The effects of small quantities of hydrogen, deuterium and helium on vibrational relaxation of carbon dioxide

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The vibrational relaxation frequency measurements were made on mixtures of carbon dioxide and the light gases using a shock tube and a Mach–Zehnder interferometer. The temperature range covered was 350–1200 °K. It was discovered that in the case of helium the effectiveness of the carbon dioxide–helium collision increases with increasing temperature while in the case of hydrogen and deuterium the collision number displays an anomalous temperature behaviour. At about 1000 °K all the three light gases are almost equally efficient in exciting the vibrational modes of carbon dioxide.

1. Introduction

Numerous sound absorption and sound dispersion measurements have been made at or near room temperature on gas mixtures containing small amounts of hydrogen, helium or deuterium. Recent contributions have been made by Parker (1961), Winter (1963) and Lewis & Shields (1967). Parker investigated the vibrational relaxation of oxygen mixed with hydrogen, helium and deuterium, both theoretically and experimentally. His experimental results indicate an equivalence between helium and deuterium in exciting the vibrational modes of oxygen, while hydrogen is about ten times more effective. Parker concluded that it is the light mass of these molecules which brings about the increased relaxation frequencies. Parker's data were confined to one temperature. Winter (1963) studied the relaxation time in carbon dioxide as a function of hydrogen and deuterium concentrations at several temperatures between 320 and 427 °K. He found that the collision effectiveness of both hydrogen and deuterium falls off slightly with increasing temperature. Kuchler (1938) reported a barely significant change in the collision number, $Z_{CO_2-H_2}$, over a temperature range of 300 °K. Lewis & Shields (1967) studied the vibrational relaxation in mixtures of carbon dioxide and helium over the temperature range 298–464 °K. Their results show that the efficiency of helium as a collision partner for energy transfer increases with temperature. This is in agreement with the Landau–Teller theory.

Marriott (1965) using a numerical method obtained theoretical values of the

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collision cross sections in mixtures of carbon dioxide and hydrogen. These values were consistent with the results of Winter (1963).

All the experimental results cited above are confined to a narrow temperature range. The present study was undertaken to investigate the temperature behaviour of the collision numbers $Z_{CO_2-H_2}$, Z_{CO_2-He}, $Z_{CO_2-D_2}$ over an extended temperature range.

The notation used in this paper is the same as that of Johannesen, Zienkiewicz, Blythe & Gerrard (1962). The term light gases will be used to denote collectively the three gases hydrogen, helium and deuterium.

2. Vibrational relaxation in gas mixtures

Consider a gas A containing small traces of another gas B. If the gaseous system is assumed to be at a sufficiently low pressure then any changes which occur can be ascribed to sequences of collisions between pairs of molecules and we may write the relaxation equation for gas A as

$$\frac{d\sigma_A}{dt} = \omega_{mix}(\overline{\sigma}_A - \sigma_A), \tag{1}$$

where $\overline{\sigma}_A$ is the local equilibrium value of the vibrational energy σ_A, and ω_{mix} is given by

$$\omega_{mix} = \alpha\omega_{AA} + \beta\omega'_{AB} + \beta\omega''_{AB}. \tag{2}$$

Here α, β are the mole fractions of gases A and B respectively. ω_{AA} and ω'_{AB} are the relaxation frequencies for the processes of translation and rotation interchange with vibration and ω''_{AB} is the relaxation frequency for the vibration–vibration energy interchange between A and B. All the above relaxation frequencies are defined at a pressure p.

If B is a monatomic gas then the third term on the right-hand side of (2) vanishes. If B is a polyatomic gas its vibrational modes are assumed to adjust so fast that gas B can be assumed to be in local vibrational equilibrium. Then

$$\omega_{mix} = \alpha\omega_{AA} + \beta\omega_{AB}, \tag{2a}$$

where $$\omega_{AB} = (\omega'_{AB} + \omega''_{AB}).$$

Equation (2a) shows that at a given temperature ω_{mix} is a linear function of β. However, it is difficult to assess the contribution of the vibration–vibration process to the measured relaxation frequency. In the case of hydrogen (characteristic temperature 5958 °K) at 1000 °K about 1 in every 400 molecules is in the first vibrational state and in the extreme case of the probability of vibration–vibration transfer being 1, one might claim that the vibration–vibration transfer process was responsible for exciting the vibrational modes of carbon dioxide. The ratio of the number of molecules in the first vibrational state to the total number of molecules falls off sharply with decreasing temperature. At temperatures below about 700 °K, even in the extreme case, the contribution from the vibration–vibration energy transfer becomes relatively insignificant. The corresponding temperature for deuterium is approximately 500 °K. However, in the

case of water vapour (to be reported) the vibration–vibration process may play a significant part over the temperature range 400–1200 °K.

The collision numbers reported in this paper correspond to the relaxation frequency ω_{AB}.

Now,

$$\omega = \rho\Phi = p\Omega, \tag{3}$$

where ρ is the density in Amagats, p is the pressure in atmospheres and Φ and Ω are respectively the relaxation frequencies at 1 Amagat and 1 atmosphere. We notice that Φ and Ω are essentially the relaxation frequencies described at two different pressures which differ by a factor of $273/T$. From $(2a)$ and (3) we have

$$\Phi_{mix} = \alpha\Phi_{AA} + \beta\Phi_{AB} \tag{4a}$$

and

$$\Omega_{mix} = \alpha\Omega_{AA} + \beta\Omega_{AB}. \tag{4b}$$

Equations (4) show that to evaluate the relaxation frequency of a carbon dioxide molecule relaxing in an atmosphere of hydrogen, say, the relevant data on the vibrational relaxation of pure carbon dioxide are essential. These data are available from the investigations of Johannesen *et al.* (1962) and Zienkiewicz, Johannesen & Gerrard (1963).

The thermodynamical properties of the system must also be adjusted to include the effect of the presence of small quantities of the lighter gases.

3. Experimental method

The shock tube used for the experiments has been described by Johannesen *et al.* (1962) and for the most part the apparatus and techniques employed in this investigation were similar to those of Johannesen *et al.* (1962).

The mixtures were prepared in a decanting volume and care was taken to ensure that the constituents of the mixture were as pure as possible. The purity of the gases, as supplied by the manufacturers, was as follows:

> carbon dioxide   99·95 % (the major impurity was water vapour);
> hydrogen   99·999 %;
> helium   99·995 %;
> deuterium   99·5 %.

Carbon dioxide was dried by passing it through a molecular sieve. The dryer lowered the dew point of the gas to −60 °C. The amount of water vapour then fell below 160 p.p.m. The effect of the remaining water vapour on the vibrational relaxation frequency was negligible. Deuterium was further purified by passing it through a liquid nitrogen trap. The main impurity left over was hydrogen. Because of the high purity of hydrogen and helium it was thought unnecessary to treat the gases in any way prior to mixing.

The decanting volume was evacuated and thoroughly outgassed. The leak rate of the vessel was negligible. In preparing a mixture, the light gas was first let into the vessel. Carbon dioxide was then allowed to flow into the decanting

volume fairly rapidly. This method apart from providing a stirring mechanism reduced the possibility of back diffusion of the light gas into the carbon dioxide supply line. The mixtures were allowed between $\frac{1}{2}$ h and 24 h to mix. Estimates based on simple kinetic theory showed that 30 min are sufficient for carbon dioxide and hydrogen to mix uniformly.

Density variations in the relaxation regions were measured using a Mach–Zehnder interferometer. For this instrument the fringe shift is directly proportional to the density change. Zienkiewicz (1959) has discussed this instrument in detail and also (1968) shown that the effects of dispersion of the white light are such that the position of the maximum contrast, i.e. the central fringe, drifts as the fringe shift increases.

Johannesen (1961) developed a method of analysis for vibrational relaxation regions. It involves no simplifying approximations and draws an analogy between the flow of the real gas and that of an ideal gas with heat extraction. This method has been adapted for use on a computer by Rees (1968) and is well suited to work involving mixtures of various compositions.

The density rise behind the diffusion resisted part of the shock wave was found to be exponential. Following the methods of Johannesen *et al.* (1962) a smoothing of the results was obtained by fitting a straight line to the logarithmic plot of the fringe shift difference $(N_2 - N)$ against x, the distance behind the diffusion resisted part. Suffix 2 denotes conditions at equilibrium. The equation of the straight line is given by

$$\log (N_2 - N) = -Ax + B',$$

where A and B' are constants for a particular shock. Johannesen (1961) shows how one can evaluate the relaxation frequencies throughout the relaxation region for each shock wave if the initial conditions, the Mach number and the A value are known.

4. Experimental results

Effects of various concentrations

To study the effect of concentration of the light gas on the relaxation frequency of the mixture, interferograms were obtained for various concentrations of hydrogen and helium at a nominal shock Mach number of 2·5. Johannesen's (1961) Rayleigh line method yields a range of values of the vibrational relaxation frequency corresponding to local temperatures in the relaxation region. The value of the relaxation frequency corresponding to 600 °K for each shock wave was selected and plotted against its respective mole fraction. Figure 1 shows the variation of Φ_{mix} with the concentration of hydrogen and figure 2 the variation of Φ_{mix} with the concentration of helium. The experimental values in both cases indicate a linear dependence of Φ_{mix} on the mole fraction of the light gas, showing that binary collisions control the excitation process. Also equation (4) has been derived assuming that the exchange of energy occurs during binary interactions and predicts a linear variation of Φ_{mix} with β. The present experimental results show that the equation is valid both for hydrogen and helium. The above study
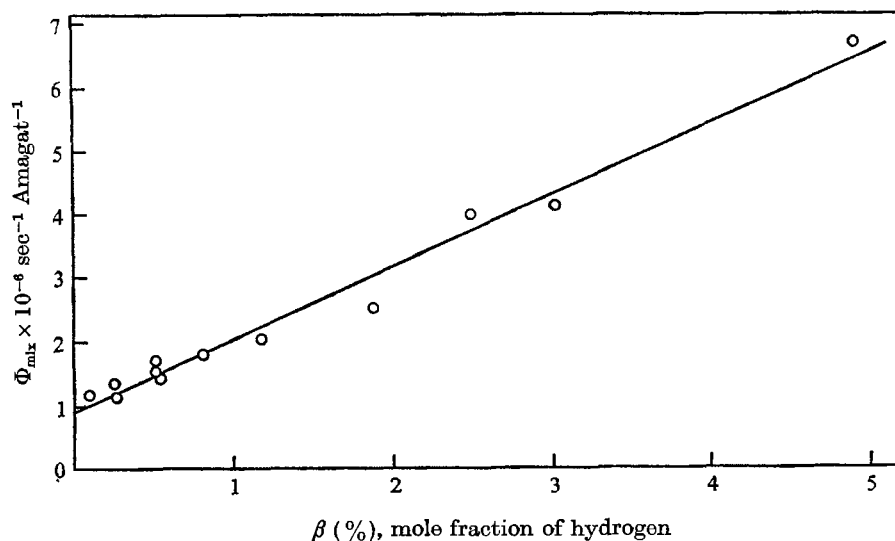
FIGURE 1. Variation of the relaxation frequency of the mixture with hydrogen concentration at 600 °K. The equation of the straight line is given by

$$\Phi_{mix} \times 10^{-6} = (1 \cdot 13\beta + 0 \cdot 91) \text{ sec}^{-1} \text{ Amagat}^{-1}.$$
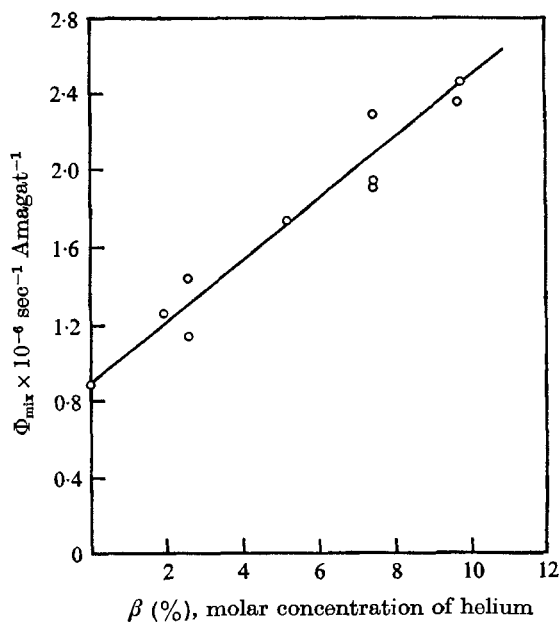

FIGURE 2. Variation of the relaxation frequency of the mixture with the concentration of helium at 600 °K. The equation of the straight line is given by

$$\Phi_{mix} \times 10^{-6} = (0 \cdot 16\beta + 0 \cdot 89) \text{ sec}^{-1} \text{ Amagat}^{-1}.$$

was not carried out for mixtures of carbon dioxide and deuterium because of shortage of the supply of deuterium. Nonetheless, it was assumed that only pairs of molecules interact.

The straight lines were drawn by the method of least squares.

Overall density ratio

The agreement between the experimental values of the equilibrium density ratio for various Mach numbers and the corresponding theoretical values was found to be excellent. The latter values were calculated using the Rayleigh line method and assuming that all modes of vibration had attained equilibrium.

The temperature dependence of the collision number

As mentioned earlier the relaxation region of a given shock wave can be characterized by a single constant A. The various A values obtained for various Mach numbers are plotted as A/ρ_2 *versus* $T_2^{-\frac{1}{3}}$ in figure 3. T_2 is the equilibrium temperature. The experimental values were smoothed out by fitting straight lines to the respective points. Using these straight line expressions it is possible to evaluate the variation of Φ_{mix} through the relaxation region of a shock wave. This was done for shock Mach numbers of 1·5, 2·0, 2·5, 3·0, 3·5 and 4·0. The temperature
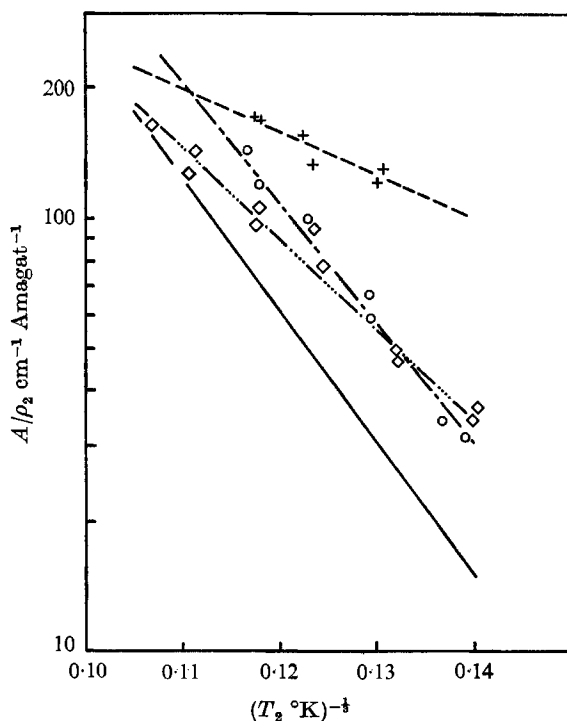

FIGURE 3. The temperature variation of A/ρ_2. $\cdots$—◇—$\cdots$, 0·51 % hydrogen; —$-+-$—, 5 % deuterium; — —O— —, 5·2 % helium; ———, pure carbon dioxide, Johannesen *et al.* (1962).

of the gas ahead of the shock wave was taken to be 295 °K. It was found that Φ_{mix} for all the light gases is not solely a function of temperature but depends in some way on the Mach number or some other related variable.

Values of $\Phi_{CO_2–LG}$ i.e. the relaxation frequency of a carbon dioxide molecule relaxing in an otherwise pure light gas at a given temperature can be obtained by using (4a) where α, β, Φ_{mix} and $\Phi_{CO_2–CO_2}$ are now known. Since both Φ_{mix} and $\Phi_{CO_2–CO_2}$ are not functions of temperature alone some uncertainty exists in correlating these values *via* (4a). This difficulty has not arisen in previous work on gas mixtures since one value was obtained for Φ which was identified to T_2 or T_{av}, the arithmetic mean of the temperature across the relaxation region.

In order to obtain a more direct interpretation of $\Phi_{CO_2–LG}$, it was converted to collision number, i.e. the number of collisions required to effect energy transfer. This was achieved as follows:

$$Z_{CO_2–LG} = [\Phi_{CO_2–LG}\tau_c]^{-1},$$

where $Z_{CO_2–LG}$ is the number of carbon dioxide–light gas collisions required for the adjustment of the energy of internal degrees of vibration of a carbon dioxide molecule and τ_c is the mean time between successive carbon dioxide–light gas collisions. τ_c is given by

$$\tau_c = \frac{10^{16}}{2n_{LG}\,\Omega_{CO_2–LG}^{(2,2)*}\,\sigma_{CO_2–LG}^2}\left[\frac{M_{CO_2}\times M_{LG}}{2\pi RT(M_{CO_2}+M_{LG})}\right]^{\frac{1}{2}}.$$

Here n_{LG} is the particle density of the light gas molecules, M_{CO_2}, M_{LG} are the molecular weights and $\sigma_{CO_2–LG}$ is in Angstroms. The quantities $\Omega_{CO_2–LG}^{(2,2)*}$ and $\sigma_{CO_2–LG}$ are defined in Hirschfelder, Curtiss & Bird (1954, p. 523).

The collision numbers for pure carbon dioxide were evaluated using two different interaction potentials, the rigid sphere model and the Lennard–Jones potential, in an effort to discover their effect on the temperature dependence of Z. It was found that the difference between the two sets of values was almost constant over the temperature range covered. This indicates that it would suffice to employ the rigid sphere model to study the temperature dependence of Z. However, in the present investigation the Lennard–Jones potential was used.

Figure 4 shows $Z_{CO_2–LG}$ plotted against $(T \text{ °K})^{-\frac{1}{3}}$. The results of other workers are also shown on the same diagram.

In figure 5 the relative efficiency of the various light gas molecules is plotted against the mean temperature across the relaxation region, T_{av}.

5. Discussion of results and concluding remarks

The behaviour of the collision numbers over an extended temperature range is very revealing. In the case of helium, the collision number behaves according to the Landau–Teller theory in that it falls consistently with increasing temperature. However, in the case of hydrogen and deuterium $Z_{CO_2–LG}$ is almost independent of temperature in the lower temperature range but rises dramatically at higher temperatures. This is in complete disagreement with the Landau–Teller theory. Both hydrogen and deuterium results display a temperature inversion. A

probable explanation for the anomalous behaviour of hydrogen and deuterium has been offered by Winter (1963). He suggests that on account of the elevated speed of the light molecules at high temperatures the time of interaction with a CO_2 molecule is too short. In normal collisions the interaction potential of the colliding molecules is not infinitely steep. Thus a finite, but short, time is
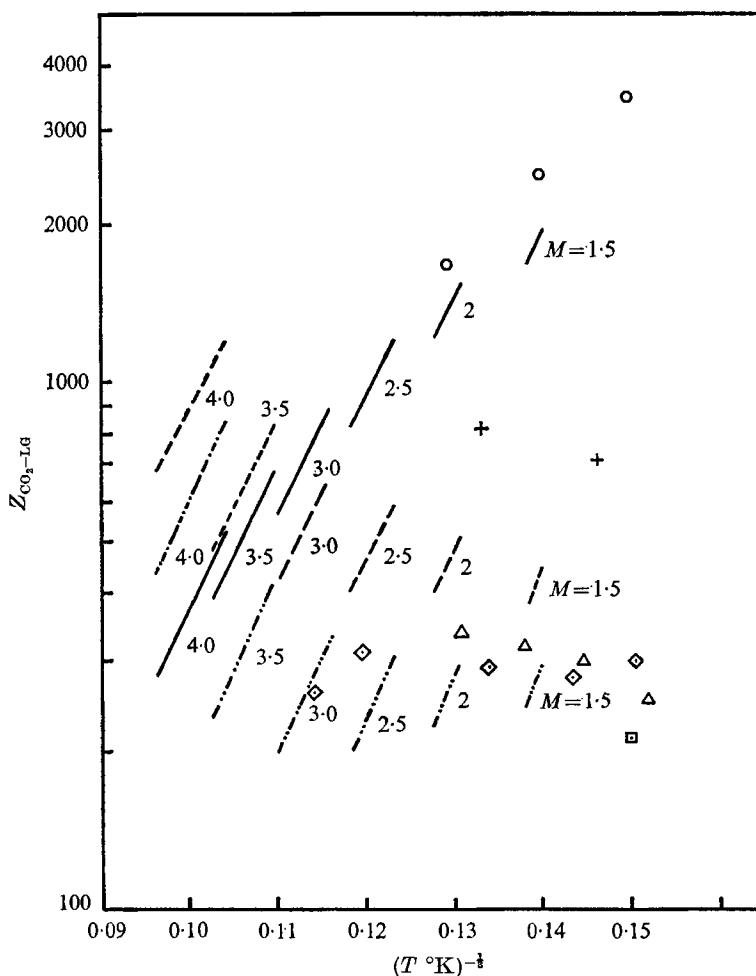

FIGURE 4. The variation of the experimental values of the vibrational collision number, Z_{CO_2-LG} with temperature. The present results are shown in the form of line segments: —··—··—, hydrogen; –––––, deuterium; ——, helium; ◇, hydrogen, Kuchler (1938); △, hydrogen, Winter (1963); ▫, hydrogen, Knudsen & Fricke (1940); +, deuterium, Winter (1963); ○, helium, Lewis & Shields (1967).

required for the transfer of energy. However, figure 4 indicates clearly that the behaviour of hydrogen and deuterium is markedly different from that of helium. This shows that the molecular mass alone is not responsible for the anomalous behaviour. A possible solution is offered by the fact that both hydrogen and deuterium are molecules while helium is an atom and that the effect of a molecule

on the potential interaction is markedly different from that of an atom. Hydrogen and deuterium with their small moments of inertia have large rotational quanta. Sharma (1969) found that the probability of rotation–vibration transfer decreases with increasing temperature.

Figure 5 illustrates more clearly the differences between the actions of the three molecules. The relative efficiency of helium is almost independent of the temperature. In the case of hydrogen and deuterium it is strongly dependent on the
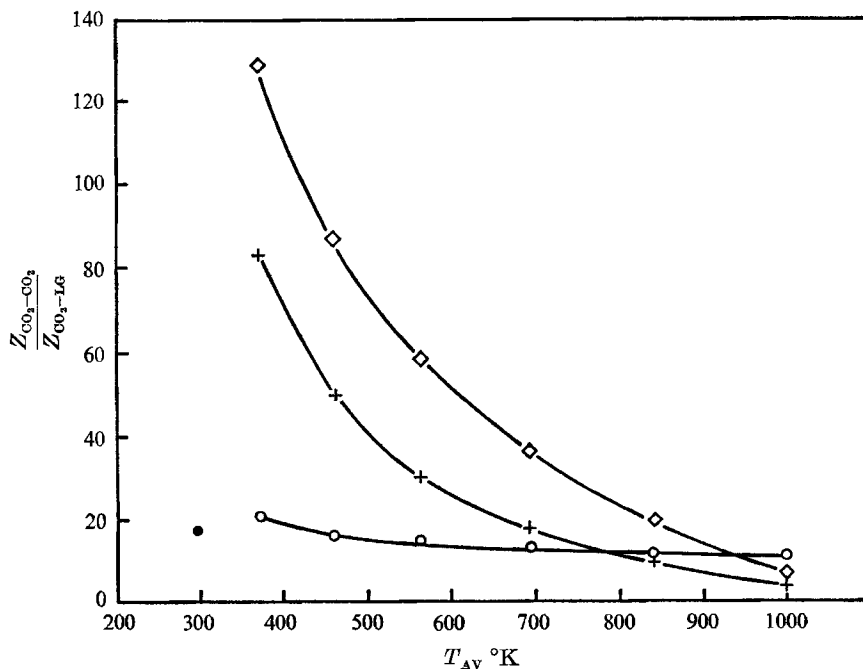

FIGURE 5. Relative efficiencies of carbon dioxide–light gas collisions. —◇—, hydrogen; —+—, deuterium; —○—, helium; ●, helium, Bauer & Liska (1964).

temperature in the lower temperature range. The relative efficiency of each light gas falls off with increasing temperature and at about 1000 °K all three gases are approximately equally efficient as collision partners with carbon dioxide.

Finally, figure 4 indicates that Z_{CO_2-LG} is not solely a function of temperature but depends in some way on Mach number or some other related variable. This effect is more pronounced in the cases of hydrogen and deuterium.

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