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Abstract

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ESTIMATION OF THE RELAXATION TIME FOR CARBON DIOXIDE DISSOCIATION FROM SHOCK-TUBE EXPERIMENTS

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From earlier experiments on the reflection of shock waves in CO_2 $^{(1-3)}$, one can judge the time required for equilibrium to be established behind the reflected wave. The measured values of the velocity of the reflected shock wave in the range of Mach numbers M_0 of the incident shock wave from 6 to 11 fit well on a curve calculated under the assumption of complete excitation of the internal degrees of freedom of the molecules and a "frozen" dissociation reaction. The change in the gas parameters behind the discontinuity, caused by the interaction of the reflected wave with the boundary layer, as well as the losses upon reflection, cannot produce such a deviation from the equilibrium calculation, since in other gases (N_2, Ar) these effects led to deviations toward a decrease, and not an increase, of the initial value of the velocity $^{(3)}$. The temperature T_2'' behind the reflected shock wave in CO_2, calculated with allowance for the temperature dependence of the heat capacity but without allowance for dissociation, is, for this group of experiments, of the order of $4—7 \cdot 10^{3\circ}$ (the temperature T_2 with allowance for dissociation for this group of experiments is $3—5 \cdot 10^{3\circ}$ (see Fig. 1). The pressure behind the reflected shock wave varies, depending on M_0, from 15 to 35 atm.

(Figure: Fig. 1)

Fig. 1. Temperature of CO_2 behind the reflected wave in the case of frozen dissociation, but with excited vibrations (T_2''), and the equilibrium temperature (T_2), $p_0 = 0.017$ atm. T_2' is the equilibrium temperature behind the reflected wave in the absence of equilibrium behind the incident wave.

It was noted that on the streak records of this series of experiments the velocity of the reflected shock wave is nonuniform. At the initial moment after reflection the velocity has larger values. They correspond to the velocity with frozen dissociation D_2''. Toward the end of the gas sample behind the incident wave, the velocity of the reflected wave decreases. Its values coincide with the values of the shock-wave velocity calculated for these values of M_0 of the incident wave under the assumption of equilibrium dissociation of carbon dioxide behind the front of the shock wave D_2.

In order to check whether the observed deceleration was a consequence of acceleration of the flow behind the incident wave from the discontinuity to the contact surface, a comparison was made between the calculated value of the gas velocity behind the incident wave and the velocity of the front face of the contact surface, which is readily measured from the streak records. The result of the comparison is shown in Fig. 2, from which it is seen that the velocity of the contact surface systematically exceeds the calculated gas velocity by 100–150 m/sec both at low and at high values of M_0 (up to 10).

As was indicated in (4), from the slope of the streak record of the motion of weak density inhomogeneities observed in schlieren photographs of the gas sample behind the shock wave, one can judge the gas velocity in different portions of the sample.

Figure 3 shows the distribution of gas velocities along the tube behind the incident shock wave in CO_2. On the basis of the data in Fig. 3, it may be assumed that from the discontinuity to the contact surface there is a smooth acceleration of the gas.

However, the acceleration of the gas has no appreciable effect on the velocity of the reflected wave, since experiment shows that this quantity remains constant at low values of M_0, despite the fact that the change in the velocity of the gas through which the wave propagates is already of the order of 50% of its velocity. This fact also agrees with the result of a calculation of the reflection of a discontinuity accompanied by a rarefaction wave (5). We therefore considered it possible to attribute the retardation of the reflected wave to its equilibrium velocity value to the attainment, by the gas behind the reflected wave, of the equilibrium state.

The time during which the velocity of the reflected wave becomes established at a value equal to that calculated under the assumption of equilibrium dissociation can be measured from the sweep records. The values of this time t for different incident-wave velocities are given in Table 1; the conditions under which the corresponding time was determined are also indicated there.

Fig. 2. Velocity of the gas behind the shock wave v_r and velocity of the contact surface v_k in CO_2.

If the assumption is regarded as valid that the overestimated values of the velocity of the reflected shock wave near the end wall are caused by the nonequilibrium composition of the gas immediately behind the front of the reflected wave, then the same mechanism should also operate as the front moves away from the end wall, since the front is moving all the time through new gas. The processes occurring in the tube behind the incident wave at $M_0 < 10$ cannot have an appreciable effect on the velocity of the reflected wave. (T_2' in Fig. 1.) Therefore the retardation of the reflected wave may be attributed to the equalization of the state of the gas behind the reflected wave after the dissociation reaction in the layer at the end wall reaches its equilibrium extent.

Table 1

Time t for establishment of the equilibrium value of the velocity of the reflected shock wave and time τ for establishment of the equilibrium concentration of

CO_2 containing 2% water

	u_0, m/sec					
	2040	2180	2265	2400	2420	2580
M_0	7.67	8.1	8.45	8.9	9.05	9.6
D_2'', m/sec	280	290	290	300	300	320
T_2', °K	2700	2900	3000	3200	3200	3300
T_2'', °K	3800	4300	4600	4900	5000	5500
P_2'', atm	14.0	17.0	19.0	21.0	22.0	26.0
a_2'', m/sec	880	920	960	1010	1020	1080
t, μsec	30	28.2	8.3	12.0	7.6	8.3
τ, μsec	20.5	19.5	5.8	8.4	5.2	5.8
$\tau p_2''$, μsec • atm	285	330	110	175	115	150

Let us estimate the minimum time during which equalization of the gas parameters can occur. Then, from the time for establishment of the equilibrium value of the velocity of the reflected wave, one can find the time for establishment of the equilibri-

equilibrium concentration in the layer of gas at the end wall, which before the other layers had been brought to rest and heated by the reflected wave.

Let, at the end wall, the gas composition reach its equilibrium value after a time τ following reflection of the wave, which propagates relative to the end wall with velocity D_2''. Then the first signal concerning the changed state at the end wall, traveling with velocity a_2'', will reach the front of the reflected wave at some time t, equal to the sum $\tau + t_1$ (t_1 is the time needed for the signal to catch up with the front of the reflected wave). The relation between these times is readily obtained by comparing the expressions for the coordinates of the front at the moment of encounter t:

$$D_2'' t = a_2'' t_1, \qquad t = \tau + t_1.$$

(Figure: Fig. 3. Distribution of gas velocity along the tube behind the incident shock wave in CO_2)

Fig. 3. Distribution of gas velocity along the tube behind the incident shock wave in CO_2

(Figure: Fig. 4. Relaxation times of CO_2 dissociation with water vapor, determined from the change in velocity of the reflected shock wave)

Fig. 4. Relaxation times of CO_2 dissociation with water vapor, determined from the change in velocity of the reflected shock wave

Then the time required for establishment of the equilibrium concentration is expressed in the following way through the time at which the signal reaches the front of the reflected wave:

$$\tau = t\,(1 - D_2''/a_2^{\alpha})\,.$$

The greatest velocity of the signal is apparently equal to the speed of sound under the conditions behind the reflected wave.

The values of t, according to the experimental data given in Table 1, vary from 30 to 7.5 μsec. (it should be noted that, because of the smoothness of the transition, the time was measured with an accuracy of the order of 20%). From these data the values of τ have been calculated, as well as the values of $\tau p_2''$, reduced to atmospheric pressure (Table 1, Fig. 4). If the reaction is completed not at the end wall, but in some middle cross-section of the tube, then the times t and τ must be reduced in proportion to the distance. The estimated times agree with the data available in the literature (^{6}).

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Note: Figure translations are in progress. See original paper for figures.