

# Departures from the linear equation for vibrational relaxation in shock waves in oxygen and carbon dioxide

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The detailed structure of the relaxation region in shock waves in oxygen was investigated using Blackman's experimental results. Oxygen was found to display a behaviour similar in many ways to that found previously for carbon dioxide with the relaxation frequency, as defined by the simple relaxation equation, depending on the departure from equilibrium as well as on temperature. The previous results for carbon dioxide were further analysed by means of a separate relaxation equation for each mode.

## 1. Introduction

In a previous paper (Johannesen, Zienkiewicz, Blythe & Gerrard 1962), we gave a detailed analysis of the vibrational relaxation phenomenon in shock waves in carbon dioxide. Using the simple relaxation equation

$$\frac{d\sigma}{dt} = \rho\Phi(\bar{\sigma} - \sigma), \quad (1)$$

where  $\sigma$  is the vibrational energy,  $\bar{\sigma}$  its local equilibrium value,  $t$  the time,  $\rho$  the density, and  $\Phi$  the relaxation frequency, it was shown that  $\Phi$  may be written

$$\Phi = \frac{v_b T_b}{\rho_b} c_{p\alpha} L(m) \frac{A(\rho_2 - \rho)}{\rho_b(\bar{\sigma} - \sigma)}. \quad (2)$$

Here  $v$  is the velocity relative to the shock wave and  $T$  the translational temperature. Suffix  $b$  indicates the sonic reference conditions of the Rayleigh line equations as discussed by Johannesen (1961) and suffix 2 refers to the final equilibrium conditions.  $c_{p\alpha}$  is the specific heat at constant pressure, ignoring vibration. It is assumed that a logarithmic plot of the difference between the final and local values of the density against distance behind the shock wave is a straight line

$$\log(\rho_2 - \rho) = -Ax + B; \quad (3)$$

this defines the constant  $A$ . The function  $L$  is defined by

$$L(m) = \left(\frac{T}{T_b}\right) \left(\frac{v}{v_b}\right)^3 (1 - m^2), \quad (4)$$

where  $m$  is the Mach number of the  $\alpha$ -gas, i.e. it is based on the sound speed ignoring vibration.

For  $\text{CO}_2$ ,  $A$  was determined experimentally over the shock Mach number range

1.4 to 4.1, and it was found that a plot of  $\Phi$  vs  $T^{-\frac{1}{2}}$  (figure 5 of Johannesen *et al.* 1962) showed that  $\Phi$  depends on the departures from equilibrium as well as on  $T$ , so that the relaxation equation in the simple form of (1) with  $\Phi$  a function of  $T$  only does not adequately describe the relaxation phenomenon.

It was suggested that this might be either because for  $\text{CO}_2$  only a system of relaxation equations (one for each mode) can give an adequate representation of the relaxation phenomena, or because a linear relaxation equation quite generally does not hold for large departures from equilibrium. If the latter explanation is the correct one, then simple diatomic gases should show the same behaviour, and it was felt that further speculation about the behaviour of  $\text{CO}_2$  should await a similar analysis for a diatomic gas.

Such an analysis, using Blackman's (1956) results for oxygen is given below. It is found that  $\text{O}_2$  behaves in many ways similarly to  $\text{CO}_2$  and does not follow the simple relaxation equation. By making certain assumptions about the relative orders of magnitude of the relaxation frequencies for the different modes of  $\text{CO}_2$ , the relaxation frequency for the bending mode is determined, and it is found to behave similarly to the previously determined over-all relaxation frequency.

## 2. Re-examination of oxygen results

Of the available experimental results for diatomic gases, only those for oxygen published by Blackman cover a sufficiently wide temperature range to make a detailed analysis possible. It is in a way unfortunate that only oxygen data can be discussed, since oxygen can hardly be described as a typical diatomic gas because of the very low energy of its first excited electronic state. In his original paper, Blackman plotted values of the relaxation time calculated by his approximate method. It would have been possible from these to work back to the slope  $A$  of the logarithmic plot. However, we were saved a good deal of work and improved the accuracy considerably by obtaining from the Palmer Physical Laboratories at Princeton University the original  $A$  values. We are grateful to Dr V. Blackman and Prof. W. Bleakney for making these data available to us.

For the  $\text{CO}_2$  results we found that a plot of  $\log(A/\rho_2)$  against  $T^{-\frac{1}{2}}$  was well fitted by a straight line. A similar plot for  $\text{O}_2$  was not a straight line. However, for  $\text{O}_2$  a plot of  $\log(A/\rho_2)$  against  $M_1$ , the shock Mach number, was well fitted by a straight line as shown on figure 1.

It should be mentioned that Camac (1961) has suggested that Blackman's values of the relaxation time are rather too small, and hence his values of  $A$  rather too high, at the lower end of the temperature scale, probably due to the effects of impurities, in particular water vapour. If this is the case, then the experimental values of  $A$  would be fitted more closely by a straight line when plotted logarithmically against  $T^{-\frac{1}{2}}$ . Attempts to check Blackman's low temperature results in our shock tube were unsuccessful, because we were unable to obtain sufficiently steady shock waves. This is thought to be because at low temperatures the length of the relaxation region was comparable with the length of the area change in the shock tube, and the distance between the area change and the working section was too short for the flow to settle down. The following discussion is therefore based on Blackman's uncorrected results.

Knowing  $A/\rho_2$  it is possible to plot for any value of  $M_1$  the variation with  $T$  of  $\Phi$  within the corresponding relaxation region in the manner discussed for  $\text{CO}_2$ . For  $\text{O}_2$  the range of  $T$  within a relaxation region is much smaller than for  $\text{CO}_2$  at the same Mach number because of the very much smaller value of the vibrational

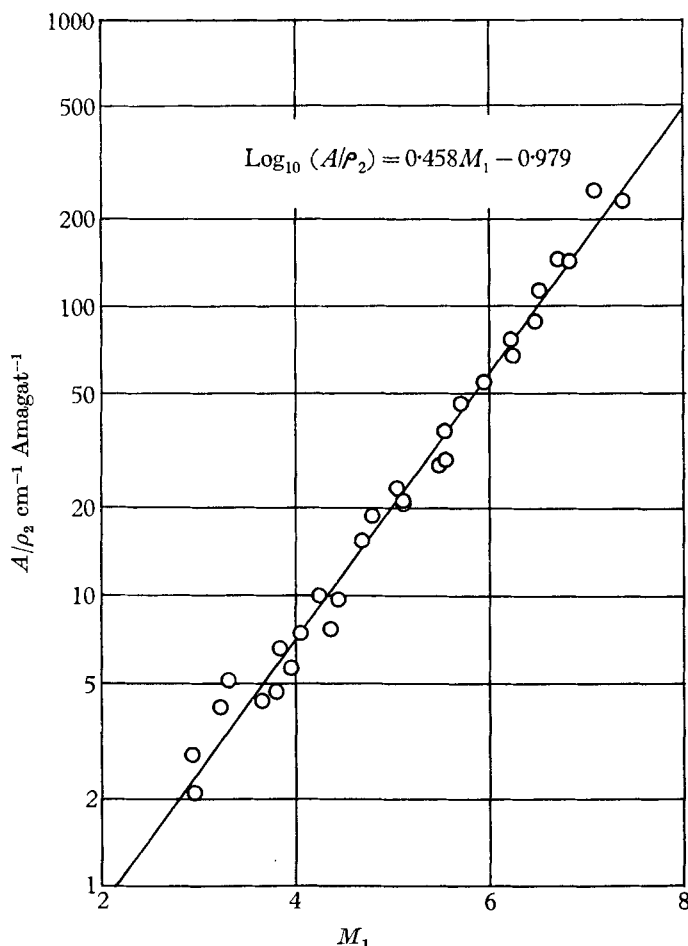


FIGURE 1. Slope  $A$  of density curves plotted logarithmically.

energy, and it was therefore necessary to use a much larger number of shock Mach numbers to get a reasonable overlap.  $\Phi$  was found for 60 different Mach numbers at intervals of 0.1 between 3.0 and 9.0, covering a slightly larger range than the experimental results. For any relaxation region the determination of  $\Phi$  becomes inaccurate close to the equilibrium condition 2, because both numerator and denominator of the fraction on the right-hand side of equation (1) tend to zero. It is possible to find the value at 2 by writing

$$\frac{(\rho_2 - \rho)}{\rho_b(\bar{\sigma} - \sigma)} \rightarrow \left[ \frac{d(\rho/\rho_b)/dT}{c_{v1b} + c_{p\alpha} dT_0/dT} \right]_{T \rightarrow T_2},$$

where  $c_{v1b}$  is the vibrational specific heat. Hence we find

$$\Phi(T_2) = v_b \frac{(\rho_2/\rho_b)^2}{T_2/T_b} L(m_2) \frac{A}{\rho_2} \left[ \frac{c_{v1b}}{c_{p\alpha}} (1 - \gamma_\alpha m_2^2) + (1 - m_2^2) \right]^{-1}, \quad (5)$$

where  $\gamma_\alpha$  is the ratio of the specific heats of the  $\alpha$ -gas and equal to 7/5 in our case. In all cases the value of  $\Phi$  at station 2 was found to lie on the continuation of that part of the  $\Phi$ -curve which could be determined accurately, but it should be remembered that there is no experimental justification for assuming that the logarithmic density plot is a straight line, and hence  $A$  constant, right up to equilibrium.

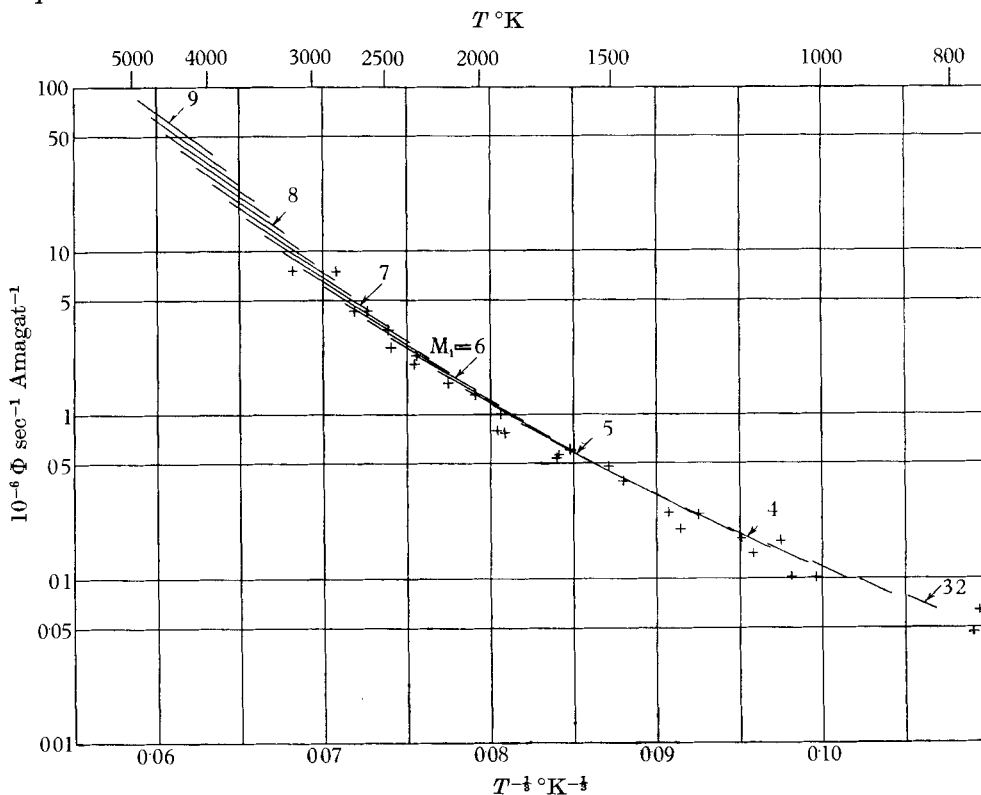


FIGURE 2. Relaxation frequencies in oxygen. — Manchester evaluation;  
+ Princeton evaluation.

Thirty of the calculated regions are shown in figure 2 which should be compared with figure 5 of Johannesen *et al.* (1962). Also shown on figure 2 are Blackman's original evaluations. They do, as predicted by Blythe (1961), tend to fall slightly below our evaluations because of the approximations used by Blackman in his evaluation method.

At low Mach numbers the behaviour of  $\Phi$  is similar to that found for  $\text{CO}_2$ : at a particular value of  $T$ ,  $\Phi$  is higher the larger the departure from equilibrium. As  $M_1$  increases the dependence on the departure from equilibrium becomes smaller (a trend also found for  $\text{CO}_2$ ) and in the neighbourhood of  $M_1 = 5$ , the

relaxation frequency is in fact a function of  $T$  only, and all the little segments overlap. Above a Mach number of 5 the dependence of  $\Phi$  on departure from equilibrium becomes reversed and at the higher end of the Mach number scale the failure of  $\Phi$  to be a function of  $T$  only is quite pronounced. It should be noted that a reduction of the  $A$  values at the lower end of the temperature scale would change the picture, and the possibility of  $\Phi$  being a function of  $T$  only at the low temperature cannot be definitely excluded.

It is difficult to define a measure for the way in which  $\Phi$  depends on 'something else' as well as on  $T$ . From the particular plot of figure 2 one would obviously tend to conclude that the failure of the individual elements to overlap to form a single curve is far more pronounced at the high Mach number end than at the low Mach number end, but this is largely due to the squeezing of the temperature scale at the high Mach number end.

In fact, it is possible to look at the results in such a way that one finds that the departures from a simple temperature dependence are about the same at the two ends of the range investigated. From the evaluated segments of the  $\Phi$ -curves it is possible to find  $\Phi/[A/\rho_2]$  and hence the value of  $d \log_{10} (A/\rho_2)/dM_1$  which will give overlap, i.e. make  $\Phi$  depend on  $T$  only. The values were about 0.60 at  $M_1 = 3.0$  and 0.25 at  $M_1 = 9.0$  as compared with the experimental (constant) value of 0.458.

### 3. Further evaluation of the results for carbon dioxide

In the previous paragraph we demonstrated that the simple relaxation equation (1) fails to describe the relaxation phenomenon even for a simple diatomic gas. In the case of  $\text{CO}_2$  we would therefore not expect the simple equation to hold either, and the behaviour found for  $\text{CO}_2$  cannot be ascribed solely to the simplifications introduced by the use of a single relaxation equation. Nevertheless, it is still interesting to see what happens if we introduce a more complicated system of relaxation equations. To do this we must make some additional assumptions. First, we assume that excitation takes place in series, i.e. that all transfer of energy from translation and rotation takes place to the bending mode (the 2-mode) and that the stretching modes (the 1- and 3-modes) are fed from the bending mode. Secondly, we assume that the rate of transfer of energy from bending to stretching is rapid compared with the transfer to bending. Both these assumptions are supported by theoretical work as discussed by Johannesen *et al.* (1962) and by our previous experimental results and their extension, see Zienkiewicz, Johannesen & Gerrard (1963).

Treating the two stretching modes together we then have

$$d\sigma_2/dt = \Phi_2 \rho (\bar{\sigma}_2 - \sigma_2) - d(\sigma_1 + \sigma_3)/dt, \quad (6)$$

and

$$d(\sigma_1 + \sigma_3)/dt = \Phi_1 \rho (\bar{\sigma}_1 + \bar{\sigma}_3 - \sigma_1 - \sigma_3), \quad (7)$$

where suffixes 1, 2 and 3 now refer to the modes rather than to positions relative to the shock wave.  $\bar{\sigma}_1$  and  $\bar{\sigma}_3$  are equilibrium values corresponding to the vibrational temperature of the bending mode, i.e. the temperature at which the vibrational energy in bending has the equilibrium value  $\sigma_2$ .

Comparing (6) and (1) we see that

$$d\sigma/dt = \Phi_2 \rho(\bar{\sigma}_2 - \sigma_2) = \Phi \rho(\bar{\sigma} - \sigma),$$

where  $\sigma = \sigma_1 + \sigma_2 + \sigma_3$ , so that

$$\Phi_2 = \Phi \frac{\bar{\sigma} - \sigma}{\bar{\sigma}_2 - \sigma_2}. \quad (8)$$

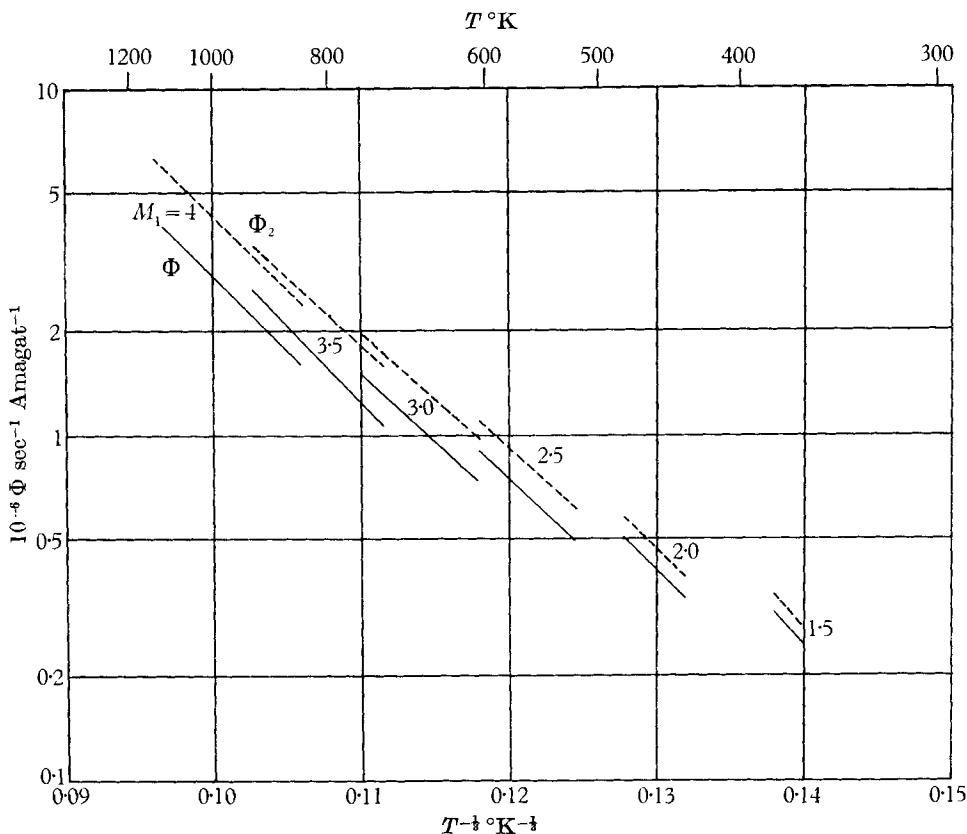


FIGURE 3. Relaxation frequencies in  $\text{CO}_2$ .

The values of  $\bar{\sigma}_1$ ,  $\bar{\sigma}_2$  and  $\bar{\sigma}_3$  as functions of temperature were found assuming each mode to behave as a harmonic oscillator. The total vibrational energy  $\bar{\sigma}$  found in this way agreed to within 1% with the values previously used and tabulated in *N.B.S. Circular 564*.

For any value of  $M_1$  we know  $\Phi$  as a function of  $T$ . We also know  $\bar{\sigma}$ ,  $\sigma$  and  $\bar{\sigma}_2$ . Then  $\sigma_2$  can be found by using the fact that  $\sigma$  is divided between  $\sigma_2$  and  $(\sigma_1 + \sigma_3)$  exactly as at equilibrium.

The values of  $\Phi_2$  are shown on figure 3 together with the previously published results for  $\Phi$ . The relaxation frequency for bending behaves similarly to the over-all relaxation frequency, but departs rather less from a single curve.

#### 4. Conclusions

We have demonstrated that both for  $\text{CO}_2$  and  $\text{O}_2$  the simple relaxation equation (1) with  $\Phi$  a function of temperature only fails to describe the relaxation phenomena in detail.  $\Phi$  depends also on some other quantity. If this is the departure from equilibrium and the correct relaxation equation is in the form of a series of powers of the departure from equilibrium with coefficients which are functions of temperature, then the correction to the linear term is positive at low temperature and negative at high temperature with an intermediate region in which the departures from the linear equation are negligible. It must be strongly emphasized that these conclusions are based on the experimentally established fact that the logarithmic plot of the departure of the density from its final equilibrium value against distance is a straight line.

We hope that our results may stimulate further theoretical work into the problem, in particular the assumptions behind the classical Landau-Teller theory. We have no direct theoretical contributions to make, but venture to suggest that the surprising fact is not perhaps that the simple equation does not hold but that it has been so universally used. In our previous work we mentioned the departure from equilibrium as a parameter which may be important in addition to the temperature, but we have been unable to suggest why this effect should change sign at a certain Mach number (or temperature).

Finally, we should like to point out that although our results may be of importance for the detailed understanding of relaxation phenomena, they do not mean that one goes far wrong in practical calculations by using the simple relaxation equation. However, one might do even better by using experimental values of  $A$  directly for calculating the structure of shock wave relaxation regions.

#### *Note added in proof*

E. Wild in an unpublished note, *ARC* 24617 (1963), has re-examined the assumptions of the classical Landau-Teller theory and the simple relaxation equation. He reaches the interesting conclusion that our suggestion that the simple equation would not be expected to hold at large departures from equilibrium is incorrect. The important parameter appears to be the vibrational energy, which is in fact smallest when the departure from equilibrium is smallest and vice versa.

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