

TABLE II. Shock wave parameters in nitrogen for the two possible values of the dissociation energy of nitrogen. Initial conditions  $T_0=25^\circ\text{C}$  and  $p_0=58$  cm.

$T^\circ\text{K}$	$DN_2=9.764$ ev				$DN_2=7.385$ ev			
	$p/p_0$	$\rho/\rho_0$	$\alpha$	$U$ (mm/ $\mu\text{sec}$ )	$p/p_0$	$\rho/\rho_0$	$\alpha$	$U$ (mm/ $\mu\text{sec}$ )
3000	65.94	6.554		2.604	66.00	6.559	$1\times 10^{-4}$	2.605
4000	92.77	6.914	$1\times 10^{-4}$	3.081	94.58	7.027	$3.2\times 10^{-3}$	3.107
5000	121.3	7.219	$1.7\times 10^{-3}$	3.514	134.9	7.843	$2.54\times 10^{-2}$	3.685
6000	155.8	7.661	$1.07\times 10^{-2}$	3.969	202.9	9.218	$9.35\times 10^{-2}$	4.476
7000	205.7	8.435	$3.88\times 10^{-2}$	4.533	308.7	10.76	0.2223	5.478
8000	281.3	9.549	$9.80\times 10^{-2}$	5.263	448.4	11.93	0.4011	6.574
9000	389.1	10.79	0.1940	6.152	602.1	12.52	0.5934	7.603
10 000	528.2	11.90	0.3238	7.136	741.9	12.61	0.7542	8.438
11 000	688.2	12.66	0.4735	8.125	851.2	12.40	0.8614	9.046
12 000	849.7	13.02	0.6210	9.019	931.4	12.04	0.9226	9.475
13 000 <sup>a</sup>	991.3	13.03	0.7449	9.742				
13 000 <sup>b</sup>	1009.8	13.12	$\beta=9.6\times 10^{-3}$	9.829				

<sup>a</sup> The thermodynamic fits are valid only to 12 000°K. This calculation was made by assuming the fits to be valid to 13 000°K. The answers are less reliable than those for lower temperatures.

<sup>b</sup> Ionization of nitrogen atoms considered. Degree of dissociation assumed unchanged by small amount of ionization.

zation, the pressure ratio behind the shock was determined from the Hugoniot equation.

$$\frac{1}{2}(p/p_0-1)\left[1+(1+\alpha+\beta)\frac{T p_0}{T_0 p}\right] \\ = \frac{H-H_0}{RT_0} + \beta\left(\frac{H^0-H_0^0}{RT_0} + \frac{W}{RT_0}\right)_{\text{electrons}}, \quad (13)$$

where  $(H-H_0)/RT_0$  is the enthalpy difference for the atoms, ions, and molecules. The results of this calculation are presented in the last line of Table II. Clearly the correction for the small amount of ionization makes only a small change in the equation of state point at the highest temperature. The correction would decrease rapidly at lower temperature. (At 12 000°K only 0.5% of the nitrogen is ionized.)

### EXPERIMENTAL RESULTS

The measured value of shock and material velocity for shock waves in nitrogen are presented in Table III. The corresponding values of pressure and density ratio calculated from Eqs. (1) and (2) are also included.

The experimental results are compared with the theoretical predictions in Fig. 1.

### DISCUSSION

Before drawing the obvious conclusion from Fig. 1 that these results show conclusively the higher value of dissociation energy for nitrogen to be correct, the very important question of relaxation time for dissociation must be considered. The time duration of the experiments reported in this paper is very short. For instance, for a representative shock wave with a final temperature of 9000°K, the transit time of the shock wave across the shortest measuring interval is less than 0.2  $\mu\text{sec}$  and across the longest interval it is only about 2.7  $\mu\text{sec}$ . If thermodynamic equilibrium cannot be established in a time shorter than 0.2  $\mu\text{sec}$ , then these results may be questioned.

Two kinetic mechanisms have been proposed which could lead to dissociation. The first considers dissociation to be the limit of vibrational excitation. If this proposal is correct, the theory of Landau and Teller<sup>5</sup> developed to explain the phenomenon of vibrational relaxation should be applicable. However, there are good reasons to believe this theory to be much too restrictive because the conditions existing behind a strong shock wave are quite different from those found in an ultrasonic wave. In particular, the energy of many of the collisions is very large compared to a vibrational quantum. Since the vibrational degree of freedom can be adequately approximated by a harmonic oscillator only for the lowest levels, imposition of the quantum mechanical restriction that the only allowed transitions are between neighboring states is unrealistic in this case. Furthermore, if the relaxation time is calculated on the basis of this theory, it is found to be so long that equilibrium could not be established in a time comparable to the time scale of these experiments. If dissociation comes about as the limit of a process of vibrational excitation, relaxation time effects should have been evident in this investigation.

TABLE III. Measured shock and material velocity and the corresponding density and pressure ratios, approximately corrected<sup>2</sup> to an initial temperature of 298°K. The maximum error in velocity measurement is  $\sim 0.5\%$ . The initial pressure and temperature at the time of each experiment are also listed.

$U$ (mm/ $\mu\text{sec}$ )	$u$ (mm/ $\mu\text{sec}$ )	$\xi=p/p_0$	$\eta=\rho/\rho_0$	$P_0$ (cm Hg)	$T_0$ (°K)
4.34	3.80	187	$8.0\pm 0.2$	60.81	305
5.02	4.46	254	$9.0\pm 0.1$	59.69	293
5.55	4.97	313	$9.6\pm 0.4$	60.91	292
5.96	5.39	364	$10.5\pm 0.3$	59.41	293
6.10	5.51	381	$10.3\pm 0.4$	60.94	297
7.18	6.55	533	$11.4\pm 0.6$	60.91	297
7.57	6.97	598	$12.6\pm 0.6$	61.09	283
9.61	8.90	968	$13.5\pm 0.5$	60.91	288
9.71	8.98	987	$13.3\pm 0.8$	60.66	298
9.74	8.99	991	$13.0\pm 0.3$	60.94	300

<sup>5</sup> L. Landau and E. Teller, Physik. Z. Sowjetunion 10, 34 (1936).



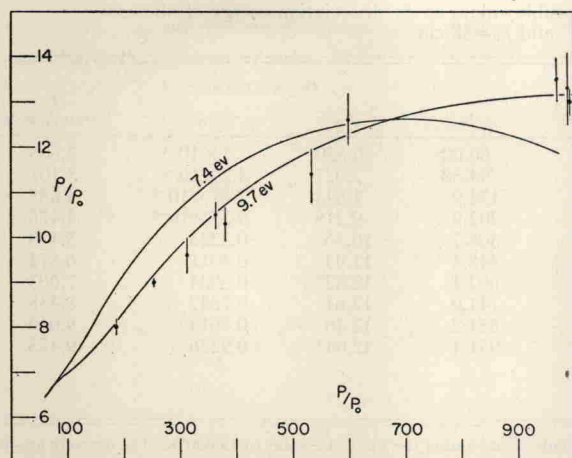


FIG. 1. This figure plots the experimental data along with the calculated Hugoniot. The initial conditions are  $T_0 = 298^\circ\text{K}$ ,  $P_0 = 58$  cm Hg. The maximum error in  $\xi$  is  $\pm 1\%$ . The error in  $\eta$  is given for each experimental point.

An alternative and more realistic mechanism is one in which some large fraction of all molecular collisions with sufficient energy are assumed to cause dissociation. The number of collisions per unit volume and time with energy greater than  $E_0$  is<sup>6</sup>

$$\omega = 2n^2\sigma^2 \left( \frac{\pi kT}{m} \right)^{\frac{1}{2}} (X_0^2 + 1) \exp(-X_0^2), \quad (14)$$

where  $X_0^2 = (E_0/kT)$ ,  $n$  is the number of molecules per unit volume,  $\sigma$  is the molecular radius, and  $m$  is the molecular mass. An order of magnitude estimate of the time required to produce the degree of dissociation  $\alpha$  calculated for a given final temperature is:  $t = (\alpha n / \omega)$ . This estimate assumes every collision with sufficient energy produces dissociation and it also neglects recombination. This latter assumption is reasonable because the three body collisions which can lead to recombination will be relatively rare until the equilibrium situation is approached. On the other hand the above expression also neglects the contribution to the dissociation rate from dissociations caused by multiple collisions.

Calculations using this relation based on a final shock wave temperature of  $9000^\circ\text{K}$  indicate that dissociative equilibrium should be attained in  $1.4 \times 10^{-7}$  second if the reaction proceeds isothermally at the equilibrium temperature and in  $4.7 \times 10^{-10}$  second if at the temperature of  $18000^\circ\text{K}$  found behind the shock before dissociation occurs. Since the temperature behind the shock changes from  $18000^\circ\text{K}$  to  $9000^\circ\text{K}$  as the reaction proceeds, a time intermediate between  $1.4 \times 10^{-7}$  second and  $4.7 \times 10^{-10}$  second should be required to

produce dissociative equilibrium. Such a time would be short compared to the time scale of the experiments and no relaxation effects should have been observed.

The velocity of the metal plate used as a piston in these experiments is determined by its thickness and the amount and type of explosive used. It is not influenced appreciably by the atmosphere in front of it; and in particular it is not influenced by changes in shock pressure caused by the relaxation process. Therefore, the particle velocity behind the shock will be constant. As the relaxation process proceeds, temperature, density and pressure behind the shock change, and the change will be manifested by a change of shock velocity. As an example, for our representative  $9000^\circ\text{K}$  shock wave the initial shock velocity should be  $6.69$  mm/ $\mu\text{sec}$ . As equilibrium is approached the velocity will drop to its final value of  $6.15$  mm/ $\mu\text{sec}$ . This represents a change of almost  $9\%$  in shock velocity—a change which would have been easily observed if it had occurred. In no instance was any variation in shock velocity observed. Therefore, the relaxation time must have been small compared to the time scale of the experiment.

A weak argument can be made that all results at pressure ratios of less than  $675$  may be questionable since they could represent nonequilibrium final states. The idea is that the density ratio immediately behind the shock is slightly less than  $6$  (the value for shock waves of infinite strength in a gas with  $\gamma = 1.40$ ). As the relaxation process proceeds, the density ratio increases at almost constant pressure. However, the rate of increase decreases as equilibrium is approached. Therefore, the results which indicate final density ratios in agreement with predictions based on  $DN_2$  of  $9.764$  eV are not conclusive since the equilibrium state could still correspond to values consistent with the  $DN_2 = 7.385$  eV curve. The observation of constant shock velocity is simply dismissed by saying that the reaction rate for the last part of the relaxation process is so slow that the velocity change is too small to be observed over the time interval in which the measurements are made.

This rather dubious argument fails completely to explain the results at pressure ratios in excess of  $675$ . In fact these results are excellent evidence that the relaxation time is very short. This conclusion is based on the fact that the degree of dissociation is a monotone function along the Hugoniot curve. Therefore, all partial reaction Hugoniot curves corresponding to fixed degrees of dissociation must lie below the equilibrium Hugoniot; and it is impossible for a density ratio corresponding to incomplete reaction to exceed the equilibrium ratio. In other words the density change behind a shock wave caused by a relaxation process is monotone in time. Thus a final density ratio greater than that predicted by the  $7.385$  eV curve is very good evidence that the dissociation energy is greater than  $7.385$  eV.

<sup>6</sup> S. Chapman and T. G. Cowling, *The Mathematical Theory on Nonuniform Gases* (Cambridge University Press, London, 1952), p. 92.