

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

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

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

where K_p is the equilibrium constant for the reaction $\frac{1}{2}\text{N}_2 \rightleftharpoons \text{N}$. The enthalpy of the mixture of atoms and molecules resulting from the partial dissociation of one mole of N_2 is

$$H = (1-\alpha)(H^0 - H_0^0)_{\text{N}_2, T} + 2\alpha(H^0 - H_0^0)_{\text{N}, T} + 2\alpha H_{0\text{N}}^0 \quad (5)$$

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

* 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.

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

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-

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.