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# Structure of Shock Waves in Polyatomic Gases*

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This paper describes the results of experiments using a shock tube and interferometer to study the role of vibrational relaxation in shock structure. Shocks of Mach number up to 5 have been observed in air, A, $N_2$, $CH_4$, $CO_2$, $N_2O$, and $CCl_2F_2$. In air and nitrogen below about $M_1=2$ and in argon the validity of the Rankine-Hugoniot relation using constant specific heat has been established within experimental accuracy. Above $M_1=2$ in both air and $N_2$, the observed density corresponds to only partial equilibrium, no appreciable excitation of vibrational modes occurring, for example, for at least 150 $\mu$sec at 900°K. Both $CH_4$ and $CCl_2F_2$ show fast adjustment with relaxation times less than 1 $\mu$sec to the expected final state. In $CO_2$ and $N_2O$, vibrational relaxation times are observed to be in reasonable agreement with published data. The downstream state, however, is at a lower density than required for complete equilibrium and the possibility of separate relaxation times for each vibrational mode is suggested; the valence vibrations adjust at least 100 times more slowly than do the bending modes. Added traces of water vapor reduce the visible adjustment greatly but leave the final state unaltered. The catalytic effect of water vapor in speeding equilibration seems therefore to be limited to the bending modes.

SINCE Ernst Mach first observed shock waves by shadow photography, a little over sixty years[1] ago, the problem of their structure has intrigued students of fluid dynamics and kinetic theory alike. It was early recognized that shock fronts are extremely thin, the order of a wavelength of visible light, but the exact manner in which collisions redistribute translational energy is still not fully understood. When other molecular energy states are excited as well, shock structure may be considerably more complex. Sound dispersion in polyatomic gases suggests that translational energy is exchanged at different rates with molecular rotation, vibration, and dissociation. A similar result may be anticipated for transfer to electronic excitation and ionization at high temperatures. The purpose of this paper is to described experiments on the role of vibrational energy lag in shock structure and its relation to the problem as a whole.

Rayleigh[2] seems to have been the first to treat the Navier-Stokes equation for the profile of a shock wave in a viscous fluid. Shortly thereafter Taylor[3] obtained an approximate expression for the density variation through a weak shock in which both viscosity and heat conduction exist. His result, that the thickness should diminish with increasing shock strength, has been substantiated by later exact solutions, in which increasingly realistic expressions for the temperature variation of the transport coefficients were used.[4] It seems safe to say that the continuous fluid theory for shock structure in monatomic gases is now complete. A new difficulty has arisen, however, because the thickness predicted for strong shocks diminishes to only a few mean free paths and one wonders whether or not the usual viscosity and heat conduction coefficients have any validity in a region of such high gradients.

Several attempts have been made to solve the problem using kinetic theory. It can be shown that a first-order correction to a Maxwellian velocity distribution leads to the same result as a continuous fluid theory which includes the ordinary coefficients of viscosity and heat conduction. Higher order corrections, including what are known as the Burnett terms, presumably improve the approximation. Formidable problems of convergence which have retarded this approach, particularly when calculations are made for Mach numbers of 2 or larger, are discussed in papers by Wang Chang,[5] Zoller,[6] and Grad.[7]

Using a slightly different approach, Mott-Smith[8] has suggested that the velocity distribution within a strong shock is composed of a mixture of two Maxwellian distributions appropriate to equilibrium conditions on either side of the shock. The resulting dependence of thickness on shock speed agrees quite well with the values from continuous fluid theory.

Experimental measurements of shock thickness in argon and other gases have been reported in a series of papers by Hornig *et al.*[9] and by Sherman.[10] Thickness

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[1] E. Mach, Akad. Wiss. Wien **98**, 1310 (1889).

[2] Lord Rayleigh, Proc. Roy. Soc. (London) **A84**, 247 (1910).

[3] G. I. Taylor, Proc. Roy. Soc. (London) **A84**, 371 (1910).

[4] R. Becker, Z. Physik **8**, 321 (1922); L. H. Thomas, J. Chem. Phys. **12**, 449 (1944); M. Morduchow and P. A. Libby, J. Aeronaut. Sci. **16**, 674 (1949); A. E. Puckett and H. J. Stewart, Quart. Appl. Math. **7**, 457 (1950); R. von Mises, J. Aeronaut. Sci. **17**, 551 (1950); Lieber, Romano, and Lew, J. Aeronaut. Sci. **18**, 55 (1951); D. Gilbarg and D. Paolucci, J. Rat. Mech. Anal. **2**, 617 (1953).

[5] C. S. Wang Chang, "On the Theory of the Thickness of Weak Shock Waves," University of Michigan, Department of Engineering Research Report APL/JHU CM-503 (unpublished).

[6] K. Zoller, Z. Physik **130**, 1 (1951).

[7] H. Grad, Comm. Pure and App . Math. **5**, 157 (1952).

[8] H. M. Mott-Smith, Phys. Rev. **82**, 885 (1951).

[9] G. R. Cowan and D. F. Hornig, J. Chem. Phys. **18**, 1008 (1950); Greene, Cowan, and Hornig, J. Chem. Phys. **19**, 427 (1951); E. F. Greene and D. R. Hornig, "Shape and Thickness of Shock Fronts in Argon, Hydrogen, Nitrogen, and Oxygen," Brown University, Metcalf Research Laboratory Report TR-4, 1952 (unpublished).

TABLE I. Exchange of rotational and translational energy in gases.

| Gas | Temp. °C | Relaxation time $t$, sec | Number of collisions $Z$ | Type of experiment | Reference |
|---|---|---|---|---|---|
| $H_2$ | 16°C | $2.1 \times 10^{-8}$ | 300 | Pitot tube | W. Griffith, J. Appl. Phys. **21**, 1319 (1950). |
| $D_2$ | 17°C | $1.5 \times 10^{-8}$ | 150 | ultrasonic dispersion | A. van Itterbeek and R. Vermaelen, Physica **9**, 345 (1942). |
| $N_2$ | 0°C | $4.85 \times 10^{-10}$ | 3 | ultrasonic dispersion | Parker, Adams, and Stavseth, J. Acoust. Soc. Am. **25**, 263 (1953). |
| $O_2$ | 0°C | $4.95 \times 10^{-10}$ | 3 | ultrasonic dispersion | Parker, Adams, and Stavseth, J. Acoust. Soc. Am. **25**, 263 (1953). |
| $NH_3$ | 20°C | $8.1 \times 10^{-10}$ | 10 | ultrasonic dispersion | S. Petralia, Nuovo cimento **10**, 817 (1953). |
| $CO_2$ | 32°C | $2.29 \times 10^{-9}$ | 16 | ultrasonic dispersion | J. C. Hubbard, J. Acoust. Soc. Am. **14**, 474 (1952). |

is usually taken to be the distance between intercepts on the asymptotic velocities of a line tangent to the velocity profile at its steepest (or mean) point. For monatomic gases good agreement between continuous fluid theory and experiment is observed, not only in the variation of shock thickness with Mach number,[9,10] but also in the actual profile as well.[10] In units of Maxwell's mean free path in the gas ahead of the shock, the thicknesses at $M_1 = 1.1$, 1.5, and 2.5 appear to be fairly well established as 16, 9, and 6, respectively. The actual number of collisions suffered by a typical molecule in passing through the shock would be 30, 19, and 13. This conclusion is important in considering the effect of additional degrees of freedom. In the ensuing discussion, it will be convenient to think of the temperature of a gas as the value appropriate to the mean translational velocity of the molecules without reference to their internal states.

The number of collisions found for fairly weak shock waves is the same order of magnitude as the number required to establish rotational equilibrium in a gas. A summary of the data available at present on rotational relaxation times is shown in Table I. This effect may be incorporated into the flow equations by introducing the rotational relaxation time itself[11] or through the concept of a second, or "bulk", coefficient of viscosity. The latter approach is well-suited to cases where the relaxation time is short compared to times characteristic of the process concerned, i.e., weak shocks.[12] Sufficiently strong shocks, on the other hand, compress the gas so rapidly that translation and rotation may adjust quite separately. Greene and Hornig conclude from their measurements that this is the case for hydrogen at $M_1 = 1.39$ and place a lower limit on the number of collisions required to bring rotational equilibrium as 150, a value compatible with the data in Table I. Since shock thickness and rotational relaxation times depend differently on temperature, it is probable that a single gas exhibits a behavior varying between the two extremes depending on the shock strength. Such is the case with nitrogen, in which translation and rotation stay in equilibrium at $M_1 = 1.13$ but appear to be somewhat out of step at $M_1 = 1.42$.[9]

Vibrational adjustment rates have been measured for a large number of gases and are generally slower by several orders of magnitude than those for translation and rotation.[13] At present, little quantitative information is available on diatomic gases because the population of excited vibrational states is exceedingly small at room temperature. Qualitatively, however, it is generally accepted that vibrational relaxation times in all diatomic gases are very long indeed. Among polyatomic gases, relaxation times are the order of microseconds and the vibrational heat capacities are appreciable so that significant effects on shock structure may be expected. Figure 1 shows interferograms of shocks in six different gases taken with a spark whose duration is less than one microsecond. In argon, the fringes jump discontinuously to their final position and the apparent thickness of the front arises solely from the motion of the shock during one-third of a microsecond. In air, the rotation adjusts so rapidly that no structure is detectable, while even at $M_1 = 2$ vibrational energy amounts to only $0.015R$, an insignificant amount. Carbon dioxide exhibits a large effect of vibrational lag, while the adjustment in freon-12 ($CCl_2F_2$) is apparently too rapid to observe. Both nitrous oxide and methane exhibit fast relaxation processes. Before turning to an analysis of such pictures, a resumé of the effect of dissociation, electronic excitation, and ionization will be included.

Dissociation frequently proceeds by bimolecular collisions, just as the processes already discussed, but its effects on shock waves has been investigated carefully only in a few cases. Carrington and Davidson[14] studied $N_2O_4$ in a carrier of nitrogen in a shock tube

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[10] F. S. Sherman, "A Low Density Wind Tunnel Study of Shock Wave Structure and Relaxation Phenomena in Gases," University of California, Berkeley, Institute of Engineering Report He-150-122, May, 1954 (unpublished).

[11] L. J. F. Broer, Appl. Sci. Research **A2**, 447 (1951).

[12] M. J. Lighthill, "Viscosity Effects in Sound Waves of Finite Amplitude" (to be published).

[13] W. Griffith, J. Appl. Phys. **21**, 1319 (1950).

[14] T. Carrington and N. Davidson, J. Phys. Chem. **57**, 418 (1953).

and measured the rate of dissociation into $NO_2$ by noting the time variation of absorption of a narrow beam of white light after a shock passed by. At 25°C they found a characteristic time of 12 $\mu$sec, in reasonable agreement with data from sound dispersion. The great advantage of using shock waves lies in the ease with which the temperature of the sample can be varied by choosing different shock strengths. Similar techniques have been applied to $Br_2$ and $I_2$. So far, little is known about dissociation of the constituents of the atmosphere but Bethe and Teller[15] make some estimates to show that times are sufficiently long for detection by shock tube studies.

Electronic excitation and ionization are expected to occur only at very high temperatures. The fact that strong shocks are indeed luminous has been observed by several workers,[16–18] and attempts to formulate a theory for the excitation process in argon have been presented by Petschek[18] and by Bond.[19] Here the structure is somewhat altered from the exponential decay to equilibrium previously encountered, because excitation and ionization are carried on most effectively by electron impact and initially, of course, there are no free electrons. The region immediately behind a shock front in argon is thus characterized by slow incubation of free electrons followed by a rapid increase in ionization quite similar to the initial processes in spark breakdown. Luminosity is not observed in the incubation region but is very intense as the gas approaches equilibrium.

In order to develop a quantitative theory for the processes discussed, it is convenient to refer directly to the one-dimensional steady-flow equations which express conservation of mass, momentum, and energy. Outside the zone ordinarily described as the shock front, where translational motion of the molecules reaches a Maxwellian distribution again, the effects of viscosity and heat conduction are relatively small. Accordingly these terms will be omitted in analyzing the remainder of the shock and attention will be centered on the redistribution of energy among internal states. The conservation equations in a frame of reference moving with the shock are as follows:

$$\text{Mass:} \qquad \rho_1 v_1 = \rho_2 v_2, \tag{1}$$

$$\text{Momentum:} \qquad p_1 + \rho_1 v_1^2 = p_2 + \rho_2 v_2^2, \tag{2}$$

$$\text{Energy:} \qquad E_1 + p_1/\rho_1 + v_1^2/2 = E_2 + p_2/\rho_2 + v_2^2/2. \tag{3}$$

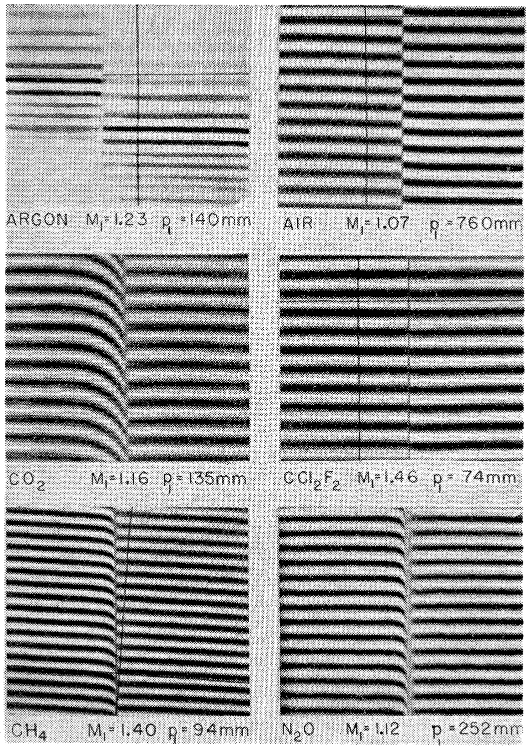

FIG. 1. Interferograms of shock waves in six different gases. In each case the shock is traveling to the right. The first picture shows how the absolute fringe shift may be obtained by using white light.

The subscripts 1 and 2 denote equilibrium conditions upstream and downstream, respectively. For most gases at ordinary densities, the ideal gas equation of state is entirely satisfactorily and may be written to include a change in number of particles from dissociation as

$$p = (1+\alpha)\rho RT. \tag{4}$$

Bethe and Teller[15] have shown that these four relations uniquely determine equilibrium conditions downstream of a shock in terms of the initial state and velocity without regard to the nature of any intervening processes. For purposes of this discussion, a shock is considered to include the zone within which quantities describing the state of the gas reach some reasonable fraction of their final value.

The method for evaluating equilibrium energy in terms of the partition function is well known and need not be repeated here.[20] Translation and rotation (in all gases but hydrogen) have the classical value, $\frac{1}{2}RT$ per degree of freedom, at room temperature and above, while additional contributions from other sources come into play at various temperatures. Dissociation and

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[15] H. Bethe and E. Teller, "Deviations from Thermal Equilibrium in Shock Waves," University of Michigan Engineering Research Institute, Ann Arbor, Michigan, 1952 (unpublished).

[16] Fowler, Goldstein, and Clotfelder, Phys. Rev. **82**, 879 (1952).

[17] Hollyer, Hunting, Laporte and Turner, Nature **171**, 395 (1953).

[18] Petschek, Rose, Glick, Kane, and Kantrowitz, J. Appl. Phys. **26**, 83 (1955); H. Petschek and A. Kantrowitz, Phys. Rev. **98**, 1141(A) (1955).

[19] J. W. Bond, Jr., Los Alamos Report, LA-1693, 1954 (unpublished).

[20] For a good description of the method see J. Mayer and M. Mayer, *Statistical Mechanics* (John Wiley and Sons, Inc., New York, 1940), or W. Doering and G. Burkhardt, "Contributions to the Theory of Detonation," Air Material Command, Wright-Patterson Air Force Base, Dayton, Ohio, Technical Report No. F-TS-1227-1A, 1949 (unpublished).

ionization appear to a significant extent only at temperatures considerably higher than those needed to excite vibrational motion, so that the latter can be studied entirely separately.

Since the energy generally depends in a complicated way on temperature, the conservation equations are most easily solved by starting with the temperature $T_2$ and finding the other quantities from this. Bethe and Teller[15] give a convenient method which makes use of a new quantity:

$$\beta(T) \equiv 1 + E(T)/RT. \tag{5}$$

The density ratio is found to be

$$\rho_2/\rho_1 = b + (b^2 + T_1/T_2)^{\frac{1}{2}}, \quad b = \beta_2 - \tfrac{1}{2} - (\beta_1 - \tfrac{1}{2})T_1/T_2. \tag{6}$$

The Mach number is

$$M_1^2 = 2(\beta_2 T_2 - \beta_1 T_1)/\gamma_1 T_1[1 - (\rho_1/\rho_2)^2], \tag{7}$$

where $\gamma_1$ is equal to $C_p/C_v$ at the temperature $T_1$. Data on the energy of a large number of gases have been compiled by the National Bureau of Standards, so that the necessary shock calculations can be readily carried out. When the specific heats are constant, as for the noble gases and air below about $M_1 = 2$, $\beta = C_p/R$ and the familiar Rankine-Hugoniot equation and other shock wave relations result.

Landau[21] and Bethe and Teller[15] have developed a simple theory for the rate of exchange of vibrational energy by collisions in gases having just one vibrational degree of freedom. They assume that internal redistribution proceeds rapidly enough for the population in various quantum levels to be described in terms of a "vibrational temperature" $T_{\text{vib}}$. Then it is possible to show that adjustment toward equilibrium is described by Eq. (8), where $E_{\text{vib}}$ is the actual value of the vibrational energy and $E_{\text{vib}}(T)$ is what it would be at temperature $T$.

$$dE_{\text{vib}}/dt = (E_{\text{vib}}(T) - E_{\text{vib}})/\tau. \tag{8}$$

The relaxation time $\tau$ is predicted to vary inversely with the bimolecular collision rate and in addition to decrease with temperature through an exponential dependence:

$$\tau = \text{const}\, T^{1/6} \exp(\text{const}/T^{\frac{1}{3}})/p. \tag{9}$$

The two constants depend on collision cross sections which are not accurately known, so that a direct calculation of $\tau$ is very difficult to make. If all experimental data are reduced to one atmosphere and the small effect of $T^{1/6}$ neglected, the linearity of a plot of $\ln\tau$ *vs* $T^{-\frac{1}{3}}$ would give a test of their theory. In gases where several vibrational modes are excited simultaneously, it is reasonable to suppose that the above theory applies to each mode and it may even be correct to say that they all adjust with the same relaxation time. We shall return to this latter question in discussing the experimental data.

In principle, Eqs. (1)–(4) and (8) can be solved to obtain a complete description of the flow behind a shock front. When the variation of specific heats and relaxation time with temperature are included, however, recourse must be had to numerical calculation for each shock strength. Broer[11] discusses the problem at some length and develops approximate solutions for certain limiting cases. In the interest of a better grasp of the physical situation, some assumptions can be made at the outset which greatly simplify the mathematics without seriously harming the result.

First, assume that translation and rotation reach equilibrium with one another before the vibrational energy has time to change at all. This intermediate condition, which will be called state $a$, is one in which the vibrational temperature $T_{\text{vib}}$ is still equal to $T_1$, while the translational temperature $T_a$ is somewhat above $T_2$. Properties at state $a$ can easily be found by omitting the contribution of vibrational specific heat to sound speed and $\gamma$ in the conservation equations. For all diatomic and linear polyatomic molecules like $CO_2$ and $N_2O$, $\gamma$ is just 7/5 so that values may be read from shock tables for air after adjusting the Mach number to compensate for the higher speed of sound. As an example, state $a$ and state 2 are shown in Fig. 2 as functions of initial Mach number $M_1$ for shocks in $CO_2$ at 23°C. $T_{\text{vib}}$ and $T$ approach $T_2$ according to Eq. (8).

The relaxation region is characterized by rapidly increasing vibrational energy, slowly falling temperature, increasing pressure and density, and a slight deceleration of the flow as a whole. From Fig. 2, it is apparent that the relative change of pressure is smaller than either change of temperature or density, the latter two being of opposite sign and nearly the same magnitude. It is this fact that makes the interferometer especially useful in studying relaxation as compared with a pressure-measuring device. In fact, little error is made in computation if the pressure is assumed to be exactly constant.

Consideration of the actual magnitudes involved in the transition from state $a$ to state 2 reveals that practically all of the energy absorbed by vibrations comes from random motion expressed as temperature. The latter energy is given by $C_p'T$, where $C_p'$ is the specific heat at constant pressure not counting vibrations. In linear molecules, $C_p'$ is equal to $(7/2)R$. Therefore,

$$dE_{\text{vib}} = -C_p' dT, \tag{10}$$

and during later portions of the approach to equilibrium, where $C_{\text{vib}}$ is not changing very much, this may be integrated to give

$$E_{\text{vib}} + C_p'T = E_{\text{vib}2} + C_p'T_2 = C_{p2}T_2. \tag{11}$$

Combining Eqs. (8), (10), and (11) and integrating

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[21] L. Landau, Physik. Z. Sowjetunion 1, 89 (1934).

again gives

$$(T-T_2)/(T_a-T_2)=e^{-C_p t/C_p'\tau}, \qquad (12)$$

showing that in the later stages, at least, the temperature drops exponentially with a time constant of $\tau C_p'/C_p$. When this result is translated into density, we find

$$\frac{\rho_2-\rho}{\rho_2-\rho_a}=\frac{\rho_2}{\rho_a}e^{-C_p t/C_p'\tau}\bigg/\left[1+\frac{\rho_2-\rho_a}{\rho_a}e^{-C_p t/C_p'\tau}\right]. \qquad (13)$$

As the fractional change $(\rho_2-\rho_a)/\rho_a$ is small and we have already decided to look at the later stages of adjustment, the denominator is nearly one so that the density also approaches its equilibrium value with an exponential decay.

The foregoing analysis has been applied to many pictures, such as are shown in Fig. 1, with the purpose of finding the state immediately behind the shock front and, if that is not a state of complete equilibrium, the time taken to reach equilibrium.[22] Two independent measurements of shock strength are made during each experiment in the shock tube. The speed of a shock is determined by noting the time taken to travel between two schlieren light screens a known distance apart. The density change across the shock can be calculated from the fringe shift measured on an interferogram taken with the fast spark while the shock is in view. The time intervals are around 1 msec and can be measured to within 1 $\mu$sec for an accuracy of one part per thousand, our most accurate measurement. For each gas tested, the theoretical speed of sound was checked by extrapolation of weak shock speeds to zero strength. Excellent agreement was obtained.[23] The Mach numbers quoted are therefore believed to be accurate within three or four parts per thousand. Repeated tests have shown that fringe shifts across plane shock waves can be consistently measured within ±1/15 fringe. To convert a fringe shift $\delta$ to density, the width $l$ of the test section, the wavelength $\lambda$ of light, and index of refraction $n_s$ at STP must be known, along with the initial gas density $\rho_1$; the relation is

$$\rho-\rho_1=\frac{\lambda T p_s}{l T_s p_1(n_s-1)}\delta. \qquad (14)$$

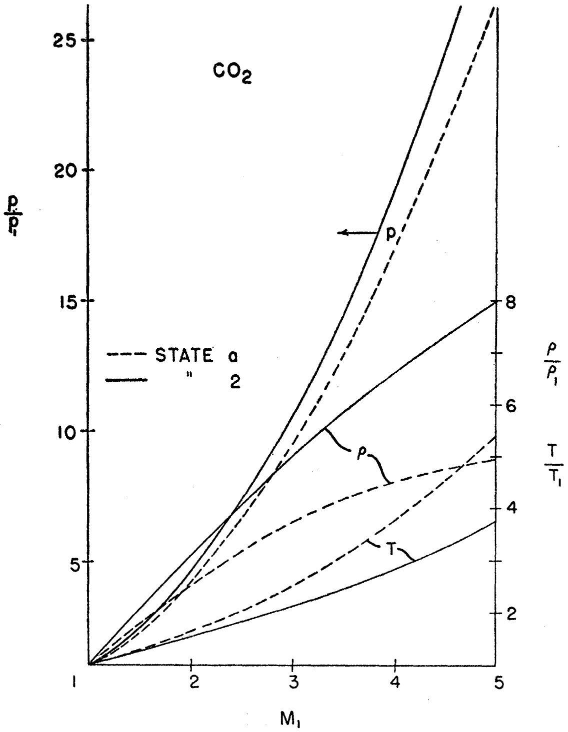

FIG. 2. Pressure, temperature, and density ratios for shock waves in carbon dioxide at final equilibrium, state 2, and at partial equilibrium, state $a$, where no adjustment of vibrational energy has taken place. Note that, for a given shock Mach number $M_1$, the greatest relative change during vibrational equilibrium occurs in the density.

Considering possible errors in measuring the initial gas pressure $p_1$ and other sources, the uncertainty in an individual density measurement is about ±1% under "normal" operating conditions, and two to four times this at the highest shock strengths conveniently obtainable with the present equipment.

As a test of the validity of the assumptions behind the Rankine-Hugoniot relation (and of the experimental technique), a number of runs were made using argon. The first electronic level is so high in energy that the constant specific heat theory should be valid for a very wide range of shock strengths. Up to $M_1=4.3$, agreement between the density measured with the interferometer and the density determined from the shock velocity and the Rankine-Hugoniot relation is within experimental error.[23] At $M_1=4.3$, the disagreement reaches a maximum of 4% in shock density ratio.

A large amount of data on shocks in air has been collected from pictures taken for other purposes over the past several years, and additional pictures in air and $N_2$ have been obtained specifically to determine the downstream state of the gas. Below $M_1=2$, so little vibrational energy is excited that there is little hope of detecting any departure from the theory using constant $\gamma$. The effect of an increased heat capacity at higher temperatures is to increase the shock density ratio as

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[22] In this regard, it might be mentioned that the possibility of studying vibrational relaxation with a shock tube and interferometer was suggested in reference 13 and an interferogram of a shock in $CO_2$ similar to that reproduced in Fig. 1 was first shown at the New York Meeting of the American Physical Society in 1952: Walker Bleakney, Phys. Rev. **86**, 610(A) (1952). Through private communication, we later learned that E. Smiley, E. Winkler, and Z. Slawsky, at the Naval Ordnance Laboratory, had started a similar study independently. Early results from Princeton were presented at the Spring Meeting of the American Physical Society in Washington: W. Griffith, Phys. Rev. **87**, 234(A) (1952). Since then two communications from the Naval Ordnance Laboratory group have appeared giving experimental results on $CO_2$ and $Cl_2$: Smiley, Winkler, and Slawsky, J. Chem. Phys. **20**, 932 (1952) and E. Smiley and E. Winkler, J. Chem. **22**, 2018 (1954).

[23] W. Griffith and W. Bleakney, Am. J. Phys. **22**, 597 (1954).

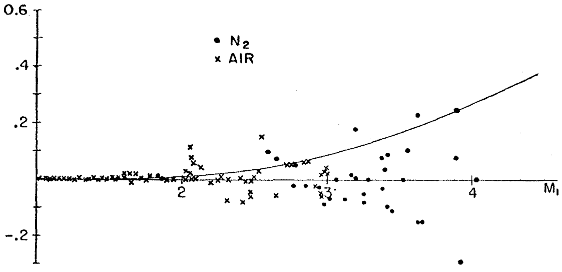

FIG. 3. Theoretical and experimental density ratios for shocks in air and nitrogen, both plotted as the difference from $\rho_2/\rho_1$ for $\gamma=1.4$. The appearance of vibrational excitation at the higher temperatures accounts for the departure of the theoretical curve from the constant $\gamma$ value. The fact that the experimental points follow the axis is taken as evidence that no vibrational excitation has actually occurred in the interferograms.

well. The solid curve in Fig. 3 shows the difference between the density ratio in $N_2$ for variable specific heat and for constant specific heat as a function of Mach number. For reference, the actual density ratio at $M_1=2$ is 2.79 and at $M_1=4$ is 4.84.

The experimental points plotted in Fig. 3 represent the density ratio measured with the interferometer minus that computed from the shock speed using constant specific heat. The fact that the points follow the axis rather than the curve means that the state observed behind the shock is only in partial equilibrium, no appreciable vibrational excitation having occurred. This result is rather surprising since the fringes remain parallel and straight to the edge of the field of view, but the conclusion is inescapable that the vibrational relaxation time in $N_2$ must be very long. From the extent of the region behind the shock in which no equilibration is observed, it is possible to place lower limits on the relaxation time: at 900°K, for instance, $\tau$ for $N_2$ must be $>150$ $\mu$sec.

Methane has been investigated in a similar way. A very fast relaxation is visible up to the limit of the present equipment at $M_1=4$. The relaxation time seems to be in rough agreement with values obtained by other methods. More interesting perhaps is the conclusion that the final density in this case is in agreement with the equilibrium values calculated by using Eqs. (5)–(7).

Freon-12 ($CCl_2F_2$) shows no visible relaxation effects in the pictures obtained so far. The known relaxation time is 0.09 $\mu$sec, so such a result is not surprising. Only when the density is very low would the region of adjustment spread out far enough to be recorded with a 0.3-$\mu$sec spark such as is now in use.

Carbon dioxide has several special molecular properties that should be mentioned before turning to the experimental data. Since it is a linear, symmetric molecule, rotation occurs about only two axes and there are four normal vibrational modes, two in bending with the same frequency of 667 cm$^{-1}$ and two in stretching at higher frequencies, 1336 cm$^{-1}$ and 2350 cm$^{-1}$—the so-called valence vibrations. There is an accidental degeneracy between the first harmonic in bending and the first excited state of the unsymmetrical valence vibration which causes both levels to shift slightly. This splitting, explained by Fermi, has only a small effect on the vibrational heat capacity but may be important in understanding the redistribution of energy among vibrational modes.

At room temperature, only the bending modes are appreciably excited. They contribute $0.89R$ to the heat capacity, while valence vibrations add only $0.065R$. The vibrational relaxation time measured by acoustic dispersion at room temperature may then be thought of as being that for the bending modes without implying anything about a simultaneous change in valence vibrations. If different rates exist for each mode, then sufficiently sensitive experiments should detect them at elevated temperatures. In the absence of any clear evidence for separate relaxation times in the past, it has usually been assumed that all vibrational modes adjust together. This assumption is strengthened by the observation that some anharmonicity exists so that mixing might occur fairly rapidly.

The density ratios across shocks in $CO_2$ from $M_1=1$ to 5 have been measured on such pictures as that shown in Fig. 1 and the corresponding Mach number computed from the timing measurement. Results are plotted in Fig. 4 where the density shown corresponds to the uniform region some distance behind the shock. The solid curve gives the theoretical ratio calculated from Eqs. (5)–(7) by using the enthalpy data published by the National Bureau of Standards.[24] For weak

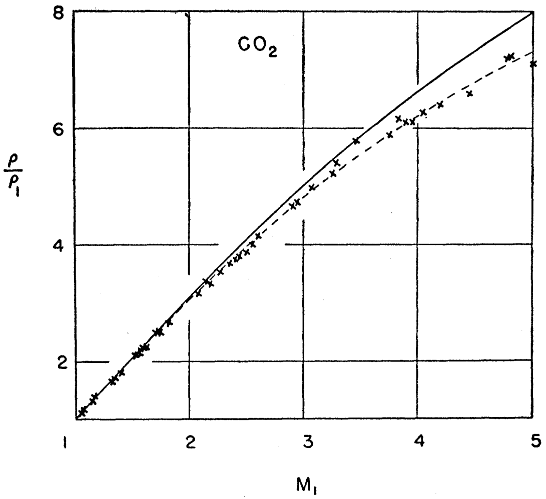

FIG. 4. Comparison of theory and experiment for the density ratio across shocks in carbon dioxide. The solid curve is the final equilibrium value calculated using data on specific heats from the National Bureau of Standards, experimental points are denoted by × 's, and the density corresponding to adjustment of the two bending modes only is shown by the dashed curve.

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[24] National Bureau of Standards Circular C641, 1947 (unpublished).

shocks, close agreement exists between experiment and computed equilibrium values, but above $M_1=2$ an appreciable discrepancy appears, the observed density falling below the anticipated value for complete equilibrium. As a supplementary check, the density for state *a* was measured and was found to fit the calculated values satisfactorily.

A vibrational relaxation time may also be obtained from each picture with the aid of Eqs. (13) and (14). The slope of a line on a graph plotting $\ln(\delta_2-\delta)$ *vs* distance $x$ behind the shock gives the relaxation time in terms of the outflow velocity $v_2$:

$$\tau=\frac{C_p}{C_p'v_2}\frac{dx}{d\ln(\delta_2-\delta)}. \tag{15}$$

Typical graphs are shown in Fig. 5, where it is seen that the lines are remarkably straight, a fact which adds confidence to our choice of assumptions leading to Eq. (13). The relaxation times are plotted in Fig. 6 on logarithmic paper against the reciprocal cube root of temperature. This should give a straight line according to the Bethe-Teller theory discussed earlier. Unfortunately, considerable scatter has arisen in the data, largely through the very strong effect of traces of gas impurities. Water vapor is known to be some five hundred times as effective in exchanging vibrational quanta with $CO_2$ molecules as are other $CO_2$ molecules. Even a very small fractional amount of water vapor therefore produces an effect entirely out of proportion to its concentration. In the large shock tube used for these experiments, there seems to be little hope of achieving the degree of purity needed, something like one part per hundred thousand, in order to get an accurate measure of the $CO_2$ relaxation time. For other gases, however, impurities are not nearly so effective so that good quantitative data can be obtained. Such is the case with $N_2O$, to be discussed shortly, and apparently with $Cl_2$.[25]

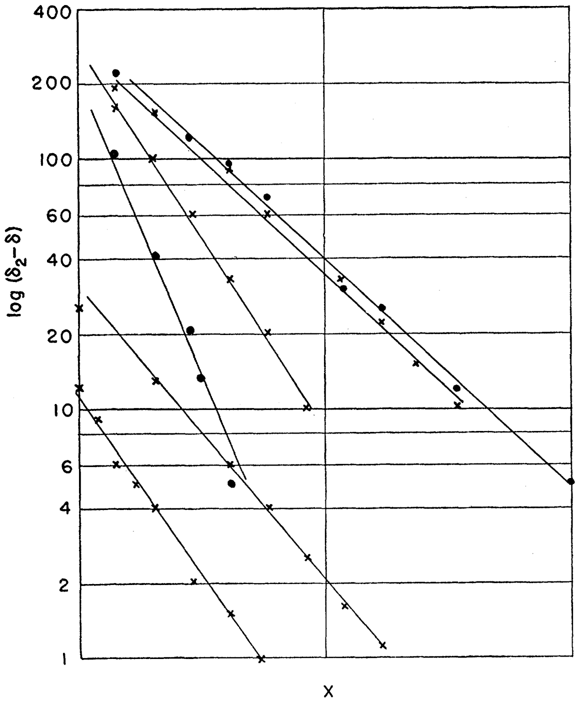

FIG. 5. Logarithm of fringe shift $(\delta_2-\delta)$ as a function of distance $x$ behind the schock. The six curves represent measurements on six different interferograms and have no relation to one another. The accuracy with which the measured points fall along a straight line is a test of the applicability of Eq. (13) for determining the vibrational relaxation time.

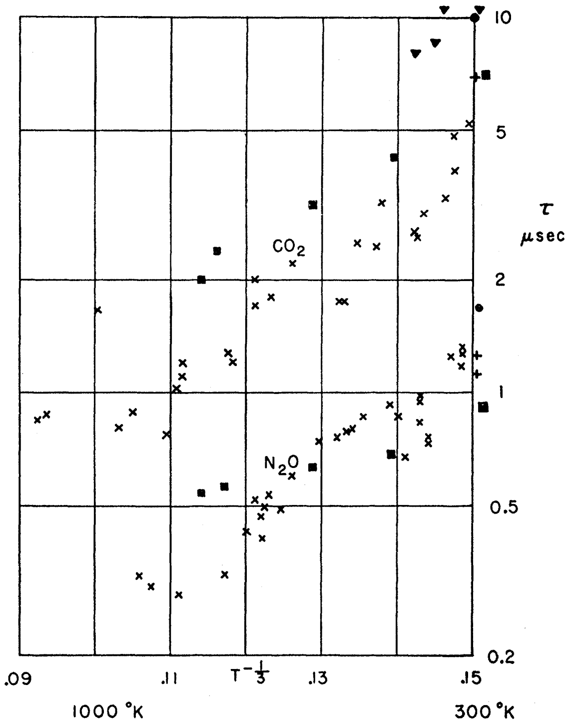

FIG. 6. Temperature dependence of relaxation times for carbon dioxide and nitrous oxide. A linear variation of $\ln\tau$ with $T^{-\frac{1}{3}}$ is suggested by a theory of Landau, Bethe, and Teller. Experimental points are: × shock tube, + pitot tube (reference 13), and sound dispersion; ■ [A. Eucken and E. Numann, Z. Phys. Chemie **B36**, 163 (1938)]; ● [E. F. Fricke, J. Acoust. Soc. Am. **12**, 245 (1940)]; ▼ [A. van Itterbeek and P. Mariens, Physica **7**, 938 (1940)].

Several alternative explanations for the failure of the fringes to reach the expected equilibrium position have been suggested. As a general observation, all processes which remove energy from the gas, such as radiation, heat conduction to the tube walls, and accidental dissociation by especially violent collisions within the shock front, will lead to *higher* final densities than expected. The only proposal which leads to a *lower* density is one in which the adjustment we see is only in the bending modes. A further increase in density to final equilibrium should appear farther back.

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[25] E. F. Smiley and E. H. Winkler, J. Chem. Phys. **22**, 2018 (1954).

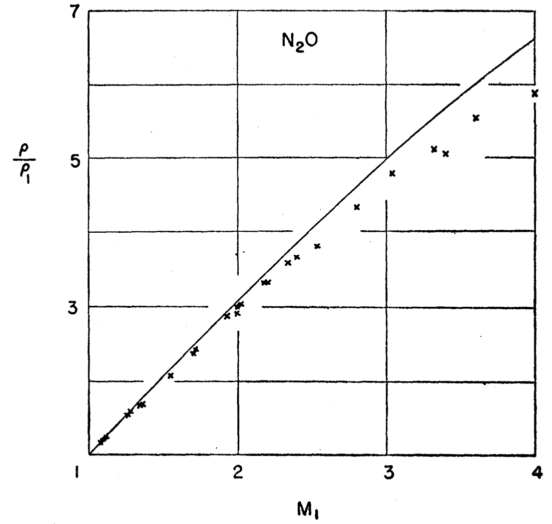

FIG. 7. Experimental and theoretical density ratios in nitrous oxide.

As a quantitative test of this hypothesis, two things may be done: compare the density calculated not counting valence vibrations with the experimental value; and search for an indication of approach to state 2 as far behind the shock as possible. When only the contribution of the bending modes is included in Eq. (5), the dashed curve in Fig. 4 results, a very good fit indeed. Thus far, a search for signs of gradual rise in density from this intermediate state has revealed nothing. From the accuracy of the measurements involved, the relaxation time for valence vibrations must be at least 100 times as long as that for bending.

Since traces of water vapor are known to hasten equilibration of the bending modes, it was suggested that final equilibrium might be reached more rapidly by the same process. When small amounts of water vapor were intentionally added to the $CO_2$, however, the visible region of adjustment did indeed become narrower, but no detectable effect was produced in the final state. Apparently the efficacy of water is very selective in its action as a catalyst.

The possibility of having two or more relaxation times depends upon transitions between vibrational modes being less probable than exchange of energy with translation or rotation during collisions. The theory of such probabilities is in an early stage of development so that little can be said for certain, one way of the other. Schwartz has analyzed the case of $CO_2$ in some detail and has developed equations which describe the nonequilibrium region when two relaxation times of appreciably different size exist.[26]

Nitrous oxide exhibits very much the same behavior as carbon dioxide. The similarity in structure of the two molecules possibly accounts for the fact that a considerable departure from final equilibrium is observed here as well. The data on density[27] are plotted in Fig. 7 and the measured relaxation times are included in Fig. 6 along with some values obtained with a Pitot tube and from sound dispersion. Less difficulty was experienced from impurities in the $N_2O$ than in $CO_2$, and the measured relaxation times may be taken to represent the values for pure gas.

In conclusion, the shock tube and interferometer prove to be an especially effective combination of instruments for research on shock waves because deviations from ideal behavior are most conspicuous in the density. The validity of assumptions used in deriving the Rankine-Hugoniot relation has been verified with shocks in argon and in air below $M_1=2$. In both air and pure nitrogen above this speed, the state behind a shock is found to be one of only partial equilibrium; vibrational levels are apparently excited so slowly by collisions that no hint of approach to equilibrium could be found. Several gases, including methane and freon-12, appear to reach the expected equilibrium density in well under 1 $\mu$sec. Carbon dioxide and nitrous oxide exhibit a relaxation effect which may be explained in terms of known relaxation times but which at shock speeds above $M_1=2$ fails to reach final equilibrium. This phenomenon can best be explained in terms of separate relaxation times for each mode, the valence vibrations requiring at least one hundred times as long to adjust as the bending modes. The well-known effectiveness of water vapor as a catalyst for equilibrium seems to be limited to the bending modes only. Extension of this work to shock strengths where vibrational relaxation in nitrogen and oxygen can be observed is now under way and the results will be reported in a later paper.

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[26] R. N. Schwartz, "Equations Governing Vibrational Relaxation Phenomena in Carbon Dioxide Gas," U. S. Naval Ordnance Laboratory NAVORD Report 3701, 1954.

[27] Enthalpy data for $N_2O$ were obtained from L. S. Kassel, J. Am. Chem. Soc. **56**, 1838 (1934).

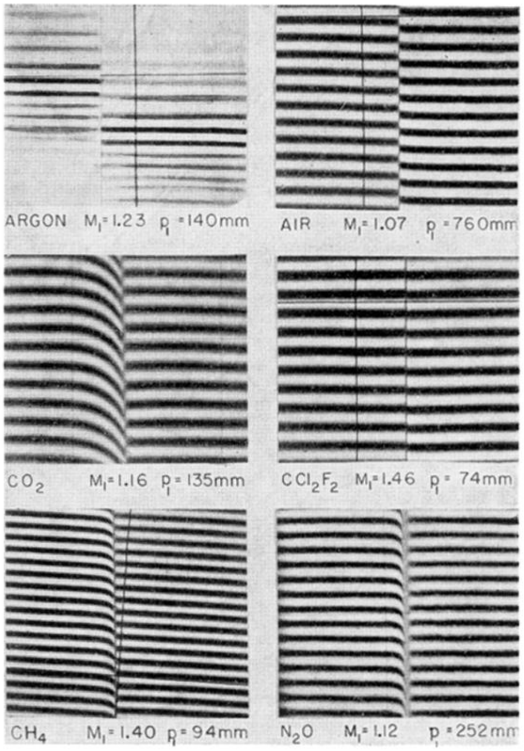

FIG. 1. Interferograms of shock waves in six different gases. In each case the shock is traveling to the right. The first picture shows how the absolute fringe shift may be obtained by using white light.