

Equation of State of Gases by Shock Wave Measurements. II. The Dissociation Energy of Nitrogen*

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(Received February 11, 1955)

The results of equation of state measurements made behind strong shock waves in nitrogen are consistent only with the higher of the two spectroscopically acceptable values of the dissociation energy of nitrogen, 9.764 ev.

RECENT experimental results¹ indicate very strongly that the correct value of the dissociation energy for nitrogen is 9.764 ev and not 7.385 ev as was formerly assumed. In particular, the work of Hendrie practically proves the higher value to be the correct one. The first evidence not of spectroscopic origin that indicated that the higher of the two possible values of the dissociation energy was correct was provided by Kistiakowsky, Knight, and Malin¹ in an investigation of the detonation velocity of cyanogen-oxygen mixtures. This work was criticized, however, because the conclusions drawn rested on the assumptions of the correctness of Chapman-Jouguet theory of the detonation process and the existence of thermodynamic equilibrium in a very complicated system of reacting gases. The present work was undertaken in an effort to circumvent these objections and to provide additional, independent evidence bearing on the question of the dissociation energy of nitrogen.

The experimental procedure whereby the pressure and density of a strongly shocked gas can be determined by measurements of shock and material velocity in the gas is described in detail in the first paper of this series.² Only a brief review of the method will be presented here.

The laws of conservation of mass and momentum applied to the flow through a shock wave lead to the following results:

$$\eta = \rho/\rho_0 = \frac{U}{U-u} \quad (1)$$

$$\xi = \frac{p}{p_0} = 1 + \frac{1}{RT_0} uU \quad (2)$$

where ρ_0 and ρ are the initial and final values of density, p_0 and p are the initial and final values of pressure, T_0

* Work done under the auspices of the U. S. Atomic Energy Commission.

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¹ Kistiakowsky, Knight, and Malin, *J. Am. Chem. Soc.* **73**, 2972 (1951); *J. Chem. Phys.* **20**, 876 (1952); Thomas, Gaydon, and Brewer, *J. Chem. Phys.* **20**, 369 (1952); A. E. Douglas, *Can. J. Phys.* **30**, 302 (1952); J. M. Hendrie, *J. Chem. Phys.* **22**, 1503 (1954).

² R. H. Christian and F. L. Yarger, *J. Chem. Phys.* **23**, 2042 (1955), preceding paper.

is the initial temperature, R is the gas constant per gram, U is the shock velocity measured relative to the medium ahead of the shock, and u is the mass velocity change across the shock. It is clear that for a gas with given initial conditions, the simultaneous measurement of shock and material velocity is sufficient to determine the values of pressure and density attained behind the shock wave.

The experimental procedure consists of driving a metal plate at constant velocity by means of high explosive into a chamber of the gas under investigation. Shock velocity is determined by measuring the transit time of the shock over many known intervals. Material velocity is similarly determined by measuring the transit time of the metal plate over the same intervals.

SHOCK WAVE CALCULATIONS

In order to deduce information concerning the correct value of the dissociation energy of nitrogen from equation of state measurements, it was necessary to make calculations of the properties of shock waves in nitrogen over an extended range of shock strength for the two disputed values of the dissociation energy.

These calculations were made by a straightforward solution of the Hugoniot or conservation of energy equation written in the form

$$H - H_0 = \frac{1}{2}(p - p_0)(v_0 + v), \quad (3)$$

where p_0 and p , H_0 and H , and v_0 and v refer to initial and final values of the pressure, enthalpy, and volume, respectively. The fraction of the nitrogen originally present dissociated at a particular temperature and pressure is given by

$$\alpha = \left[\frac{K_p^2}{K_p^2 + 4p} \right]^{\frac{1}{2}}, \quad (4)$$

where K_p is the equilibrium constant for the reaction $\frac{1}{2}N_2 \rightleftharpoons N$. The enthalpy of the mixture of atoms and molecules resulting from the partial dissociation of one mole of N_2 is

$$H = (1 - \alpha)(H^0 - H_0^0)_{N_2, T} + 2\alpha(H^0 - H_0^0)_{N, T} + 2\alpha H_{0N}^0 \quad (5)$$

where $H^0 - H_0^0$ is the enthalpy per mole of the component relative to an absolute zero reference state and

TABLE I. Fit coefficients for thermodynamic functions for N₂ and N between 3000 and 12 000°K.

	<i>a</i>	<i>b</i>	<i>c</i>	<i>d</i>	<i>k</i>
N ₂	2.51443	2.58314×10 ⁻⁴	-2.84107×10 ⁻⁸	1.24154×10 ⁻¹²	2.74113
N	1.70375	-1.41798×10 ⁻⁴	2.84705×10 ⁻⁸	-1.17894×10 ⁻¹²	3.06136

H_0^0 is the heat of formation per mole of the component at absolute zero, zero for nitrogen molecules and $\frac{1}{2}$ the dissociation energy for nitrogen atoms. The ideal gas equation of state is used to relate pressure, volume, and temperature.

$$pv = (1 + \alpha)RT. \quad (6)$$

The calculational procedure was to assume a final temperature and iterate the Hugoniot equation until a value of pressure was found which satisfied all of the above equations. Shock velocity and material velocity behind the shock measured relative to a medium at rest were then calculated from the well-known relations.

$$U = v_0 \left(\frac{p - p_0}{v_0 - v} \right)^{\frac{1}{2}} \quad \text{and} \quad u = U \left(1 - \frac{v}{v_0} \right). \quad (7)$$

These calculations were performed on an IBM card programmed calculator.

The thermodynamic functions for N₂ used were calculated by Fickett and Cowan,³ those for N were calculated by one of the authors (R.E.D.) using the standard statistical mechanical procedure as outlined in Mayer and Mayer.⁴ The four excited levels designated ²D⁰ and ²P⁰ were considered in this calculation. The values of $(E^0 - E_0^0)/RT$ in the temperature range from 3000° to 12 000°K were fit by least-squares procedures to an expression of the form

$$(E^0 - E_0^0)/RT = a + bT + cT^2 + dT^3. \quad (8)$$

The entropy was obtained by integrating the second law of thermodynamics using the above expression to determine dE .

$$S^0/R = k + (a+1) \ln T + 2bT + \frac{3}{2}cT^2 + 4/3dT^3, \quad (9)$$

where k is an integration constant chosen to give the best agreement with the statistical mechanical calculations. The equilibrium constant for the dissociation of nitrogen was calculated from the fundamental relation

$$RT \ln K_p = -\Delta F^0 \quad (10)$$

where F^0 , the free energy, can be determined from the energy and entropy expressions given above.

$$(F - F_0^0)/RT = (a+1)(1 - \ln T) - bT - \frac{1}{2}cT^2 - \frac{1}{3}dT^3 - k. \quad (11)$$

The values of the least-square constants used in these

³ W. Fickett and R. D. Cowan, Los Alamos Scientific Laboratory Report, LA 1727.

⁴ J. E. Mayer and M. G. Mayer, *Statistical Mechanics* (John Wiley & Sons, Inc., New York, 1940), p. 440.

calculations are presented in Table I. The average deviation between the calculated value of energy and the value given by the least square cubic fit of the data is about 0.1%.

The results of the shock wave calculations are presented in Table II. Initial conditions are $T_0 = 25^\circ\text{C}$ and $p_0 = 58$ cm Hg (58 cm is used because this is approximately local atmospheric pressure). Since the thermodynamic fits are correct to 0.1%, the shock parameters are probably reliable to about the same degree. However, the partition function for diatomic molecules becomes slightly uncertain at high temperatures because the anharmonicity correction becomes large and also because there is uncertainty as to how to estimate the contribution from highly excited electronic levels. Any errors in the thermodynamic functions themselves arising from present limitations of the fundamental theory will of course cause corresponding errors in the shock wave parameters.

At 12 000°K the anharmonicity correction for N₂ contributes roughly 3% of the calculated value of the internal energy. The contribution from electronic excitation is about twice as large but the accuracy of the correction is certainly greater than for the anharmonicity. Therefore, if one can assume that these contributions are accurate to at least 25% the thermodynamic functions for nitrogen are good to about 1%. The shock wave parameters should be at least as accurate.

The calculations outlined above are correct at temperatures sufficiently low that no ionization occurs. However, at the highest temperatures assumed, a small amount of ionization should be expected. The effect of this ionization on the calculated equation of state point was estimated by using the Saha equation in the following form:

$$2 \log \beta = 5/2 \log T - \frac{W}{2.303RT} - 5.830 - \log p_N, \quad (12)$$

where β is the fraction of the nitrogen atoms ionized and W is the ionization potential of nitrogen, and p_N is the pressure of nitrogen atoms. The statistical weight of the ground state of the atom was taken as 4 and that for the ion as 9. At 13 000°K $\beta = 9.6 \times 10^{-3}$; thus slightly less than one percent of the nitrogen atoms are ionized. The ionization of nitrogen molecules was neglected because the ionization potential is higher and because the molecules constitute only 15% of the gas present at this temperature.

Under the assumption that the degree of dissociation would not be changed by this small amount of ioni-

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			U (mm/ μsec)	$DN_2 = 7.385$ ev			U (mm/ μsec)
	p/p_0	ρ/ρ_0	α		p/p_0	ρ/ρ_0	α	
3000	65.94	6.554		2.604	66.00	6.559	1×10^{-4}	2.605
4000	92.77	6.914	1×10^{-4}	3.081	94.58	7.027	3.2×10^{-3}	3.107
5000	121.3	7.219	1.7×10^{-3}	3.514	134.9	7.843	2.54×10^{-2}	3.685
6000	155.8	7.661	1.07×10^{-2}	3.969	202.9	9.218	9.35×10^{-2}	4.476
7000	205.7	8.435	3.88×10^{-2}	4.533	308.7	10.76	0.2223	5.478
8000	281.3	9.549	9.80×10^{-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 ^a	991.3	13.03	0.7449	9.742				
13 000 ^b	1009.8	13.12	$\beta = 9.6 \times 10^{-3}$	9.829				

^a 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.

^b 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 μsec and across the longest interval it is only about 2.7 μsec . If thermodynamic equilibrium cannot be established in a time shorter than 0.2 μsec , 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 Teller⁵ 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 corrected² 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/ μsec)	u (mm/ μsec)	$\xi = p/p_0$	$\eta = \rho/\rho_0$	P_0 (cm Hg)	T_0 (°K)
4.34	3.80	187	8.0 ± 0.2	60.81	305
5.02	4.46	254	9.0 ± 0.1	59.69	293
5.55	4.97	313	9.6 ± 0.4	60.91	292
5.96	5.39	364	10.5 ± 0.3	59.41	293
6.10	5.51	381	10.3 ± 0.4	60.94	297
7.18	6.55	533	11.4 ± 0.6	60.91	297
7.57	6.97	598	12.6 ± 0.6	61.09	283
9.61	8.90	968	13.5 ± 0.5	60.91	288
9.71	8.98	987	13.3 ± 0.8	60.66	298
9.74	8.99	991	13.0 ± 0.3	60.94	300

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

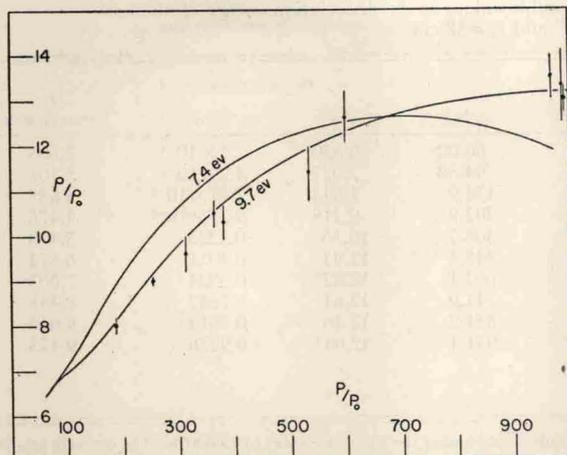


FIG. 1. This figure plots the experimental data along with the calculated Hugoniot. The initial conditions are $T_0 = 298^\circ\text{K}$, $P_0 = 58$ cm Hg. The maximum error in ξ is $\pm 1\%$. The error in η is given for each experimental point.

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 is⁶

$$\omega = 2n^2\sigma^2 \left(\frac{\pi kT}{m} \right)^{\frac{3}{2}} (X_0^2 + 1) \exp(-X_0^2), \quad (14)$$

where $X_0^2 = (E_0/kT)$, n is the number of molecules per unit volume, σ 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 α 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°K indicate that dissociative equilibrium should be attained in 1.4×10^{-7} second if the reaction proceeds isothermally at the equilibrium temperature and in 4.7×10^{-10} second if at the temperature of 18000°K found behind the shock before dissociation occurs. Since the temperature behind the shock changes from 18000°K to 9000°K as the reaction proceeds, a time intermediate between 1.4×10^{-7} second and 4.7×10^{-10} second should be required to

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

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°K shock wave the initial shock velocity should be 6.69 mm/ μsec . As equilibrium is approached the velocity will drop to its final value of 6.15 mm/ μsec . 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 D_{N_2} of 9.764 eV are not conclusive since the equilibrium state could still correspond to values consistent with the $D_{N_2} = 7.385$ 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.

CONCLUSIONS

The results of equation of state measurements behind strong shock waves in nitrogen show conclusively that the dissociation energy of nitrogen is the higher of the two spectroscopically acceptable values. Furthermore the kinetic mechanism leading to dissociation is probably not the step-by-step excitation of the vibrational degree of freedom. This investigation provides another

illustration of how shock waves can be used to investigate physical chemical problems at very high temperatures.

ACKNOWLEDGMENTS

The authors are happy to acknowledge the encouragement and assistance of Professor G. B. Kistiakowsky and R. G. Shreffler in various phases of this work.