\nu_3(2223.5 \text{ cm}^{-1})$ vibrational mode excited; phase lags are compared with the 1.6 μsec theoretical relaxation line.

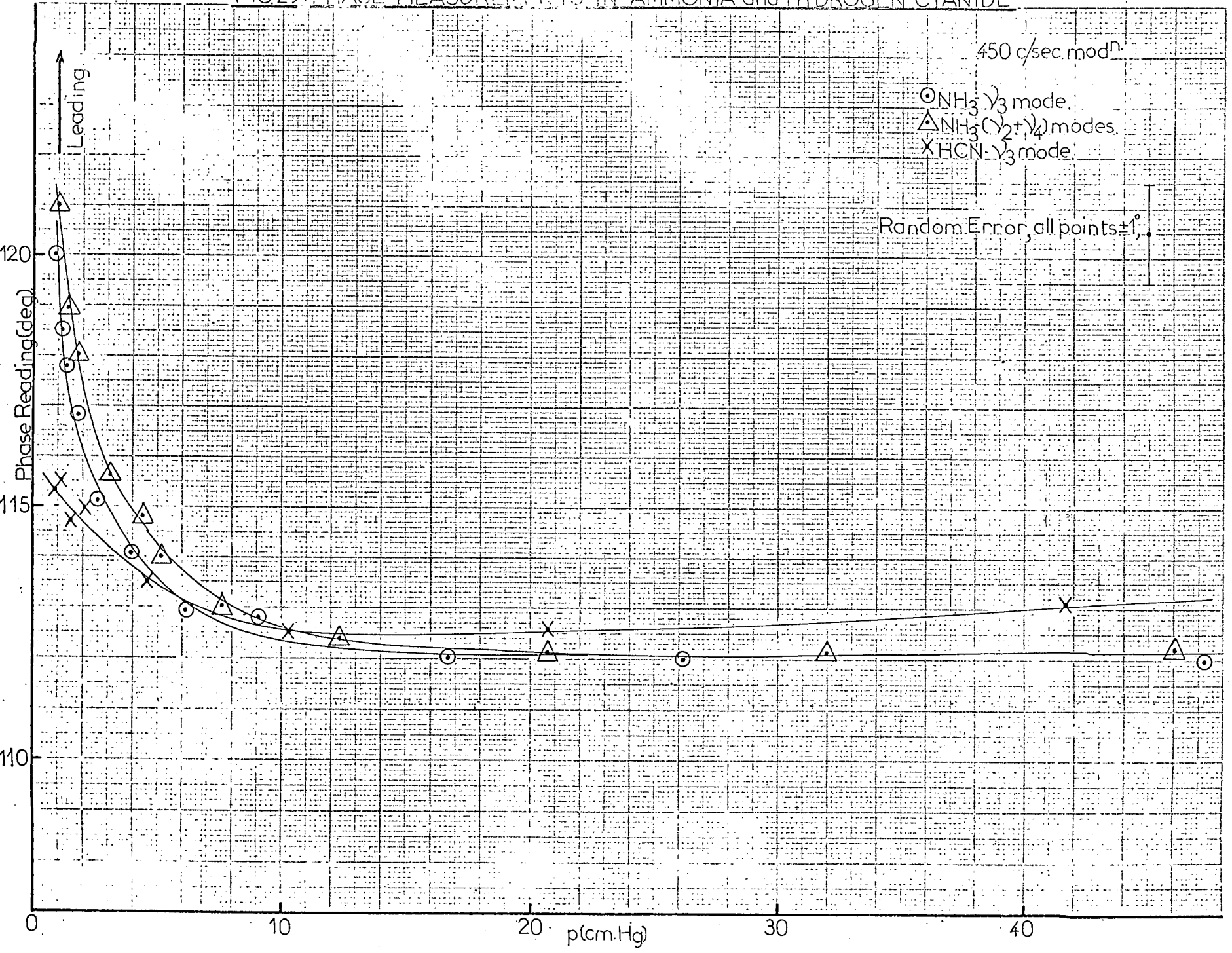
(2) low energies ($<2,100 \text{ cm}^{-1}$): simultaneous excitation of the $\nu_1(1285.0 \text{ cm}^{-1})$ and the $\nu_2(588.8 \text{ cm}^{-1})$ vibrational modes; phase lags, limited to pressures $>2 \text{ cm.}$ by the low signal level, are compared with the 1.1 μsec theoretical relaxation line.

As in carbon dioxide thermal effects are negligible.

CARBONYL SULPHIDE, Fig.28: irradiated at

high energies: $\nu_3(2079 \text{ cm}^{-1})$ vibrational mode excited with possible small contributions from overtone and combination bands; phase lags, measurable down to 0.50 cm. pressure because of the high signal levels, are compared with the 0.7 $\mu\text{sec.}$ theoretical relaxation line. No thermal effects need be considered (M.W. = 60).

FIG 29: PHASE MEASUREMENTS IN AMMONIA and HYDROGEN CYANIDE



AMMONIA, Fig.29: irradiated at

(1) high energies ($> 1,700 \text{ cm}^{-1}$): $\nu_1(3336.5 \text{ cm}^{-1})$ vibrational mode excited; phase behaviour followed to within 1° the results from irradiation at,

(2) low energies ($< 2,100 \text{ cm}^{-1}$): $\nu_2(950 \text{ cm}^{-1})$ and $\nu_4(1627.5 \text{ cm}^{-1})$ modes simultaneously excited and showing a thermal diffusivity phase lead with decreasing pressure, as discussed earlier (p.56)

HYDROGEN CYANIDE, Fig.29: irradiated at

(1) high energies: $\nu_3(3312 \text{ cm}^{-1})$ vibrational mode excited giving phase results identical with those from irradiation at

(2) low energies: $\nu_2(712 \text{ cm}^{-1})$ vibrational mode and its first overtone ($2\nu_2 = 1412 \text{ cm}^{-1}$) excited; no relaxation lag shown, only a slight thermal lead.

CHLOROTRIFLUOROMETHANE (Arcton 13), Fig. 25: irradiated at

low energies, gave no phase shift over a range of pressures from 0.75 to 60 cm.

SUMMARY:

Relaxation times for the gases studied in this work are gathered in Table III; the errors quoted are based on the fit between the experimental points and the theoretical curves, taking into account the possible influence of the thermal conduction effect.

TABLE III

Gas	Fundamental Vibration Excited	Relaxation Time(μ sec)	Ultrasonic β (μ sec)
CO ₂	$\nu_3, 2349 \text{ cm}^{-1}$	7.0 ± 0.5	6.5 (2)
CH ₄	$\nu_3, 3020 \text{ cm}^{-1}$	1.6 ± 0.2	
CH ₄	$\nu_4, 1306 \text{ cm}^{-1}$	1.6 ± 0.4	1.5 (54)
N ₂ O	$\nu_3, 2223.5 \text{ cm}^{-1}$	1.6 ± 0.2	
N ₂ O	$\nu_1 + \nu_2, 588.8 \text{ cm}^{-1} + 1285 \text{ cm}^{-1}$	1.1 ± 0.2	0.9 (62)
COS	$\nu_3, 2079 \text{ cm}^{-1}$	0.7 ± 0.1	0.69 (63)
NH ₃	$\nu_1, 3336.5 \text{ cm}^{-1}$	< 0.1	
NH ₃	$\nu_2 + \nu_4, 950 \text{ cm}^{-1} + 1627.5 \text{ cm}^{-1}$	< 0.1	0.001 (53)
HCN	$\nu_3, 3312 \text{ cm}^{-1}$	< 0.1	
HCN	$\nu_2 + 2\nu_2, 712 \text{ cm}^{-1} + 1412 \text{ cm}^{-1}$	< 0.1	0.1 (60)
CClF ₃	All fundamental modes	< 0.1	0.09 (52)

DISCUSSION:

Before reviewing this work in the light of available experimental and theoretical results, some discussion about the fundamental significance of the spectrophone's measurements is required. A 'relaxation time', as defined in terms of (1.1), the simple relationship derived by Landau and Teller (66) from the harmonic oscillator model of a molecule, can be measured strictly for a particular mode only by a technique sensitive to energy change within that mode. Since in the spectrophone, the energy change is observed not in the vibrational mode excited but in translation, is it justifiable to equate the delay time measured with the relaxation time of the specific mode? Decius has argued (67) that "the hope of studying 'separate modes' by the spectrophone is quite illusory". Considering a polyatomic molecule as a set of coupled oscillators, the decay of vibrational energy will be governed by a rate matrix whose eigenvalues, involving mixtures of the fundamental processes, will be the observables for the system. That these characteristic times are independent of how the system has been excited forms the basis for Decius's arguments: periodic variation of a selected vibrational temperature, as in the spectrophone, can reveal no more than that of the translational temperature, as in ultrasonics. However, the amplitudes of the different 'normal modes' may be particularly sensitive to the nature of the driving function and if several have similar but not identical characteristic times then Decius's statement will be invalidated. Another important

factor must be the degree of coupling between the molecule's fundamental modes. Decius's description of relaxation cannot account for the double dispersions found in ultrasonics and assigned to the separate excitation of different groups of vibrations. Two cases, those of sulphur dioxide (68) and ethane (69), have been well-established. Both involve a low energy mode (at 290 cm^{-1} in ethane) separated by a large energy gap from the lowest (821 cm^{-1} in ethane) of the next group of vibrations. Such assignments of different relaxation times to separate vibrational groups within a molecule seem to invalidate the general applicability of the Decius hypothesis and hence its comment on the spectrophone's potential.

Stretton (10) has determined the eigenvalues of the rate matrix for methane, producing a set of relaxation times which can be associated with the fundamental processes normally considered in simple de-excitation mechanisms: the excited ν_3 -mode transferring its energy to the first overtone of the ν_2 -mode and so on. At the present level of theoretical development it would therefore seem justifiable to interpret the results in terms of the redistribution of energy amongst the fundamental vibrational levels by a series of complex collisions.

Since the fate of the relaxing energy is immaterial to equation (1.1), its definition of the 'relaxation time' for a specific higher energy vibrational mode refers to the first of the series of energy transfer processes. The spectrophone sums the 'relaxation times' for all the processes required to reduce the

energy to translation. If a single 'relaxation time' (τ) is measured ultrasonically for a group of vibrations then, by assuming that energy slowly enters the group from translation via the lowest mode before being rapidly distributed amongst the others, a 'reduced relaxation time β ', associated with the lowest mode, can be derived from,

$$\beta = (C_1^{\text{vib}} / \sum_s C_s^{\text{vib}}) \tau, \quad (6.1),$$

where C_1^{vib} is the vibrational heat capacity of the lowest mode and $\sum_s C_s^{\text{vib}}$ the total heat capacity of all the modes.

By comparing a 'spectrophone relaxation time' with the 'reduced relaxation time β ', a measurement is obtained of the facility with which energy, injected at a high vibrational level, can be degraded by complex collisions to the lowest vibrational mode in the molecule.

The well-developed theory of energy transfer from the lower vibrational levels (1) is based upon a simple model which can be invoked during speculation about complex collisions. For a molecule to make a vibrational transition ($E_1 \leftrightarrow E_2$) it must suffer, during a collision with another, an oscillatory perturbation of frequency ν defined by the energy gap:

$$\nu = (E_1 - E_2) / h \quad \dots \dots \dots (6.2)$$

where h is Planck's constant. The perturbation experienced, effectively a measure of the sharpness of the collisional interaction, is a function of the molecules' relative velocities and the shape

of the intermolecular potential. The number of effective perturbations generated in a gas under given conditions in unit time defines the 'collision efficiency' whose value is exponentially related to the energy gap: the larger the gap the less frequent the critical collisions. From a knowledge of the relaxation time of the lowest mode in a particular polyatomic molecule the rates of possible complex collision processes for de-exciting a higher mode can therefore be roughly estimated by comparing the widths of the energy gaps involved.

Measurements, agreeing with the ultrasonic β 's for five groups of low energy modes, emphasise both the spectrophone's consistent performance for a wide range of molecules and the justifiability of the thermal diffusivity correction. None of the fast-relaxing modes ($\text{NH}_3(\nu_2+\nu_4)$, $\text{HCN}(\nu_2)$, CClF_3) lagged in phase but their small thermal leads permitted an estimation of this minor effect which, applied to methane, gave a corrected relaxation time for the ν_4 -mode in good agreement with ultrasonic values (2).

Of the higher energy levels only the ν_3 -modes in nitrous oxide and carbon dioxide appear to remain vibrationally excited for a detectable time before their energy is degraded to the lowest level in the molecule. Relaxation of the ν_3 -mode in methane was indistinguishable from that of the ν_4 -mode. The ν_1 -mode in ammonia and the ν_3 -mode in hydrogen cyanide relax, as do the lowest modes in these molecules, too rapidly for measurement in the spectrophone. In carbonyl sulphide, despite the wide energy gap

below the high energy mode ($\nu_3:2079\text{cm}^{-1}$, $\nu_1:859\text{cm}^{-1}$, $\nu_2:527\text{cm}^{-1}$), the relaxation time measured for the ν_3 -mode agrees well with Fricke's (63) ultrasonic result ($\sqrt{\nu_1 + \nu_2}$ modes) but is lower than that of Eucken and Aybar (64) ($\beta = 1.35 \mu\text{sec}$). For these molecules there is an easy path for the degradation of energy to the lowest levels. In each case there is close energy matching between the level excited and overtone of a lower mode; an energy gap $< 100\text{cm}^{-1}$ followed by a resonant 'cascade' from the overtone to the fundamental suggests a rapid process.

A direct comparison was possible between the ν_3 -mode in nitrous oxide and those of lower energy ($\nu_1 + \nu_2$) because the symmetric stretch is I.R. active. A careful ultrasonic study (62), using both absorption and dispersion techniques, has established that the relaxation of the low modes is governed by a single time constant. Although interference from the 'Moving signal centre effect' (p.56) cannot be discounted, only limiting signal levels being available from the ($\nu_1 + \nu_2$) modes at the lowest gas pressures, the maximum deviation possible is equivalent to $\sim 0.3 \mu\text{sec.}$, insufficient to account for the difference of $0.5 \mu\text{sec.}$ measured between their relaxation time and that of the ν_3 -mode. That the experiment, comparing different modes within the same molecule, reaches the peak of the spectrophone's potential supports the claim that the measured difference, albeit small, is real. Borrell and Hornig (23), by watching the growth of I.R. emission from shock-heated nitrous oxide measured the relaxation time for the ν_3 -mode at 650°K as $11 \mu\text{sec.}$, rather longer than found here but shorter

than the result of a flow experiment devised by Gauthier and Marcoux (31). Their estimate of 100 μ sec. at $\sim 370^\circ\text{K}$ is however outwith the limits set by the current interpretations of these effects.

Within its error spread, the spectrophone found the ν_3 -mode in carbon dioxide relaxing at the same rate as the lowest mode (ν_2), which has been the subject of repeated ultrasonic examinations (2). Because the symmetric stretch is only Ramanactive the signal level generated by the low energy group was inadequate for a direct comparison with the ν_3 -mode as was made in nitrous oxide. However, experiments on carbon dioxide mixtures (Chapt.8) require for an explanation of the relaxation times' concentration dependence that the removal of energy from the ν_3 -mode is an inefficient process with a relaxation time of about 0.5 μ sec. Such a difference is allowable, and indeed is indicated, by the measurements on pure carbon dioxide and is supported by the observation of an equivalent process in the similar molecule, nitrous oxide.

Discussion of the nitrogen-dilution studies on carbon dioxide by Delany (41) and Slobodskaya and Gasilevich (46) is postponed until the next chapter. Both report a relaxation time of ~ 12 μ sec. for the ν_3 -mode but the analysis of their results depended upon an unjustified assumption about the concentration dependence of the mixture relaxation times. At high temperatures, a small difference between the relaxation times of the ν_3 and ν_2 -modes will be undetectable by current shock-tube technique which there-

-fore should, according to the spectrophone, see all the vibrational modes relaxing together. This is in general agreement with the work of Witteman (70) and Camac (22) but in disagreement with that of both Gaydon and Hurlle (71) and Borrell and Hornig (23). Whereas the latter, examining the ν_3 -mode directly, measured a relaxation time of 7 μ sec. at 600°K (cf. N_2O), the former, using sodium line reversal to follow the vibrational temperature in carbon dioxide shocked to ultimate dissociation, deduced very long relaxation times for the ν_3 -mode e.g. 54 μ sec. at 2,520°K. The ~~nature~~ ^{nature} of the conditions in the latter experiment suggests a cautious approach to the interpretation of its results. Since Borrell is attempting to reduce the scatter in his measurements by repeating the experiments, a detailed comparison with the spectrophone work would be premature at this time.

Because of the lack of experimental results there have been few theoretical determinations of the rate of energy transfer from higher energy levels. Herzfeld (72) calculated the relaxation time of the ν_3 -mode of carbon dioxide to be approximately ten times that of the lowest (ν_2) mode, whilst Marriott (11) in a more recent work concludes that the various modes will all relax at very similar rates, the maximum difference in relaxation times being 0.5 μ sec. Stretton (10) has shown that for methane the relaxation time of the ν_3 -mode is less than 0.1 μ sec. longer than that of the ν_4 -mode, in agreement with the spectrophone results.

In agreement with the latest theoretical work the spectrophone has demonstrated a strong coupling, presumably through complex collision processes, between the higher and lower

energy vibrational modes of even the simplest polyatomic molecules. Only the studies on nitrous oxide and carbon dioxide suggested the existence of a barrier to the degradation of vibrational energy within a molecule but the effects were small, at the apparatus's limit of detection. It has been found that the 'B. and K. Spectrophone', while capable of measuring 0.5 μ sec. relaxation time to within 0.1 μ sec. for very strongly absorbing modes, has a more general limit of practicability at $\sim (1.0 \pm 0.2)$ μ sec. A rapid survey soon shows the majority of ultrasonic measurements (1), (2) made at room temperature to be shorter than 1 μ sec. (at 1 atm.). Therefore, until a much higher radiation density (laser?) can be supplied to the gas in the cell further work on pure gases is unlikely to be instructive. However, certain of the noble and diatomic gases are known to be inefficient in vibrationally de-exciting polyatomic molecules (1), (2). Although a pure gas relaxes at a rate close to the spectrophone's lower limit of detection the addition of an inefficient collision partner will give a mixture with a longer relaxation time, falling within the spectrophone's optimum range of operation (1 μ sec --- 100 μ sec.). A series of experiments on carbon dioxide mixed with nitrogen, neon and xenon are described in the next chapter.

CHAPTER 7

THE B. and K. SPECTROPHONE EXPERIMENT : GAS MIXTURES.

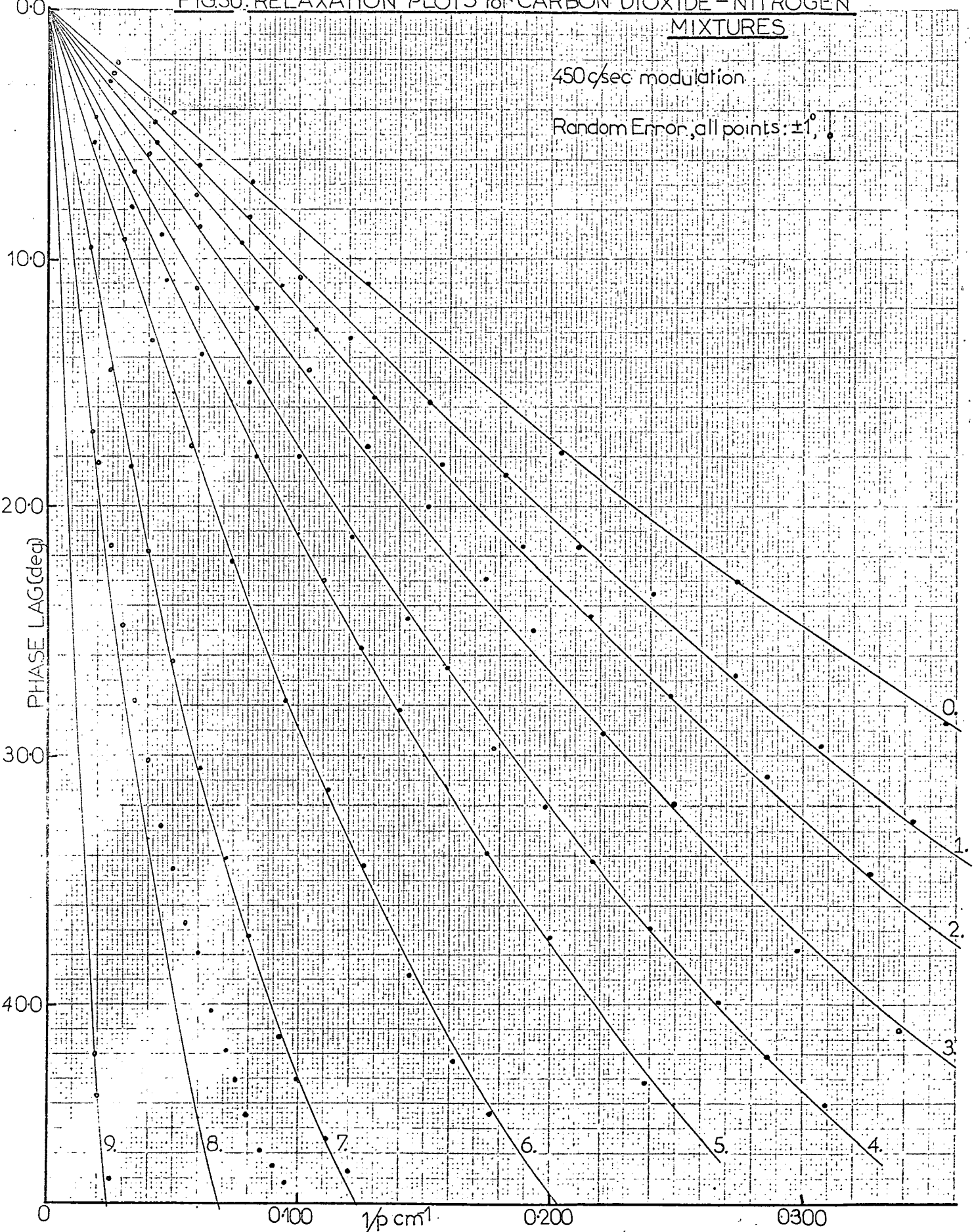
In addition to revealing the easy degradation of vibrational energy from the higher to the lower levels in simple molecules the work on pure gases showed the lower limit for the average 'B and K. Spectrophone' measurement to be at about 1 μ sec. Most of the few gases with relaxation times longer than 1 μ sec. were studied. However, several of these, mixed with inefficient collision partners, give long-relaxing mixtures which offered a promising field for investigation. Precise ultrasonic measurement of long relaxation times ($>10 \mu$ sec.) is technically difficult; transverse wave effects (56), for instance, can interfere at the low sound frequencies required. Little accurate work on such mixtures has therefore been reported.

That both neon and xenon are inefficient in de-exciting the ν_2 -mode in carbon dioxide has been ultrasonically established (73) while the early spectrophone workers (41), (46) founded their technique upon nitrogen's inefficiency in de-exciting the ν_3 -mode. Mixtures of carbon dioxide with nitrogen, neon and xenon were studied in the 'B. and K. spectrophone' at two modulation frequencies: 250 c/sec. and 450 c/sec. The ν_3 -mode was excited (Barr and Stroud filter). As in the single gas work the 250 c/sec. results, being more affected by thermal deviation, served only to check roughly the reliability of the more precise 450 c/sec. measurements. Gas purities are quoted in Table II (opposite p.60). Mixtures were

prepared by firstly freezing the required amount of pure carbon dioxide into a trap attached to the P_2O_5 -coated mixing globe. Nitrogen was admitted via a tube filled with glass wool-supported P_2O_5 . Both the neon and the xenon were supplied from sealed bulbs (B.O.C. Ltd.), the former being transferred with the aid of a Töpler pump, and underwent no further purification. After the second gas was added and the carbon dioxide allowed to expand, twenty-four hours were allowed for mixing before measurements were made in the spectrophone.

The phase lags were analysed in the manner described for the single gases.

FIG.30: RELAXATION PLOTS for CARBON DIOXIDE-NITROGEN MIXTURES



RESULTS: (a) CARBON DIOXIDE-NITROGEN MIXTURES

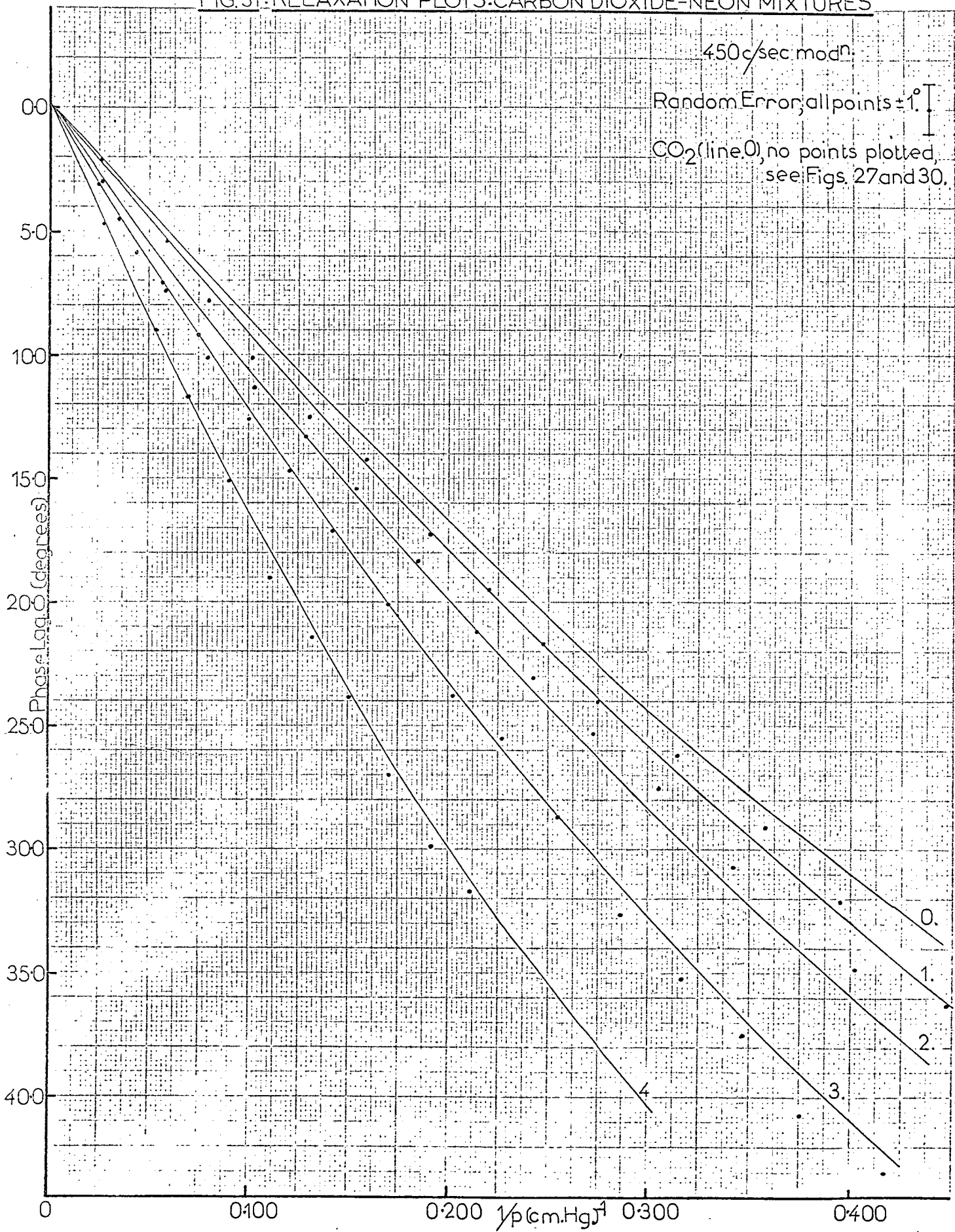
Fig. 30

Measurements at 450 c/sec. gave:

<u>Curve Number</u>	<u>Mole Fraction CO₂</u>	<u>τ (μsec.)</u>	<u>$(1/\tau \times 10^{-5}) \text{ sec}^{-1}$</u>
0	1.000	7.0 \pm 0.5	1.430 \pm 0.100
1	0.851	8.7 \pm 0.5	1.149 \pm 0.070
2	0.747	10.0 \pm 0.5	1.000 \pm 0.050
3	0.650	12.0 \pm 0.6	0.833 \pm 0.040
4	0.550	14.6 \pm 0.7	0.685 \pm 0.030
5	0.500	17.8 \pm 1.0	0.562 \pm 0.033
6	0.350	25.4 \pm 1.5	0.394 \pm 0.025
7	0.200	43.3 \pm 5.0	0.231 \pm 0.030
8	0.101	76.0 \pm 15.0	0.132 \pm 0.030
9	0.049	223 \pm 50.0	0.045 \pm 0.012

Errors have been estimated from the fit between the experimental points and the theoretical curves, taking into account the possible effect of thermal conduction phase shifts. The gradual expansion of the error limits between curves 0 and 6 reflects the reduced sensitivity of the fitting process at longer relaxation times but the large increase between curves 6 and 9 arises from the breakdown of the simple theory at very long relaxation times, as can be seen for curve 8. This will be more fully discussed later.

FIG. 31: RELAXATION PLOTS: CARBON DIOXIDE-NEON MIXTURES



(B) CARBON DIOXIDE-NEON MIXTURES

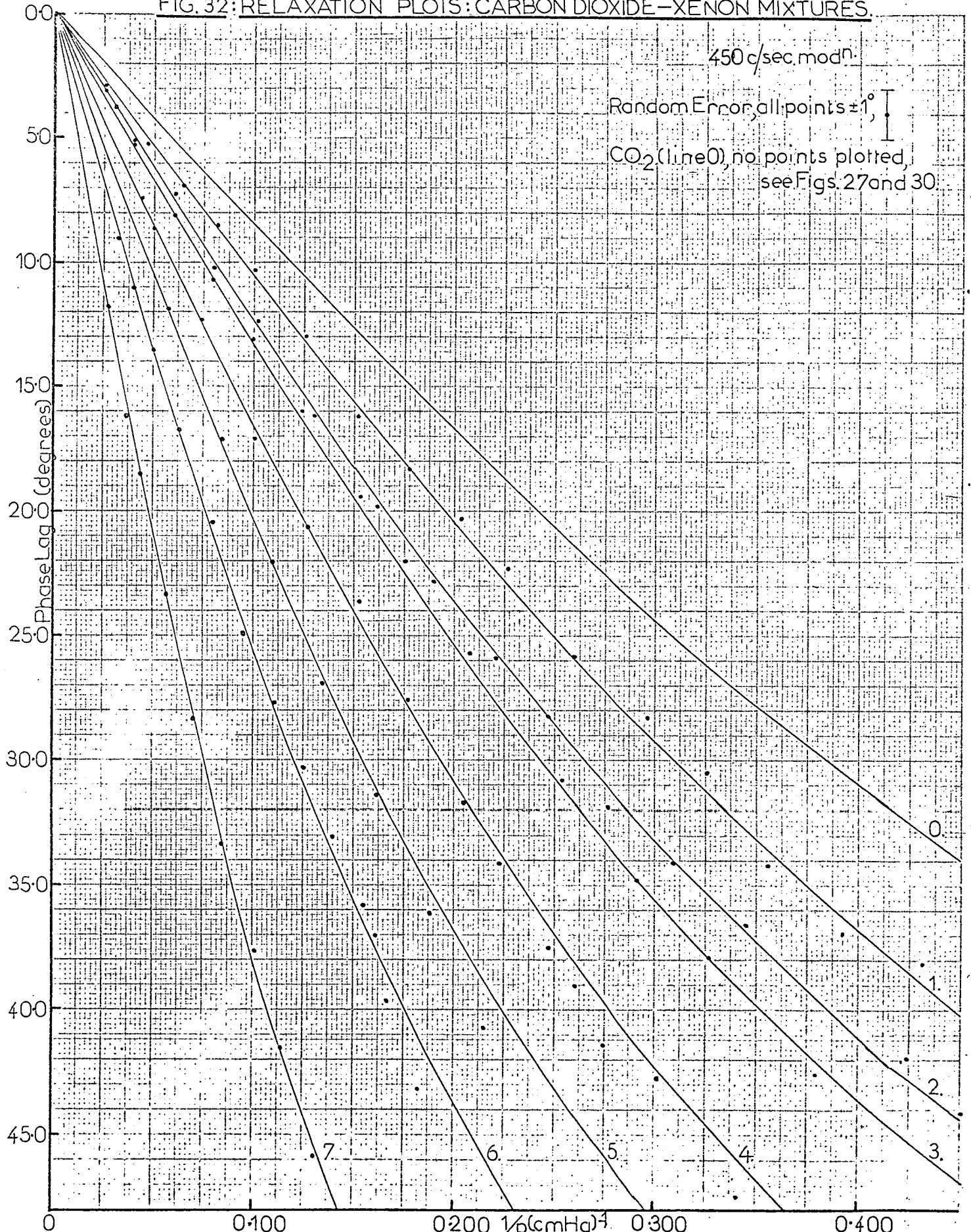
Fig. 31.

Measurements at 450 c/sec. gave:

<u>Curve Number</u>	<u>Mole Fraction CO₂</u>	<u>τ (usec.)</u>	<u>$(1/\tau \times 10^{-5}) \text{sec}^{-1}$</u>
0	1.000	7.0 \pm 0.5	1.430 \pm 0.100
1	0.792	7.5 \pm 0.5	1.333 \pm 0.090
2	0.587	8.4 \pm 0.5	1.190 \pm 0.070
3	0.400	9.9 \pm 0.5	1.010 \pm 0.050
4	0.202	13.0 \pm 0.6	0.769 \pm 0.040

Note that the thermal diffusivity of these mixtures increases with the concentration of neon, a light molecule (M.W. = 20).

FIG. 32: RELAXATION PLOTS: CARBON DIOXIDE-XENON MIXTURES.



(C) CARBON DIOXIDE-XENON MIXTURES

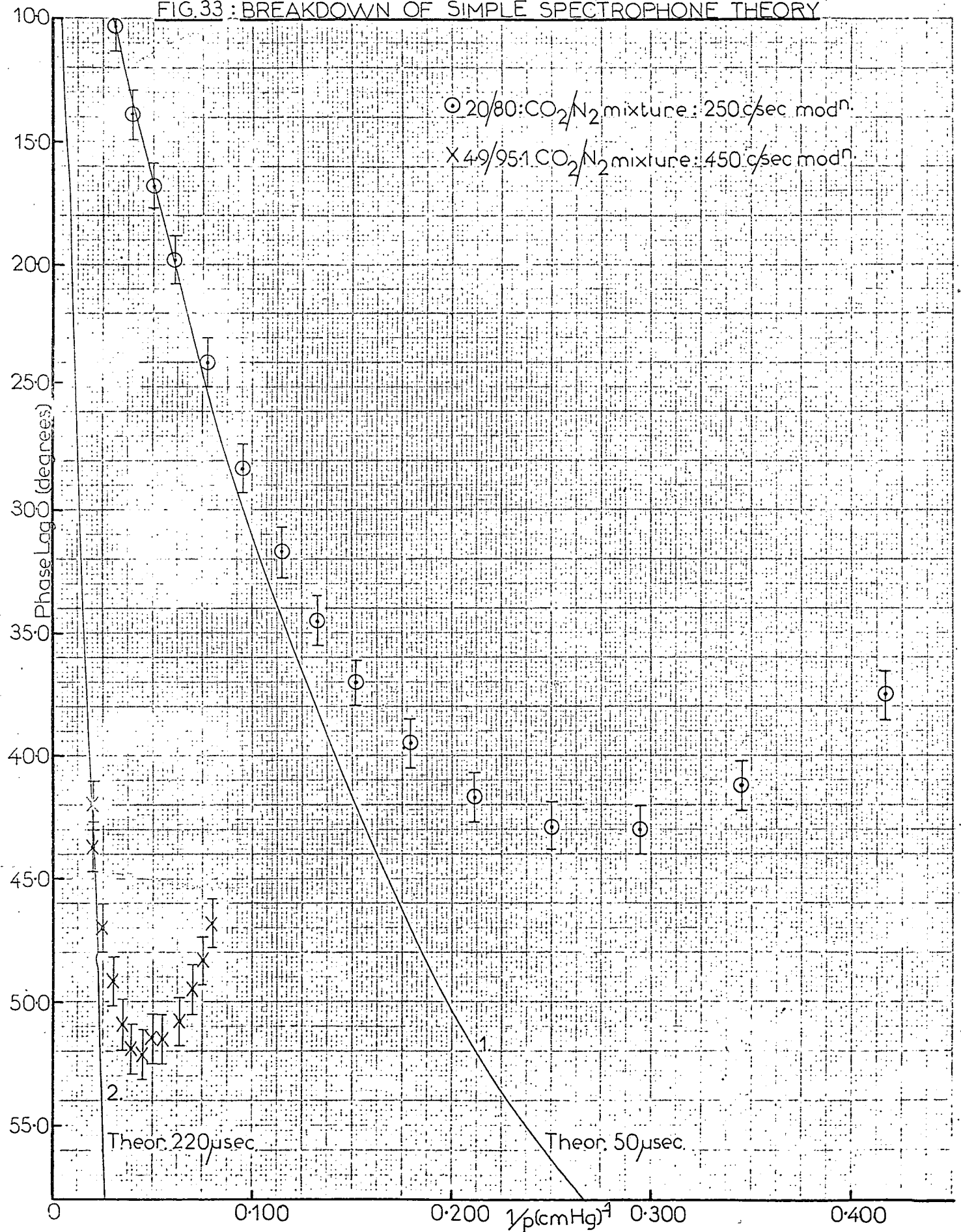
Fig.32.

Measurements at 450 c/sec. gave:

<u>Curve Number</u>	<u>Mole Fraction CO₂</u>	<u>τ (μsec)</u>	<u>$(1/\tau \times 10^{-5} \text{sec}^{-1})$</u>
0	1.000	7.0 \pm 0.5	1.430 \pm 0.100
1	0.844	8.6 \pm 0.5	1.163 \pm 0.070
2	0.724	10.1 \pm 0.5	0.990 \pm 0.050
3	0.667	11.0 \pm 0.6	0.909 \pm 0.050
4	0.526	13.9 \pm 0.7	0.719 \pm 0.040
5	0.379	17.3 \pm 1.0	0.578 \pm 0.035
6	0.285	22.2 \pm 1.5	0.451 \pm 0.030
7	0.115	36.7 \pm 3.0	0.273 \pm 0.025

In contrast to the neon mixtures, here the thermal diffusivity decreases with increasing concentration of xenon, a heavy molecule (M.W. = 131), and an exact correspondence between the 450 c/sec and 250 c/sec measurements was obtained for every mixture.

FIG. 33 : BREAKDOWN OF SIMPLE 'SPECTROPHONE THEORY'



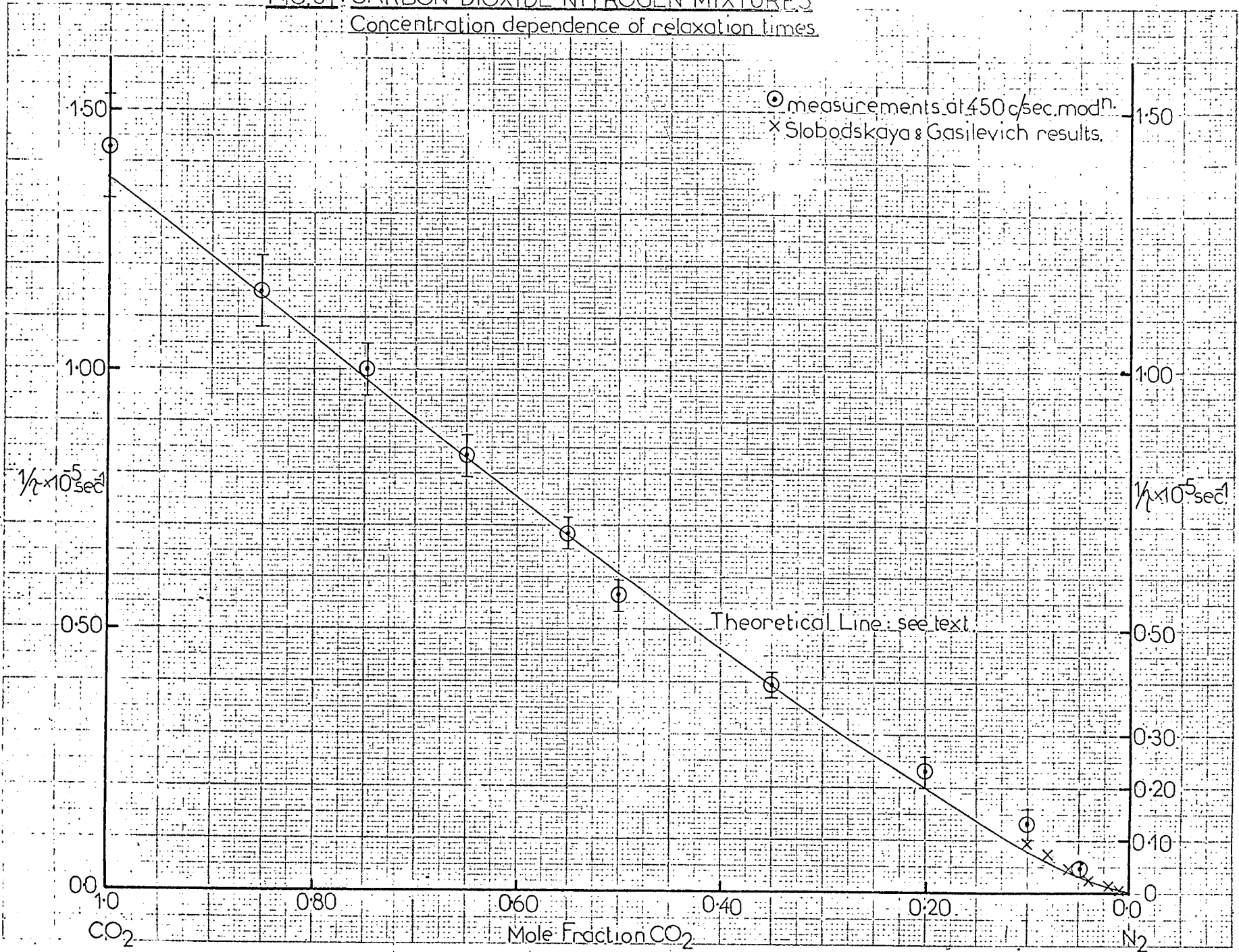
DISCUSSION:

Breakdown of the Simple Theory: The validity of the simple theory, predicting a tangential relationship between relaxation phase lag and reciprocal gas pressure in the spectrophone, depends upon the satisfaction of the inequality,

$$\alpha \gg \beta_1, \beta_2 \quad (\text{see P.18}).$$

which summarises the assumption that energy transfer from vibration to translation (α) is much more rapid than the interaction of the gas with its environment (β_1, β_2) i.e. the cell walls. Purely thermal effects (β_1, β_2), treated theoretically by Delany(41), produce small phase leads which have been observed in the light, fast-relaxing gases e.g. NH_3 , HCN (Chapt.5) and are dependent on gas properties and the modulation frequency. With the carbon dioxide-nitrogen mixtures, particularly at high nitrogen concentrations, α can become very small and in addition to the development of small thermal leads the basis of the theory used to interpret the measurements becomes questionable. If the mole fraction of carbon dioxide is 0.100 then the relaxation time for the mixture at 1 atm. is 100 $\mu\text{sec.}$, but at 0.1 atm., representing the lowest pressure used in the determination, it has risen to 1,000 $\mu\text{sec.}$ Furthermore as the concentration of the lighter N_2 increases so does the thermal diffusivity of the mixture. Under these conditions it would not be surprising if the assumption that $\alpha \gg \beta_1, \beta_2$ proved unrealistic, and the simple theory broke down. That the tangential relationship does in fact become inadequate in describing the measurements is seen in Fig.33.

FIG. 34: CARBON DIOXIDE-NITROGEN MIXTURES
 Concentration dependence of relaxation times



Curve (1) represents a 50 μ sec. relaxation line fitted to the phase lags measured at 250 c/sec. in the higher pressures of a 20/80 : CO₂/N₂ mixture. Similarly curve (2), a 220 μ sec. relaxation line, cannot fit the set of measurements made in a 4.9/95.1 : CO₂/N₂ mixture at 450 c/sec. Almost identical in their failure to follow the theoretical lines, at low pressures the two sets of results demonstrate how the applicability of the simple theory may be extended by raising the modulation frequency. An upper limit however is imposed by the phase characteristic of the microphone; at 1 kc/sec the phase shift in the B. and K. one inch Type 4132 has already reached 5°.

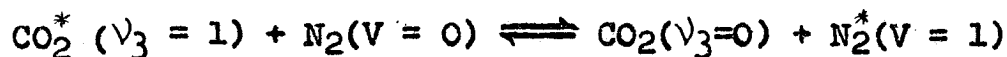
Carbon Dioxide-Nitrogen Mixtures: In Fig.34 the reciprocal relaxation times for the mixtures are plotted against the mole fraction of carbon dioxide.

Both Delany(41) and Slobodskaya and Gasilevich (46), using a nitrogen dilution technique (p.20), deduced the relaxation time of the ν_3 -mode in pure CO₂ from their spectrophone measurements, by assuming a linear relation between the reciprocal relaxation time and the mole fraction of CO₂. They quoted results of 11 μ sec. and 12 μ sec. respectively. Since the measurements were made at constant gas pressure, although Slobodskaya did use several modulation frequencies, a close check on the concentration dependence of the relaxation times was impossible, particularly at the higher concentrations of CO₂ ($X > 0.500$) when the phase lags were at the limit of detection. That their assumption of

linearity was unjustified is apparent from Fig.34. Considering only those mixtures with higher N₂ concentrations ($X_{CO_2} < 0.500$), a linear extrapolation from the B. and K. results predicts a τ_{CO_2} of 9.0 ± 1.0 usec., similar to the conclusions of the earlier workers.

What is already known of the behaviour of the system which might lead to an explanation of the observed concentration dependence? It has been shown that:

- (1) the relaxation time of the ν_2 -mode in carbon dioxide is $\beta = 6.5 \pm 0.4$ μ sec. (2) : *ultrasonic work.*
- (2) Nitrogen is very inefficient in de-exciting the ν_2 -mode of carbon dioxide (74) : *ultrasonic work.*
- (3) The ν_3 -mode in carbon dioxide ($2,349\text{cm}^{-1}$) is nearly resonant with the fundamental vibration frequency of nitrogen ($2,331\text{cm}^{-1}$). This almost perfect matching between the levels should make the energy exchange process



very rapid, occurring every few collisions. Experimental confirmation is supplied by work on the CO₂-quenching of vibrationally excited nitrogen (14) and from the development of the CO₂/N₂ laser (6).

(4) Homogeneous deactivation of N₂ is extremely slow and at room temperature in small vessels virtually all the deactivation occurs on the walls. (14). (cf. p5)

From these facts one end of the concentration curve can be qualitatively defined. A single vibrationally excited carbon

dioxide molecule injected into nitrogen gas will transfer its energy almost immediately to one of its molecules. Since the probability that the CO_2 molecule again encounters its lost quantum is virtually zero, the energy will be degraded to translation at a rate characteristic of the nitrogen: $1/\tau = 0$. The system is little changed by adding another one, ten or a hundred excited CO_2 molecules; therefore the curve must leave the point ($X_{\text{CO}_2} = 0, 1/\tau = 0$) asymptotically along the mole fraction axis. This is in agreement with the Slobodskaya and Gasilevich measurements which are also plotted on Fig. 34.

One postulate is required for an explanation of the remainder of the curve: that a vibrational quantum has a finite existence time in the ν_3 -mode of carbon dioxide. The following evidence supports the claim.

(1) The single gas work reported in Chapter Six allows a difference in relaxation times of $\sim 0.5 \mu\text{sec.}$ between the ν_3 -mode and the ν_2 -mode in carbon dioxide ($\tau = 7.0 \pm 0.5 \mu\text{sec.}$; $\beta = 6.4 \pm 0.3 \mu\text{sec.}$)

(2) Marriott's theoretical treatment (11) of the relaxation of the carbon dioxide molecule predicts a $0.5 \mu\text{sec.}$ lag between the ν_3 -mode and the remainder of the vibrations.

(3) An analogous molecule, sulphur dioxide, displays a well-substantiated ultrasonic double dispersion (68), (75). The higher energy stretching modes are considered to be slower relaxing ($\tau_2 = 1.2 \mu\text{sec.}$) than the low energy bending mode ($\tau_1 = 0.06 \mu\text{sec.}$) Since the obvious schemes for degrading

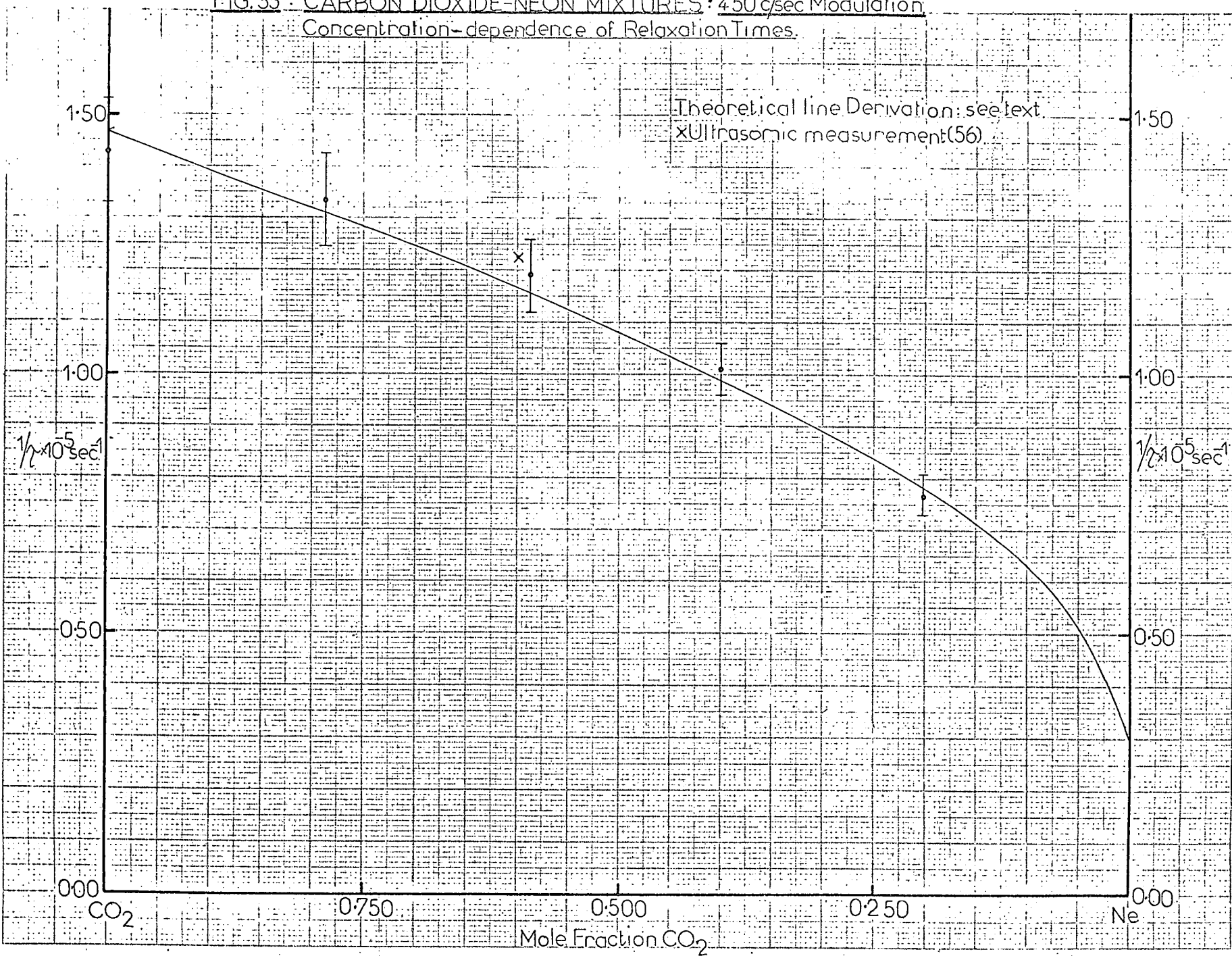
energy from sulphur dioxide's higher levels are almost identical with those possible in carbon dioxide, being based on transferring the quantum into an overtone of the bending mode, their relative inefficiency is suggestive of a similar state of affairs in carbon dioxide.

Energy from the $\nu_3(2,349\text{cm}^{-1})$ mode in carbon dioxide would seem to be most easily transferred into the second (1932.5cm^{-1}) or third (2553.3cm^{-1}) overtone of the ν_2 -bending mode, then rapidly 'cascaded' down the nearly resonant levels to the fundamental. That the conversion of an anti-symmetric stretch into a bend is a relatively inefficient process is not too surprising, a critical geometric factor may have to be satisfied during collision.

Agreeing that it is not unreasonable to postulate a relaxation time of ~ 0.5 $\mu\text{sec.}$ for the ν_3 -mode, how does it help to explain the results? If τ_{ν_3} in the pure gas is given a value X, then in a 50/50 mixture with an inefficient collision partner it will have a value 2X. But in nitrogen, because of the almost perfect matching between the relevant energy levels, the quantum will spend half its time associated with a nitrogen molecule (the 'principle of microscopic reversibility' stating that the transfer in one direction is as easy as in the reverse). Since the energy only stands a chance of degradation in a collision between two carbon dioxide molecules, this nitrogen 'storage-effect' will further double the relaxation time to 4X. Extending the argument, in a 10/90:CO₂/N₂ mixture only 1 in 10

FIG. 35 : CARBON DIOXIDE-NEON MIXTURES : 450 c/sec Modulation

Concentration-dependence of Relaxation Times.



of an excited CO₂ molecule's collisions stand a chance of being efficient, but the quantum only spends a tenth of its time associated with the CO₂ molecule, the rest in 'nitrogen-storage'. The total relaxation time for ν_3 is then (10).(10). X = 100X. Only vibrational quanta in the ν_3 -mode of carbon dioxide can, of course, participate in this exchange process and if their existence time is short the effects described above will be unimportant.

The theoretical line drawn in Fig.34 was calculated by assuming:

- (a) $\tau_{\nu_3} = 0.7 \mu\text{sec.}$
- (b) $\tau_{\nu_2} = 6.7 \mu\text{sec.}$
- (c) N₂ is completely inefficient in deactivating the ν_2 -mode.
- (d) easy energy exchange between CO₂(ν_3) and N₂.

Carbon Dioxide-Neon Mixtures: The reciprocal relaxation times are plotted against the mole fraction of carbon dioxide in Fig.35. The relation is not linear. Ultrasonic work(56) has produced a value of $12 \pm 3 \mu\text{sec.}$ for the ν_2 -mode's relaxation time infinitely dilute in neon. As in the CO₂/N₂ mixtures the spectrophone results require a vibrational quantum to have a finite existence time in the ν_3 -mode. The probable importance of a geometric factor in transferring energy from a stretching mode to a bending mode has been previously emphasised. It is not difficult to imagine that the small neon molecule might be inadequate in this respect, and therefore be only an inefficient collision partner for the transition. Using these ideas the theoretical line in

FIG. 36: CARBON DIOXIDE-XENON MIXTURES: 450c/sec Modulation.
Concentration-dependence of Relaxation Times.

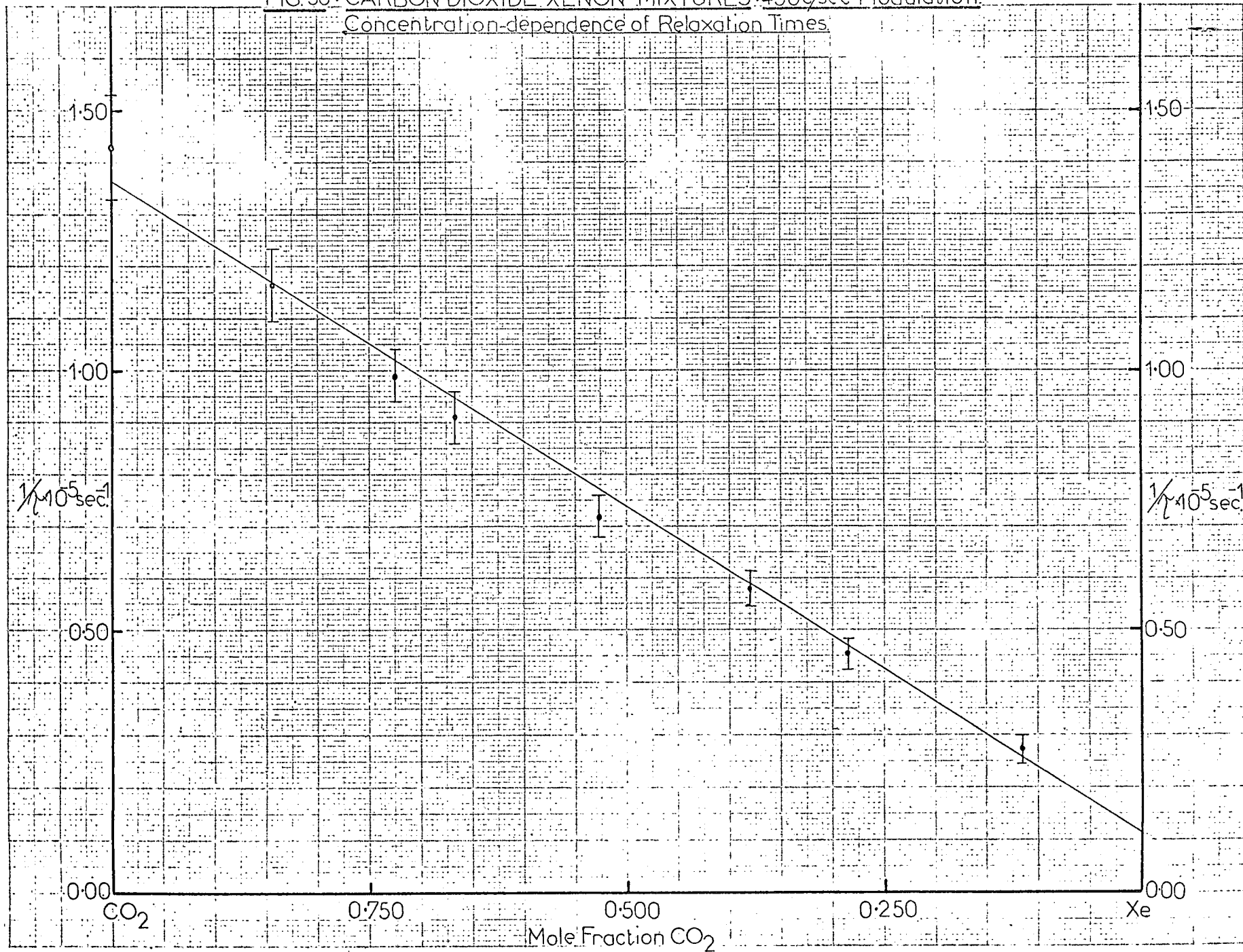


Fig.35 was calculated by assuming the values:

- (a) In pure CO₂, $\tau_{\nu_3} = 0.6 \mu\text{sec}$ and (b) CO₂∞ly dil. in Ne, $\tau_{\nu_3} = 20.0 \mu\text{sec}$.
" " " $\tau_{\nu_2} = 6.2 \mu\text{sec}$. " " " $\tau_{\nu_2} = 12.5 \mu\text{sec}$.

Carbon Dioxide-Xenon Mixtures: The reciprocal relaxation times are plotted against the mole fraction of carbon dioxide in Fig.36 and the results are adequately represented by a straight line. It would therefore seem that xenon is approximately as inefficient in de-exciting the ν_3 as the ν_2 -mode. Ultrasonic work (56) has found the relaxation time of carbon dioxide infinitely dilute in xenon to be $\gg 30 \mu\text{sec}$; the spectrophone gives a value of $85 \pm 10 \mu\text{sec}$.

CONCLUSIONS and FUTURE WORK.

The spectrophone allows the rates of energy transfer processes from the infra-red active vibrational modes of gas molecules to be accurately and swiftly measured. Whereas the precise determination of a relaxation time by ultrasonic interferometry requires several days effort by the experimenter the spectrophone can produce a result within an hour. In its present form the B and K Spectrophone is suitable for studying relaxation times in the range 1 μ sec to 100 μ sec. These limits may be extended by a factor of two in favourable cases. Further work is therefore possible on gases such as carbon dioxide, nitrous oxide, etc. mixed with inefficient collision partners.

Expansion of present limits: At the fast-relaxing end of the scale more energy must be made available to generate a stronger optic-acoustic signal in the gas. Once the extra energy has been supplied however the thermal diffusivity effect will preclude the extension of measurements to lower gas pressures and the modulation frequency will have to be raised. Similarly, to study slow-relaxing gases, unless a more sophisticated theory is developed, a higher modulation frequency is necessary to damp wall effects and preserve the validity of the simple theoretical interpretation of the results. Hence, assuming that the delivery of a higher radiation density is possible, the spectrophone's range is extendable to both shorter and longer relaxation times by raising the modulation frequency. The device used to detect the optic-acoustic signal now becomes the limiting factor. With one inch

condenser microphones the zero phase shift condition is not preserved beyond 1 kc/sec. A balance will therefore require to be struck between the sensitivity of the detecting device and its resonance frequency - half inch microphones may be an improvement.

It is felt that the information provided by the spectrophone about the relaxation times of higher energy vibrational modes widens our appreciation of the collisional interactions between gas molecules and that the spectrophone has still more to contribute in the field of energy transfer.

C H A P T E R 8

THE ULTRASONIC METHOD FOR STUDYING GAS IMPERFECTION.

The pressure-dependence of the velocity of sound in a gas has been widely studied in the measurement of vibrational relaxation times(1). Another gas property, however, also causes a pressure dependence which must be corrected for in energy transfer work: gas imperfection. Velocities are corrected by a factor (S), a function of the gas's second virial coefficient (B). Studying sound velocities outside the dispersion region therefore provides an opportunity for measuring a gas's imperfection by a method independent of adsorption effects. This is an important factor in establishing the virial coefficients of polar gases. The development of a technique and its application to two polar gases, ammonia and hydrogen cyanide, is described in Appendix 1.

APPENDIX I

Gas Imperfection in Ammonia and Hydrogen Cyanide Determined by an Ultrasonic Method

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Measurement of the velocity of ultrasound in ammonia and hydrogen cyanide, outside the vibrational dispersion region, confirms the expected linear pressure dependence of this quantity. The values of the gas imperfection parameter S at the temperatures 30 and 75°C are in fairly good agreement with values calculated from P, V, T data. Small discrepancies are discussed in terms of possible errors in the latter.

Various properties of gases, such as the compressibility and the Joule-Thomson coefficient, have been used to determine the extent of gas imperfection. Another convenient property is the velocity of sound, which depends on the quantity $\sqrt{(dp/d\rho)_{\text{ad}}}_{\text{iabatic}}$. This quantity is independent of pressure for an ideal gas, but does show a small pressure dependence in an imperfect gas. It may be shown^{1,2} that, to the first order in the correction term, the velocity V of sound in a gas is given by

$$V = \left[\frac{RT}{M} \left(1 + \frac{R}{C_v^0} \right) \right]^{1/2} \left(1 + \frac{Sp}{RT} \right), \quad (1)$$

where

$$S = B + \frac{T}{c} \frac{dB}{dT} + \frac{T^2}{2c(c+1)} \frac{d^2B}{dT^2}. \quad (2)$$

The factor in square brackets is the ideal gas contribution, the second factor the imperfection correction. B is the second virial coefficient, C_v^0 is the ideal molar heat capacity at constant volume, and $c = C_v^0/R$.

The sound velocity has the advantage, particularly for polar gases, that its measurement is unaffected by adsorption of the gas on the surface of the vessel. It can be measured^{1,2} to about 1 part in 1000, so that a gas imperfection correction of about 1% at 1 atm can readily be determined. The quantity S is not so familiar to physical chemists as is B , so it may be helpful to note that if B is given (for example), by the Berthelot equation (where P and Q are essentially positive functions of the critical constants),

$$B = P - QT^{-2}, \quad (3)$$

then

$$S = P - GT^{-2}, \quad (4)$$

where

$$G = Q \left(1 - \frac{2}{c} + \frac{3}{c(c+1)} \right). \quad (5)$$

The factor $\left(1 - \frac{2}{c} + \frac{3}{c(c+1)} \right)$ is always positive and does not vary greatly from one gas to another, being 0.54 for diatomic molecules and about 0.7 for moderately

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complicated polyatomic molecules. This means that S generally follows B in its behaviour, but is somewhat greater.

In this paper S values for the polar gases ammonia and hydrogen cyanide are determined ultrasonically and compared with values derived from P, V, T data.

EXPERIMENTAL

Commercial anhydrous ammonia was purified as already described.³ Hydrogen cyanide (I.C.I. Ltd.) was dried over phosphoric oxide, and distilled from solid CO_2 +acetone and ice+salt freezing mixtures. Infra-red analysis of both gases showed no impurities.

The sound velocities were measured in a conventional ultrasonic interferometer. Except for the results for ammonia at 30°C , which have been reported previously,³ all the measurements were made with a quartz crystal transducer at ~ 93 kc/sec. The analysis of the results in terms of eqn. (1) will only be valid if no dispersion of the velocity because of vibrational relaxation is taking place under the experimental conditions. Dispersion does not take place in ammonia up to $13 \text{ Mc sec}^{-1} \text{ atm}^{-1}$,⁴ nor in hydrogen cyanide up to $3 \text{ Mc sec}^{-1} \text{ atm}^{-1}$.⁵ The present experiments cover the range 0.06 – $0.9 \text{ Mc sec}^{-1} \text{ atm}^{-1}$.

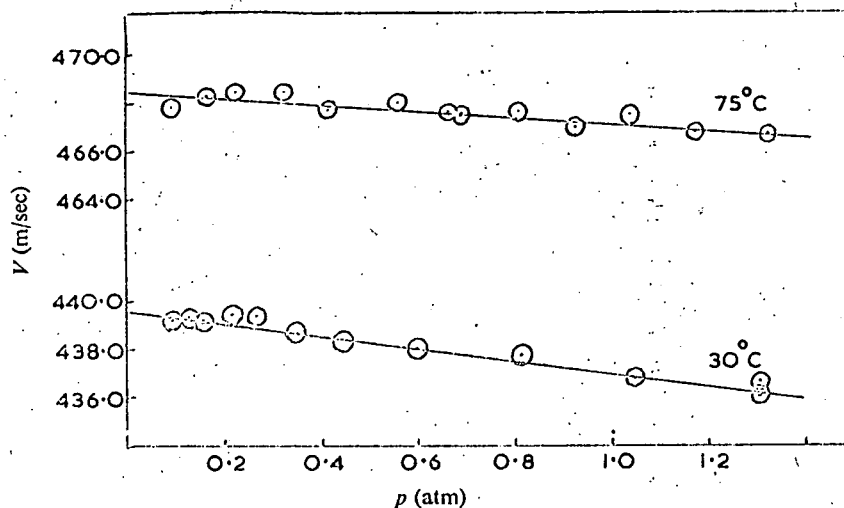


FIG. 1.—Sound velocity in ammonia as a function of pressure. Frequency at 30°C , 694.8 kc/sec; at 75°C , 93.148 kc/sec.

The observed velocities, particularly at 93 kc/sec, required the application of a transverse wave correction, to give the true plane-wave velocity.³ This was determined by adjusting the extrapolated value of the ideal velocity for HCN at 30.8°C to fit the theoretical value. The correction amounted to 0.15% , slightly less than we have found before for a crystal of this frequency. The same correction was applied at the higher temperature. Provided the transverse wave correction is independent of pressure its magnitude is not important since the absolute value of the velocity is not significant in connection with the determination of S . Measurements on air, whose second virial coefficient is well established,

TABLE 1.— S VALUES ($\text{cm}^3 \text{ mole}^{-1}$) FOR NH_3 AND HCN

	S (ultrasonic, this work)		S (P, V, T , see text)
NH_3	30°C	-142 ± 10	-145
	75°C	-80 ± 10	-98
HCN	30.8°C	-1118 ± 20	-930
	75°C	-513 ± 20	-512

showed the correction to be independent of pressure. The reasonably satisfactory agreement of the correction with expectation, and the consistency of the HCN and NH_3 results confirm that the gases must be free from impurities of substantially different molecular weight.

The observed velocities, with transverse wave correction, are plotted against pressure in fig. 1 and 2. Least-squares analysis gave the S values, with standard deviations, shown in table 1.

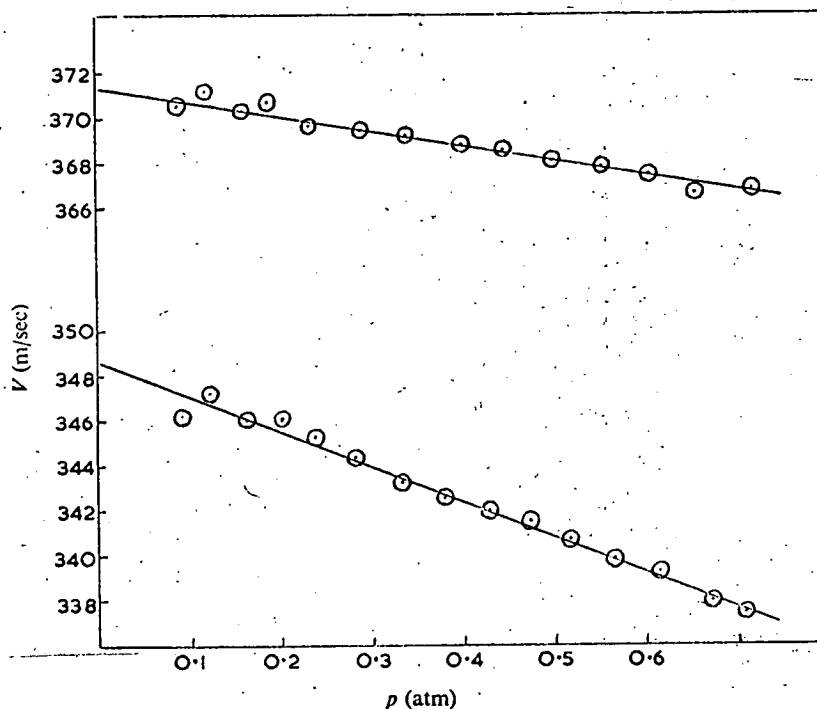


FIG. 2.—Sound velocity in hydrogen cyanide as a function of pressure. Frequency at both temperatures, 93.148 kc/sec.

DISCUSSION

Most discussions⁶⁻⁸ of gas imperfection in ammonia have started from Keyes'⁹ analysis of Meyers' and Jessup's¹⁰ P, V, T measurements, in which the pressure exerted by a known weight of gas in a variety of fixed volumes was measured as a function of temperature, the pressures being as high as 30 atm at the higher temperatures. Keyes' analysis has, however, been criticized,¹¹ and we re-analyzed the original data by fitting them to the relation

$$\frac{pV}{RT} = 1 + \frac{B(T)}{V} + \frac{C(T)}{V^2}, \quad (6)$$

where V is the molar volume, with results in agreement with Hirschfelder, McClure and Weeks.¹¹ The B values thus obtained were then fitted to an equation of the form used by Keyes,

$$B(T) = \alpha - \frac{\beta}{T} \exp\left(\frac{\gamma}{T^2}\right), \quad (7)$$

the constants being $\alpha = 41 \text{ cm}^3 \text{ mole}^{-1}$, $\beta = 4.088 \times 10^4 \text{ cm}^3 \text{ mole}^{-1} \text{ deg.}$, $\gamma = 6.83 \times 10^4 \text{ deg.}^2$. This equation fitted the B values exactly in the temperature range 25-200°C. From it were calculated the values of S given in table 1.

Whereas agreement is excellent at 30°, the P, V, T value is more negative than the ultrasonic value at 75°, by an amount which may just be significant. The pressures in the higher temperature P, V, T work were rather high, and if it is assumed that the experimental B values at higher temperatures are slightly too negative, dB/dT will be slightly too small, and d^2B/dT^2 will be too negative, in that the gradient will be flattening off too quickly, and hence the derived S value will be too negative. Thus, although the agreement between the ultrasonic and P, V, T results is reasonably good, the slight discrepancy found could be explained on the assumption that the higher temperature P, V, T results for B are a few $\text{cm}^3 \text{ mole}^{-1}$ too negative.

The P, V, T data for hydrogen cyanide¹² were obtained in the same way as those for ammonia. At lower temperatures, particularly at 0°C, measurements were made near the saturation point and large adsorption effects were reported. We analyzed the data in the same way as for ammonia, and found for the constants in eqn. (7): $\alpha = 295 \text{ cm}^3 \text{ mole}^{-1}$, $\beta = 1.838 \times 10^5 \text{ cm}^3 \text{ mole}^{-1} \text{ deg.}$, $\gamma = 10.30 \times 10^4 \text{ deg.}^2$. The equation gave a good fit in the region 0-100°C. The gas density of hydrogen cyanide has been measured¹³ at 30, 70 and 110°C, and these results may be interpreted in terms of the second virial coefficient, giving the results noted in table 2.

TABLE 2.— $B(\text{HCN})$ ($\text{cm}^3 \text{ mole}^{-1}$)

temp. °C	P, V, T	gas density	ultrasonic (this work)
30	-1564	-1602	-1332 ± 100
70	-989	-811	
75	-940	-760*	-765 ± 75
110	-672	-507	

* interpolated

The P, V, T virial coefficients were used to calculate the S values given in table 1. Whereas the agreement is excellent at 75°C, the P, V, T S -value is ~~larger~~ ^{smaller} negatively than the ultrasonic one. This is the direction in which errors due to adsorption ^{at 30°C} would be expected to operate.

In order to go from the observed S -values to the virial coefficient B , it is necessary to make a simple assumption about the form of $B(T)$. A convenient expression which requires only two-empirical constants is derived on the assumption that the virial coefficient consists of two terms, one due to dispersion forces and given by the Berthelot equation, and the other due to dimerization (assumed small) so that¹⁴

$$B(T) = P - QT^{-2} - RT/K_p, \quad (8)$$

where

$$P = 9RT_c/128p_c, \quad (9)$$

$$Q = 27RT_c^3/64p_c, \quad (10)$$

and

$$K_p(T) = P_A^2/P_{A_2}, \quad (11)$$

where T_c and p_c are the critical temperature and pressure, p_A is the partial pressure of monomer, and p_{A_2} is the partial pressure of dimer. We then have for S

$$S = P - GT^{-2} - \frac{RT}{K_p} \left[1 + \frac{1}{c} \left(1 - \frac{\Delta H}{RT} \right) + \frac{1}{2c(c+1)} \left(\frac{\Delta H}{RT} \right)^2 \right], \quad (12)$$

where G is given by eqn. (5) and ΔH is the enthalpy of dissociation of the dimer. The expression in square brackets is positive for all c and ΔH , so that dimerization must make the value of S more negative.

An analysis of the S -values along these lines was attempted for ammonia, but it was found that S calculated from the Berthelot equation at 75° was approximately equal to the S value found ultrasonically. This means that K_2 is so large that the analysis cannot be usefully applied, or that the Berthelot equation gives too large a negative value of S . This difficulty does not appear to arise for hydrogen cyanide, however, and the B values calculated by fitting eqn. (12) are given in table 2. They are slightly smaller (negatively) than those from the P, V, T data at both temperatures, but in exact agreement with the gas density value at 75°C . On the other hand, since the modified Berthelot equation does not fit the P, V, T data very well, it may be that this particular method of analysis of the ultrasonic data is not fully justified.

It appears, then, that the ultrasonic method is an acceptable one for considering gas imperfections, and that the existing P, V, T data for second virial coefficients may be slightly in error at the higher temperatures for ammonia and at low temperatures for hydrogen cyanide.

- ¹ Cottrell and McCoubrey, *Molecular Energy Transfer in Gases* (Butterworths, 1961).
- ² Herzfeld and Litovitz, *Absorption and Dispersion of Ultrasonic Waves* (Academic Press, 1959).
- ³ Cottrell and Matheson, *Trans. Faraday Soc.*, 1963, 59, 824.
- ⁴ Lambert and Salter, *Proc. Roy. Soc. A*, 1959, 253, 277.
- ⁵ Macfarlane, unpublished work.
- ⁶ Rowlinson, *Trans. Faraday Soc.*, 1949, 45, 974.
- ⁷ Stockmayer, *J. Chem. Physics*, 1941, 9, 398.
- ⁸ Lambert and Strong, *Proc. Roy. Soc. A*, 1950, 200, 566.
- ⁹ Keyes, *J. Amer. Chem. Soc.*, 1938, 60, 1761.
- ¹⁰ Meyers and Jessup, *Refrig. Eng.*, 1925, 11, 345.
- ¹¹ Hirschfelder, McClure and Weeks, *J. Chem. Physics*, 1942, 10, 201.
- ¹² Sinosaki and Hara, *Tech. Rept. Tohoku Univ.*, 1949, 8, 297.
- ¹³ Felsing and Drake, *J. Amer. Chem. Soc.*, 1936, 58, 1714.
- ¹⁴ Lambert, Roberts; Rowlinson and Wilkinson, *Proc. Roy. Soc. A*, 1949, 196, 113.

REFERENCES.

1. Cottrell and McCoubrey, 'Molecular Energy Transfer in Gases', Butterworths, London, 1961.
2. Read, 'Progress in Reaction Kinetics', Pergamon Press, 1965.
3. Bauer, Annual Reviews of Physical Chemistry, 1965, 16
4. Rowlinson, Mol. Phys., 1961, 4, 317
5. Benson and DeMore, Annual Reviews of Physical Chemistry, 1965, 16
6. Patel, Phys. Rev. Letters, 1964, 13, 617.
7. Ferguson, unpublished work.
8. Herzfeld and Litovitz, 'Absorption and Dispersion of Ultrasonic Waves', Academic Press, New York, 1959.
9. Zener, Phys. Rev. 1931, 37, 556; 38, 227.
10. Stretton, Trans. Faraday Society, 1965, 61, 1053.
11. Marriott, Proc. Phys. Soc. 1964, 84, 877
12. Ferguson and Read, Trans. Faraday Soc. 1965, 61, 1559.
13. Read, Thesis, University of Edinburgh, 1963.
14. Morgan and Schiff, Canad. J. Chem, 1963, 41, 903.
15. Schwartz, Slawsky and Herzfeld, J. Chem. Phys. 1952, 20, 1591.
16. Rapp and Englander-Golden, J. Chem. Phys. 1964, 40, 573; 3120.
17. Millikan and White, J. Chem. Phys. 1963, 39, 98.
18. Millikan, J. Chem Pys. 1965, 43, 1439.
19. Rabinowitch and Flowers, Quart. Rev. 1964, 18, 122.
20. Hooker and Millikan, J. Chem. Phys. 1963, 38, 214.
21. Millikan and White, J. Chem. Phys. 1963, 39, 98.
22. Camac, Avco.-Everett Res. Lab. Rept. No. 164, Everett, Mass, 1964.
23. Borrell and Hornig, 'Molecular Relaxation Processes', Academic Press, 1966.
24. Clouston, Gaydon and Glass, Proc. Roy. Soc., 1958, 248A, 429.
25. Richards and Sigafos. J. Chem. Phys. 1965, 43, 492
26. Millikan, J. Chem. Phys. 1963, 38, 2855.

27. Millikan, J. Chem. Phys. 1964, 40, 2594.
28. Millikan and Osburg, J. Chem. Phys. 1964, 41, 2196.
29. Lipscomb, Horrieh and Thrush, Proc. Roy. Soc. 1956, 233A, 455.
30. Charters and Polanyi, Disc. Faraday Soc. 1962, 33, 107.
31. Gauthier and Marcoux, Canad. J. Phys. 1964, 39, 1130.
32. Tyndall, Proc. Roy. Soc. 1881, 31, 307; 478.
33. Rontgen, Phil. Mag. 1881, 11, 308.
34. Bell, Phil. Mag. 1881, 11, 510.
35. Luft, Zeit. tech. Physik, 1943, 24, 97.
36. Pfund, Science, 1939, 90, 326.
37. Veingerov, Dokl. Akad. Nauk. S.S.S.R. 1938, 19, 687.
38. Veingerov, Comp. Rendus (Doklady) 1945, 46, 182.
39. Gorelik, Dokl. Akad. Nauk. S.S.S.R. 1946, 54, 779.
40. Cottrell, Trans. Faraday Soc. 1950, 46, 1025.
41. Delany, Thesis, University of London, 1959.
42. Kaiser, Canad. J. Phys. 1959, 37, 1499.
43. Delany, Science Progress, 1959, 459.
44. Slobodskaya, Izvest. Akad. Nauk. S.S.S.R. 1940, 12, 656.
45. Woodmance and Decius, J. Chem. Phys. 1962, 36, 1831.
46. Slobodskaya and Gasilevich, Optika i Spectroscopia, 1959, 7, 58
47. Jacox and Bauer, J. Phys. Chem. 1957, 61, 833.
48. Schaefer, Zeit. fur Ang. Physik, 1965, 19, 55.
49. Decius, Private communication.
50. Cottrell, Unpublished work.
51. Cottrell, Hunter and Read, Proc. Chem. Soc. 1963, 272.
52. Anne and Legvold, J. Chem. Phys. 1959, 30, 163.

53. Lambert and Salter, Proc. Roy. Soc. 1959, 253A, 277.
54. Cottrell and Matheson, Trans. Faraday Soc. 1962, 58, 2336.
55. Heading, *Mathematical Methods in Science and Engineering*, Edward Arnold, 1963.
56. Day, Thesis, University of Edinburgh, 1965.
57. Dushman, 'Scientific Foundations of Vacuum Technique', Wiley, 1962.
58. Clusius and Riccobini, Z. Phys. Chem. 1938, 38B, 81.
59. Stephens and Bate, 'Wave Motion and Sound', Arnold, 1950.
60. Cottrell, Macfarlane and Read, Trans. Faraday Society, 1965, 61, 1632.
61. Lambert, Edwards, Pemberton and Stretton, Disc. Faraday Society, 1962, 33, 61.
62. Holmes, Parbrook and Tempest, Acustica, 1960, 10, 155.
63. Fricke, J. Acoust. Soc. Amer. 1940, 12, 245.
64. Eucken and Aybar, Z. Phys. Chem, 1940, 46B, 195.
65. Eucken and Numann, Z. Phys. Chem. 1937, 36B, 163.
66. Landau and Teller, Phys. Leit. Sowjetunion, 1936, 10, 34.
67. Decius, Private communication.
68. Lambert and Salter, Proc. Roy. Soc. 1957, 243A, 78.
69. Valley and Legvold, J. Chem. Phys. 1960, 33, 627.
70. Witteman, J. Chem. Phys. 1962, 37, 655.
71. Gaydon and Hurler, Nature, 1959, 184, 1858.
72. Herzfeld, Disc. Faraday Soc. 1962, 33, 22.
73. Cottrell and Day, 'Molecular Relaxation Processes', Academic Press, 1966.
74. Day, Unpublished work.
75. McCoubrey, Milward and Ubbelohde, Proc. Roy. Soc. 1961, 264A, 299.

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