Experimental and theoretical analysis of vibrational relaxation regions in carbon dioxide

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The density distribution in the relaxation regions of shock waves in carbon dioxide were determined in the Mach number range 1·4 to 4·0 using an interferometer. The over-all density ratios were found to agree with the theoretical final equilibrium values. Detailed analysis of the relaxation regions showed that the simple relaxation equation is inadequate, the relaxation frequency depending on departures from equilibrium as well as on temperature.

1. Introduction

Vibrational relaxation in shock waves in carbon dioxide has been studied experimentally by Smiley & Winkler (1954) and by Griffith, Brickl & Blackman (1956). Both groups used a Mach–Zehnder interferometer to evaluate the density distribution through the wave. Apparently some measurements in shock waves have also been made by Witteman (1961*a*, *b*) using a schlieren-type instrument, but his full results are not yet available.

Both Smiley & Winkler and Griffith *et al.* found the density variation in the relaxation region to be exponential with distance measured downstream from the shock front (so did Witteman 1961*a*). However, they disagreed about the final value of the density far downstream. Smiley & Winkler found this to agree with the value at final equilibrium, whereas Griffith *et al.* found it to correspond to the lowest mode of vibration (the doubly degenerate bending mode of characteristic temperature 959 °K) being in equilibrium and the other two modes (symmetrical stretching (1920 °K) and asymmetrical stretching (3380 °K)) unexcited.

Greenspan & Blackman (1957) in a short note claimed that at higher temperatures the final density values gave strong evidence for the existence of three separate relaxation frequencies (reciprocal relaxation times), the bending mode having the largest and the asymmetric stretching mode the smallest.

These results by Griffith *et al.* and by Greenspan & Blackman are not consistent with theoretical predictions by Schwartz (1954) and Witteman (1961*b*). Carbon dioxide is a special case since there exists an accidental degeneracy between the bending modes and the symmetric stretching mode (the frequency of the latter being almost exactly twice that of the bending modes). Schwartz pointed out that of the two possible means by which the symmetric stretching mode can be excited, namely, direct excitation by energy exchange with translation and indirect excitation by energy exchange with the bending modes, the latter is the more probable, and he derived the corresponding relaxation equations. Witteman

(1961 *b*) has also given a treatment of the same problem, including a calculation of the temperature dependence of the two relaxation frequencies. He found that the relaxation frequency for the energy exchange between the vibrational modes was at least an order of magnitude greater than the relaxation frequency for the bending modes.

The experimental results of Griffith *et al.* and of Greenspan & Blackman indicate that the stretching modes always have smaller relaxation frequencies than the bending modes (at least at temperatures greater than 400 °K). Witteman (1961 *b*), however, has reported values which indicate that the reverse is true.

In the present paper we report experimental results on carbon dioxide in the temperature range 350 to 1200 °K. Throughout this range the density profiles were found to be exponential and the final density ratio agreed within the experimental error with that corresponding to complete equilibrium.

A previously developed method of detailed analysis of the structure of the relaxation region was extended and used to plot relaxation frequencies, as defined by the simple relaxation equation, within the relaxation region. The relaxation frequency was found not to be a simple function of translational temperature, but to depend strongly on the departure from equilibrium. The simple relaxation equation is therefore not adequate. This may be because the relaxation phenomenon can only be described by separate relaxation equations for the different modes, but may also be because the simple equation with linear dependence on departure from equilibrium only holds when this departure is small. If the latter reason is the main one, then simple diatomic gases should exhibit the same behaviour, and it is concluded that a detailed discussion of the carbon dioxide results must await a similar analysis for diatomic gases.

2. Extension of theory

Johannesen (1961) showed how the variables inside a vibrational relaxation region can be simply related by means of the Rayleigh line equations. He also suggested a numerical method for determining relaxation frequencies throughout the relaxation region from an experimental record giving the density at a number of discrete points within the region.

When this method was applied to the experimental records discussed later it was found that although the density values themselves varied smoothly with distance, the slope of the density curve, obtained from the experimental points, varied very irregularly, and it was therefore necessary to smooth the experimental density records before evaluating them further.

This smoothing process involved finding an approximate functional relationship between density, ρ, and distance, x, and with this relation known it was possible to use analytical differentiation and thus determine point values of the relaxation frequency.

As in the previous paper we shall use the simple relaxation equation

$$\frac{d\sigma}{dt} = \omega(\bar{\sigma} - \sigma), \tag{1}$$

where σ is the vibrational energy and $\bar{\sigma}$ its local equilibrium value. It may be argued that there is little justification for using this equation to correlate data for a complicated gas, such as carbon dioxide, with several modes of vibration, and therefore possibly several relaxation frequencies. However, the equation has been used by previous investigators, and we shall therefore start by finding the consequences of using it with the more detailed evaluation method.

It was pointed out in the paper by Johannesen (1961) that according to the simple theory ω may be written as

$$\omega = p\Omega(T), \tag{2a}$$

where Ω is a function of temperature only. Several authors have referred the relaxation frequency to unit density, and we shall adopt this practice and write

$$\omega = \rho\Phi(T). \tag{2b}$$

The unit of pressure is one atmosphere, and the unit of density (Amagat) is that at one atmosphere and 273·16 °K.

In the Rayleigh line method proposed by Johannesen (1961) use is made of an ideal gas with constant specific heats (the α-gas) which has the same density, pressure and velocity distributions as the real gas, and whose temperature equals the translational temperature of the real gas. The ratios of the α-gas variables to their sonic values (suffix b) are simple functions of the α-gas Mach number m.

If the experimental density curve is approximated by

$$x = f(\rho/\rho_b), \tag{3}$$

we have

$$\frac{d(\rho/\rho_b)}{dx} = 1/f'(\rho/\rho_b). \tag{4}$$

Using the relations (15) to (18) in Johannesen (1961) Φ may be written

$$\Phi = \frac{v_b T_b}{\rho_b} L(m)\, c_{p\alpha} \frac{d(\rho/\rho_b)/dx}{\bar{\sigma} - \sigma}, \tag{5}$$

where $c_{p\alpha}$ is the specific heat at constant pressure of the α-gas, v the velocity relative to the shock, and

$$L(m) = \frac{T}{T_b}\left(\frac{v}{v_b}\right)^3 (1 - m^2). \tag{5a}$$

In this equation v_b, T_b and ρ_b are known from the conditions in front of the shock wave. Also known for a particular shock wave are the values of the α-gas Mach numbers m_a and m_2 just behind the α-shock and at final equilibrium. By choosing a number of values of m between m_a and m_2, corresponding values of T and Φ can be determined.

3. Experimental equipment and procedure

The high-pressure section and the first part of the low-pressure section of the shock tube are of cylindrical cross-section of 12 in. diameter. A slowly converging channel scoops out a rectangular area $7\frac{1}{2}$ in. by 8 in. and reduces it to a 2 in. by 8 in. rectangular section which continues through the timing section and the working section which is fitted with 2 in. by 12 in. windows. After the working section the area increases abruptly to 12 in. diameter circular in a dump chamber.

Both high- and low-pressure sections of the tube can be evacuated to 0·05 mm Hg by rotary pumps. Oil diffusion pumps make it possible to pump the low-pressure section for any length of time at a pressure below 10^{-5} mm Hg. Low pressures are measured with Pirani and ionization gauges, which have been calibrated against a McLeod gauge.

In experiments on relaxation phenomena the purity of the gas is of utmost importance. In particular, for CO_2, water vapour impurities are known to have a marked effect on the relaxation frequency. Although no systematic experiments on the effects of water vapour were performed, some fairly crude experiments showed that at 350 °K CO_2-H_2O collisions are between 500 and 1000 times as efficient as CO_2-CO_2 collisions in giving energy exchange between translation and vibration. This agrees with the results obtained by Smiley & Winkler (1954) who also showed that the effect becomes less important at higher temperatures.

These results were used to determine the maximum amount of water vapour permissible in the experiments for the effect to be negligible. In the experiments there are two sources of impurities, first, those present in the commercial gas used, and secondly those introduced during the experiments by leaks and outgassing.

To remove the water vapour present in the commercial CO_2 it was passed slowly through a molecular sieve which is claimed by the makers to reduce the dewpoint to a value approaching -100 °C.

When the tube is first brought down to 10^{-5} mm Hg the apparent leak rate is of the order of 10^{-3} mm Hg per minute. With further pumping this leak rate decreases, reaching a fraction of 10^{-3} mm Hg per minute in about an hour. The time between the closing of the valves to the diffusion pumps and the firing of the tube was of the order of 2 min, and the apparent leak rate was always low enough to ensure that even if all the leakage was H_2O it would not affect the results.

The pressure p_1 of the gas in the tube was measured either directly on an oil manometer or indirectly using a decanting procedure in which the gas was first filled into a smaller volume (1/100 to 1/20 of the tube volume) and the final pressure in the tube calculated from the pressure in the decanting volume and the known volume ratio. In all cases p_1 was known to within 1 %.

The timing section contained three gold film timing elements spaced at equal intervals of 7 in. The signals from the gold films were amplified and fed into two binary counters, and thus two determinations of the shock speed were obtained. These always agreed to within the accuracies of the counts. The last timing station also started a delay circuit which triggered the spark light source of the optical system when the shock wave was in the field of view. The distance from the last timing station to the position of the shock wave at the time of firing of the spark was of order 25 in. Accurate measurements of this distance on the photographs together with the known delay provided a third measurement of the shock speed. This was systematically about 1 % lower than the speed based on the counts. Checks with low Mach number shocks in air, for which the density ratio is known accurately theoretically and could be compared with that obtained interferometrically, showed that the density ratio agreed with the Mach number based on the delay. The delay was therefore used in all experiments to determine M_1, which may be assumed known to within 1 %.

The interferometer used in evaluating the density distributions in the shock waves is of the conventional Mach–Zehnder type and has a 4 in. square field of view. As the working section is 2 in. high the dimensions of the flow regions photographed were 2 × 4 in.

White light photographs were obtained using the unfiltered light from a spark source of half a microsecond duration triggered from the delay circuit. A typical photograph is shown in figure 7, plate 1, where the shock is travelling from right to left. When white light is used the fringes on either side of the central one fade out, and the central fringe can be followed across the shock.

The corresponding no-flow fringes were obtained by using a continuous tungsten source and a 4425 Å filter of bandwidth 40 Å. A typical photograph is shown on figure 8, plate 1. On both plates the rectangular shadow is due to a $\frac{1}{2}$ in. diameter cylindrical rod inserted at the downstream end of the working section. This does not affect the flow but serves to define a co-ordinate system in the working section.

A number of procedures were tried for evaluating the interferograms. The one finally adopted, which was both the quickest and the most accurate method, was as follows. First, an enlarged image of the white light negative was projected on to a sheet of white paper. The positions of the marker and the shock wave were drawn together with the centre lines of the central fringe and its two neighbours. It was found that the scatter in the variation of the fringe shift through the relaxation region was much reduced by using an average fringe shift determined from these three fringes. Next the monochromatic negative was projected on to the sheet of paper and the image of the marker made to coincide with the outline already drawn.

The white light fringes and the monochromatic fringes should be parallel ahead of and far downstream of the shock. The few experiments in which there was a tilt of the two sets of fringes relative to each other, which could be ascribed to a shift in the interferometer setting between the two photographs, were discarded. A few records had to be discarded because one or more ‘bumps’ occurred on one set of fringes and not on the other. These bumps were caused by convection currents which might be created by accidental disturbances to the air in the observation room.

When the monochromatic image had been correctly aligned the centre lines of the monochromatic fringes were drawn in the region covered by the central white light fringe and its neighbours. A series of constant-x lines were then drawn perpendicular to the shock-tube axis. The spacing was chosen small close to the α-shock and increased further downstream. The fringe shifts for the three white light fringes were then measured in terms of the monochromatic fringes and averaged, and the resulting plot of fringe shift $N - N_1$ against x was used for further evaluation.

It was found that the fringe shift could be measured to about $\pm 1/25$ fringe. Most errors caused by imperfections of the interferometer cancel out in the present method of analysis, because they have the same effect on the monochromatic and the white-light negatives. Chromatic variations and refraction errors were found to have a smaller effect than the uncertainty in the measurement of fringe shift.

From the measured fringe shift ΔN the density change can be found as

$$\Delta\rho = \frac{\lambda\rho_0}{DK}\Delta N. \tag{6}$$

Here λ is the wavelength of the monochromatic light, ρ_0 is the density of the gas at N.T.P., D is the width of the working section, and K is the Gladstone–Dale constant corresponding to the value of λ used. The evaluation factor λ/DK can be determined experimentally by measuring the fringe shift for a known density change. Its value was found to be 209·0. The calculated value based on the known values of λ and D together with a value of K obtained from data given by Landolt & Börnstein (1935) was 209·2, and this was used in the evaluation.

The room temperature in all the experiments reported here was 295 °K. The driver gas used was nitrogen.

The estimated accuracies of some of the measured quantities involved in the evaluation of the experiments have already been quoted. A full assessment of all the errors was attempted and their combined effects on the measured relaxation frequencies estimated. It is not, however, easy to obtain a valid estimate because the use of standard error theory which assumes random errors would be unjustified. Many of the errors involved in the experiments are in fact systematic (but unknown) rather than random. Furthermore, the errors in the relaxation frequency depend greatly on the Mach number. We shall therefore confine ourselves to the statement that the scatter of the experimental points is probably a good indication of the random errors and that the estimated maximum (but unlikely) errors which occur at the highest Mach number are 3 % in ρ_2/ρ_1 and 5 % in Φ.

4. Experiments and conclusions

The series of experiments discussed in the present paper were the last of three performed in CO_2. The two series not discussed here served to refine the experimental techniques and also included experiments to check that at a particular Mach number the values of Φ were independent of the density level of the experiment. The Mach number range covered was from 1·4 to 4·0 corresponding to a temperature range from 350 to 1200 °K. Experiments above Mach number 4 showed a rapidly decreasing accuracy and are not included. The pressure in front of the shock wave varied from 70 mm Hg at the lowest Mach number to 3 mm Hg at the highest Mach number.

The first quantity to be evaluated is the over-all density ratio ρ_2/ρ_1. This is shown in figure 1 together with the theoretical curve assuming complete equilibrium at station 2. This curve was based on the properties of CO_2 given in N.B.S. Circular 564. The points on the whole lie *above* the theoretical curve but within the limits set by the possible errors in ρ_2/ρ_1 and M_1. We can therefore only conclude that the experiments agree with the theory to within the experimental error. The results of Griffith *et al.*, mentioned earlier, fall as much as 10 % below our values at the highest Mach number, a difference which seems quite incompatible with the possible errors in our results. Our theoretical curve agrees with the one given by Griffith *et al.* No satisfactory explanation has yet been given for the above discrepancy, and the question obviously requires further examination.

The density ratio ρ_a/ρ_1 across the α-shock cannot be determined from the records with the same accuracy as ρ_2/ρ_1 because the density curve is very steep at the beginning of the relaxation region and the density value therefore very sensitive to small changes in x. There was no indication that the values of ρ_a/ρ_1 differed from those predicted by theory.

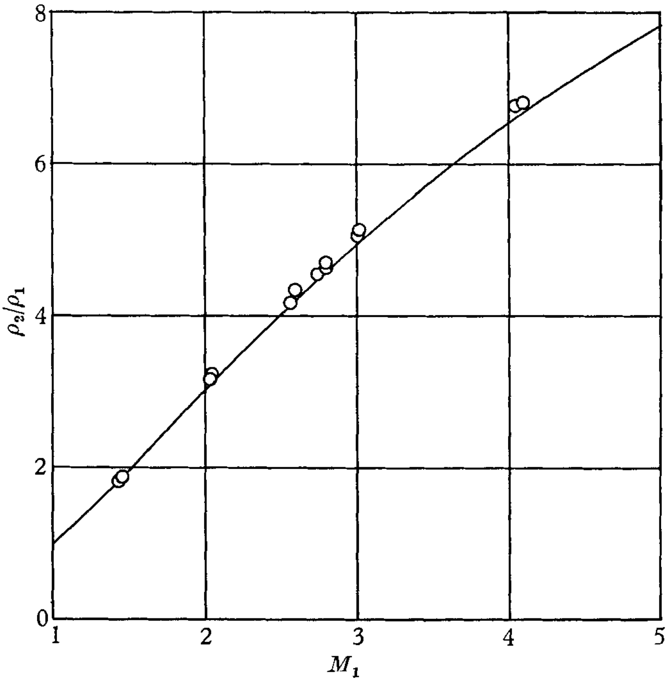

FIGURE 1. Over-all density ratios for shock waves in CO_2.

For all experiments evaluated in this and in previous series it was found that a logarithmic plot of fringe shift difference $N_2 - N$ against x was a straight line to within the experimental scatter. In fact, there was nothing in all the evaluations to indicate any systematic deviations from a straight line. As an example figures 2 and 3 show the experimental points and the corresponding straight line on logarithmic and linear plots. The straight line was fitted only to points over about 80 % of the density change, because closer to the equilibrium value the scatter in $N - N_1$ and the possible error in $N_2 - N_1$ become increasingly important as $N_2 - N$ decreases. It can therefore not be concluded from our results that an exponential curve represents the density variation right up to equilibrium.

Although one would expect all quantities to approach their equilibrium values roughly exponentially, there is no obvious reason why the fringe shift curve and hence the density curve should be so closely fitted by an exponential when plotted

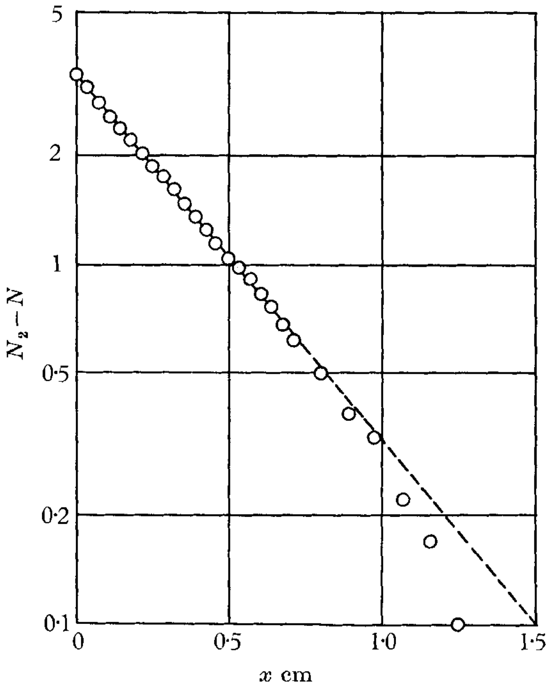

FIGURE 2. Fringe shift for shock wave in CO_2. $M_1 = 1{\cdot}47$, $p_1 = 69$ mm Hg.

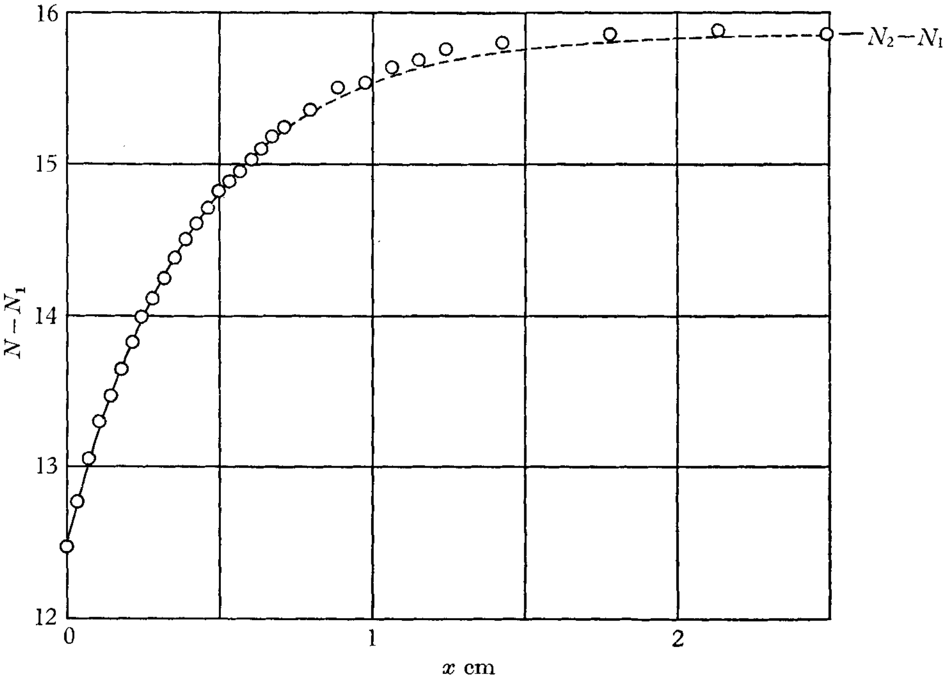

FIGURE 3. Fringe shift for shock wave in CO_2. $M_1 = 1{\cdot}47$, $p_1 = 69$ mm Hg.

against x. A number of other variables, e.g. σ and v, were plotted both against x and against t, but in all cases the departure from the exponential was clearly detectable. It should be mentioned that previous investigators have found the same property of their density curves for a large number of different gases. Apparently no explanation has been offered.

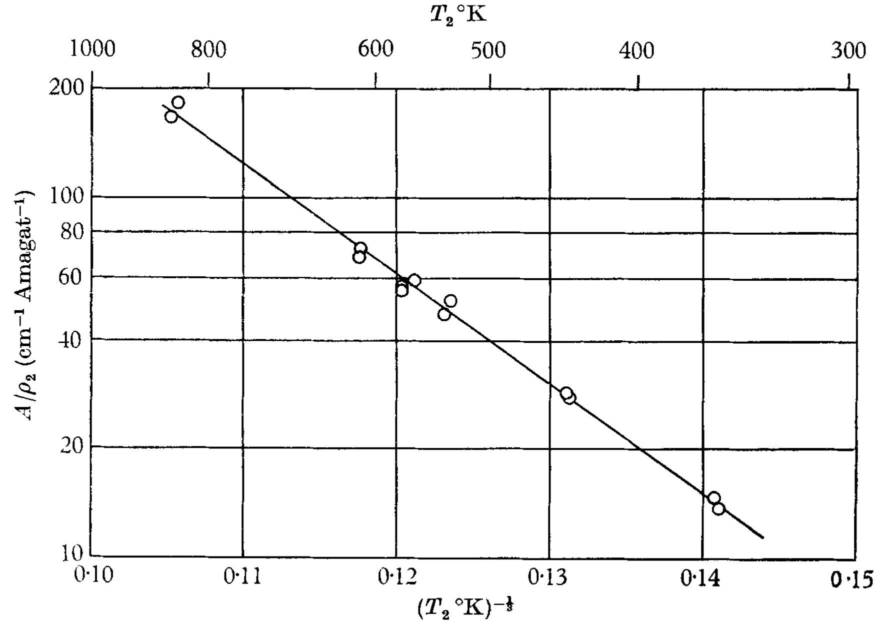

FIGURE 4. Slope A of logarithmically plotted density curves.

Writing
$$\log(N_2 - N) = ax + b, \tag{7}$$
we may write
$$\log(\rho_2 - \rho) = -Ax + B, \tag{8}$$
and have
$$\frac{d(\rho/\rho_b)}{dx} = A\,(\rho_2 - \rho)/\rho_b, \tag{9}$$

where A is a constant for each particular shock wave, and therefore a function of shock Mach number and initial density. A number of different plots were tried, and it was found that A/ρ_2 plotted against $T_2^{-\frac{1}{3}}$ was well fitted by a straight line as shown on figure 4. It is not felt that any special significance should be attached to this particular way of plotting the A values.

The structure of shock waves in CO_2 (at least for $T_1 = 295$ °K) may be predicted directly from figure 4 without any reference to a relaxation equation.

With the smooth representation of A, equation (5) can be written

$$\Phi = \frac{v_b T_b}{\rho_b} c_{pa} L(m) \frac{A(\rho_2 - \rho)}{\rho_b(\bar{\sigma} - \sigma)}. \tag{10}$$

It is interesting to note that although this expression gives the variation of Φ through the relaxation region, the experimental results do not contribute to this variation as they are contained in the constant multiplication factor A.

The variation of Φ within the relaxation region depends only on the thermodynamic properties of the gas in the temperature range covered by the relaxation region.

The variation of Φ within the relaxation region corresponding to $T_1 = 295$ °K and $M_1 = 1{\cdot}5, 2{\cdot}0, 2{\cdot}5, 3{\cdot}0, 3{\cdot}5$, and $4{\cdot}0$ were computed. The corresponding A values were found from figure 4 and the resultant curves are shown in figure 5. It is clearly seen that Φ is not a simple function of T but depends on M_1 and hence on the departure from equilibrium. Without prior knowledge of the experimental results it might have been expected that A would vary in such a manner as to make the curve segments on figure 5 collapse into a single curve. Undetectable departures from the simple exponential density curve together with possible errors in the A values would have an effect on the shape and position of the curve segments but this would be far too small to allow a collapse to a single curve.

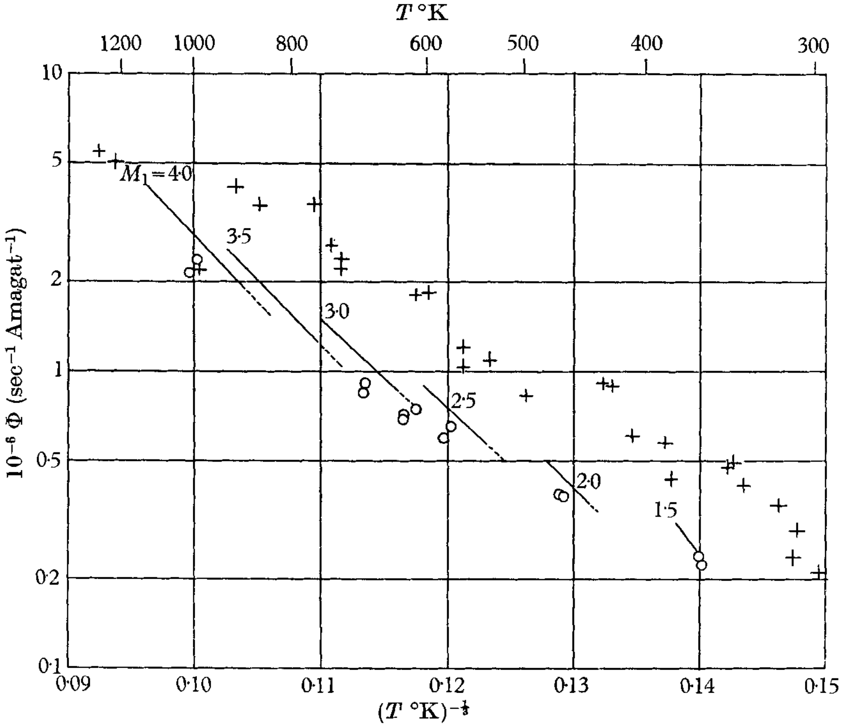

FIGURE 5. Relaxation frequencies in CO_2. —, Present results; ○, present results Griffith evaluation; +, Griffith results.

Also shown on figure 5 are the values of Φ determined from our experimental results using the evaluation method of Griffith *et al.* As predicted by Blythe (1961) they fall somewhat below the values obtained using our evaluation method. By evaluating our data the Griffith *et al.* way we can compare them with their data which are also shown on Fig. 5. They lie consistently above our points, an effect which could be due to more impurities (in particular H_2O) being present in their experiments than in ours.

The experimental data of Smiley & Winkler are not shown in the figure. In their paper they stated that the data had been reduced to standard density. Herzfeld & Litowitz (1959) and Greene & Toennis (1959) have, however, quoted these results as corresponding to atmospheric pressure. If we take them to correspond to standard density they lie on roughly the same level as the Griffith *et al.* data at the lower temperatures, but have a larger overall slope. Since their method of analysis leads to an increasing overestimate of Φ as the temperature increases, this tendency is not surprising.

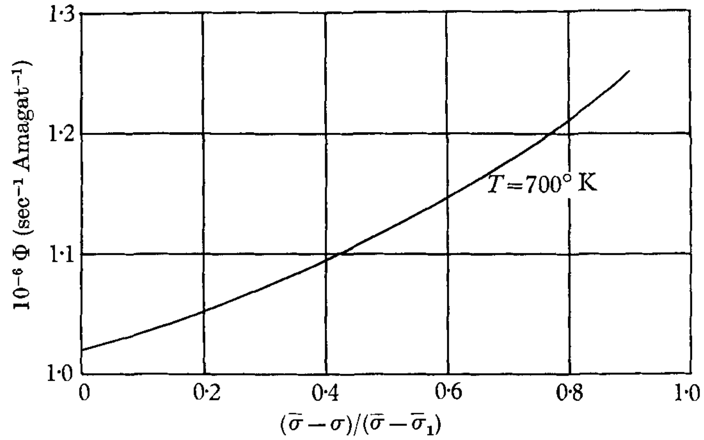

FIGURE 6. Relaxation frequency in CO_2 for $T = 700$ °K and $T_1 = 295$ °K.

In an attempt to learn more about the true form of the relaxation equation, curves for the variation of Φ with $\bar{\sigma}-\sigma$ for a fixed T can be computed. One such curve, corresponding to $T = 700$ °K, is shown in figure 6.

For a diatomic gas the relaxation phenomena could be adequately described by curves such as the one of figure 6, because the general relaxation equation

$$\frac{d\sigma}{dt} = \rho F(T, \bar{\sigma}-\sigma) \tag{11}$$

might be written

$$\frac{d\sigma}{dt} = \rho\Phi(T, \bar{\sigma}-\sigma)(\bar{\sigma}-\sigma) \tag{12}$$

and the curves would be universal ones, not depending on initial conditions.

However, for CO_2, such a simple representation is not possible because the state of the gas is not fully determined by ρ, T and σ. σ is made up of three parts corresponding to the three vibrational frequencies, and no direct information about the composition of σ can be obtained using our experimental techniques. This means that curves like the one in figure 6 would not be universal ones but only represent shock waves of initial temperature $T_1 = 295$ °K.

The inadequacy of the simple relaxation equation is perhaps not surprising in the case of CO_2, for which quite possibly only a system of equations (one for each mode) can give an adequate representation of the relaxation phenomena. However, to our knowledge, no attempt has previously been made to find the detailed variation of Φ within the relaxation region, and no evidence is therefore available to show that the simple relaxation equation is valid for large departures from equilibrium.

If, in fact, the inadequacy of the equation is partly or wholly due to the large departures from equilibrium, then simple diatomic gases should show the same behaviour. It is therefore felt that further speculation about the CO_2 results should be postponed until similar detailed analyses are available for diatomic gases. Such work is in progress using Blackman's (1956) results for O_2 and N_2, and will be reported later.

If diatomic gases turn out to obey the simple relaxation equation with Φ a function of temperature only, we reach the interesting conclusion that if the density distribution is exponential, one single experiment will in principle suffice to determine the whole Φ curve. This is because *all* segments (as on figure 5) can be calculated independently of experiments and if one experiment has determined the location of *one* segment the whole curve can be built up from overlapping segments.

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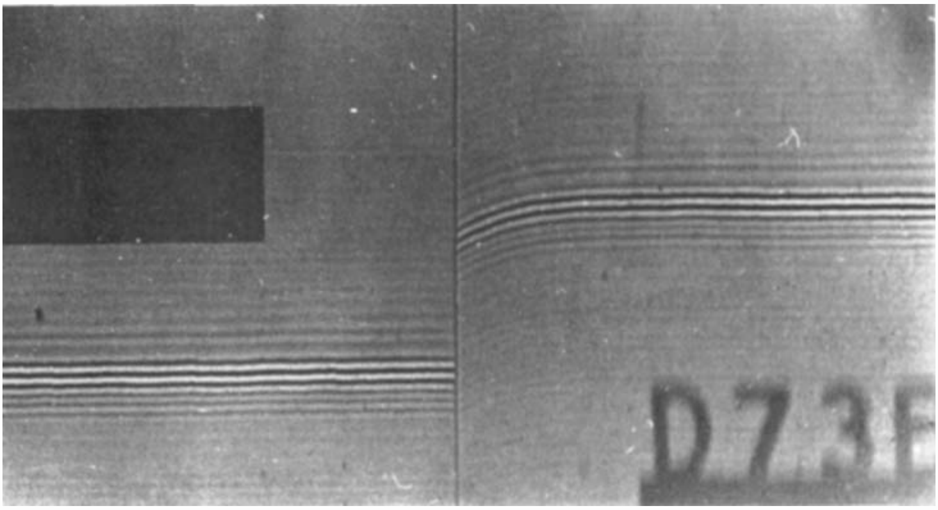
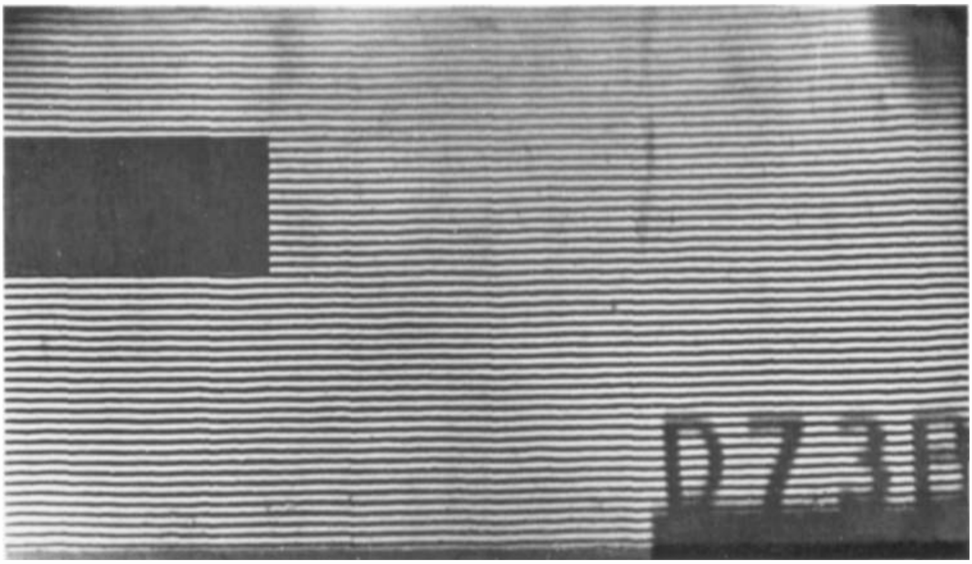


FIGURE 7. White-light interferogram of shock wave in CO_2, $M_1 = 1{\cdot}47$, $p_1 = 69$ mm Hg.



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