Shock-Tube Study of Nitrogen Dissociation Rates Using Pressure Measurements

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The thermal dissociation rate of undiluted nitrogen has been studied behind strong shock waves using time-resolved pressure measurements on a shock-tube end wall. Improved rate coefficients for N_2 dissociation by impact with N_2 and N were inferred for temperatures from 5700–12,000°K, and the results are

$$k_{d,N_2} = 3.9 \times 10^{33} T^{-4.5} \exp(-1.13 \times 10^5/T)$$

and

$$k_{d,N} = 2.2 \times 10^{26} T^{-2.5} \exp(-1.13 \times 10^5/T)$$

(cm^{-3}-mole^{-1}-sec^{-1}). The magnitudes of these rate coefficients are in reasonable agreement with most previous work, but their temperature dependences are stronger than previously reported.

Introduction

THE collisional dissociation rate of nitrogen, the primary constituent of the Earth's atmosphere, is still not well known. Several shock-tube studies of nitrogen dissociation have been made,[1–4] yielding rate data over a temperature range from 6000–15,000°K, but in the regions of temperature overlap the rates inferred in the various studies differ by as much as a factor of 6. By virtue of employing a new diagnostic technique and making use of a wider range of shock conditions, the present work provides improved values for the rate coefficients.

A fast-response pressure gage, mounted on the end wall of a conventional shock tube, was used to obtain pressure-time histories following reflection of strong shock waves in undiluted nitrogen. Using a rather simple theory,[5,6] one can show that such pressure histories are directly equivalent to records of the spatial variation in density throughout the incident-shock relaxation zone. On the assumption that the dominant mechanism for dissociation was the bimolecular process

$$N_2 + M \underset{k_r}{\overset{k_d}{\rightleftarrows}} 2N + M \qquad (1)$$

where the collision partner M may be either N_2 or N, theoretical incident-shock density profiles and end-wall pressure histories were computed using assumed values for the reaction-rate coefficients $k_{d,N}$ and k_{d,N_2}. A comparison of a large number of measured and predicted pressure histories, for incident-shock speeds from 4 to 7 km/sec, enabled selection of rate coefficients which apply over the temperature range from about 5700–12,000°K.

Previous shock-tube studies of nitrogen dissociation using an interferometer to measure the density profile in the incident-shock relaxation zone have been conducted by Byron[1] and Cary.[2] The bulk of their data was obtained with nitrogen diluted in an inert gas, however, and data obtained with undiluted nitrogen were limited to a narrow range of incident-shock speeds. Consequently, the uncertainty in the rate coefficients inferred for dissociation of N_2 by impact with N_2 or N is rather large, and the accuracy with which the temperature dependence of the rate coefficients could be extracted from the data suffered accordingly.

Allen et al.[3] inferred the dissociation rate in undiluted nitrogen from measurements of the emission from the $N_2(1+)$ band system during the approach to final equilibrium behind incident shocks. Their data were restricted to a narrow range of temperature, and only a single data point for the rate coefficient $k_{d,N}$ was presented (at 6400°K). Their results were inadequate to define the temperature dependence of the rate coefficients.

In a more recent study, Appleton et al.[4] utilized vacuum-ultraviolet absorption at 1176 Å to monitor the disappearance of molecular nitrogen behind reflected shock waves. The nitrogen was highly diluted in argon so that only the rate coefficient for argon as a collision partner can be considered accurately determined. The temperature range covered in Appleton's investigation, 8000–15,000°K, is greater than that studied in any other work, and the scatter of his data seems quite small, so the temperature dependence of his rate coefficient for argon as the collision partner should be the most reliable of published results. The magnitudes of all three rate coefficients ($M = N_2$, N and Ar) presented by Appleton et al. fall substantially below those presented by others, and the reason for this difference is not yet clear.

Theoretical Considerations

The theoretical model used to compute end-wall pressure histories for given shock conditions and assumed dissociation-rate coefficients has been discussed previously.[5,6] The model takes advantage of the fact that the characteristic relaxation time behind a reflected shock wave is generally much shorter than the characteristic relaxation time behind the preceding incident shock wave (for the same chemical reaction). This is, of course, primarily a result of the increase in temperature and density across the reflected shock wave. If observations are made on a time scale comparable with the incident-shock relaxation time, then, for practical purposes, the gas in the reflected region may be considered to be in local chemical equilibrium. In such cases, the reflected shock acts primarily to stagnate the incoming gas,

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and the pressure immediately downstream of the reflected shock is readily computed in terms of the density immediately upstream. This value of pressure is then communicated to the end wall at the local speed of sound. If one assumes a reasonable trajectory for the reflected shock wave (in the present case, a constant-speed trajectory was used based on the final, equilibrium reflected-shock speed), it is then a simple matter to map a known or computed incident-shock density profile into an end-wall pressure history. Pressure histories calculated with this technique are in excellent agreement with those computed using the (more lengthy) method of characteristics.[5-7]

The techniques for computing incident-shock relaxation profiles in an inviscid, chemically relaxing gas are well known and need not be discussed here. A reaction-rate expression must be supplied, of course, and the expression used here describing the reaction in Eq. (1) was simply

$$(\rho/W)(D\alpha/Dt) = k_{d,\mathrm{N}_2}\{[\mathrm{N}_2]^2 - [\mathrm{N}]^2[\mathrm{N}_2]/K\} + k_{d,\mathrm{N}}\{[\mathrm{N}_2][\mathrm{N}] - [\mathrm{N}]^3/K\} \quad (2)$$

where ρ is the mass density, W is the molecular weight of N_2, α is the mass fraction of the N-atom species, K is the usual equilibrium constant, and the square brackets are used to denote species concentrations. This form of the rate equation includes the common assumption that the ratio of the dissociation and recombination rates is equal to the equilibrium constant evaluated at the local translational temperature.

Other chemical reactions known to occur in the relaxation zone (for example, ionization reactions of N_2 and N and reactions involving excited electronic states of N_2) are omitted here on the grounds that they have a negligible thermal effect and do not significantly influence the rate at which the dissociation relaxation proceeds.[8,9] The present model also neglects vibration-dissociation coupling and assumes that the vibrational temperature is equal to the translational temperature throughout the incident-shock relaxation zone. Of course, the same mapping technique could be used to compute end-wall pressure histories from incident-shock density profiles obtained with a coupling model, or with additional reactions, but it was believed to be premature to use a sophisticated kinetics model in analyzing experimental results at this stage of development. Furthermore, most previous studies of N_2 dissociation have neglected these complications and it was felt that a more instructive comparison could be made with previous work if a similar kinetics model was employed.

Experimental Procedure

The experiments were performed in two shock tubes, a 3-in.-diam stainless-steel tube, 35 ft long (driven section), at Ames Research Center, and a 2-in.-sq aluminum tube, 25 ft long, at Stanford University (Aerophysics Laboratory). Both shock tubes were operated in the combustion-driven mode using a stoichiometric mixture of hydrogen and oxygen diluted with helium. Incident-shock speeds were varied from about 4–7 km/sec and were measured with a series of piezoelectric pressure sensors spaced along the last few feet of each driven tube upstream of the end wall. The uncertainty in the incident-shock speed at the end wall was generally less than 1%; the attenuation of the incident shocks varied up to 2%/ft. Because of the brevity of the observation times (and hence the short distance of incident-shock travel involved), shock-attenuation effects were neglected in the data analysis.

Initial pressures ranged from 0.5–5 torr in the Ames facility and from 2–5 torr in the Stanford shock tube. Measurements were made with a McLeod gage or a bellows-type pressure gage calibrated against the McLeod gage. The uncertainty in measured initial pressure was estimated to be 1%.

The test gas used in both facilities was taken directly from a commercial cylinder of high-purity nitrogen (minimum purity 99.996%). At Stanford, the shock tube was evacuated to an ultimate pressure of about 10^{-5} torr, and the apparent leak rate owing to outgassing and vacuum leaks after pumping for a minimum of 1 hr between runs was less than 0.5×10^{-3} torr/min. The elapsed time between isolating the vacuum system and firing the tube was a few minutes so the maximum partial pressure of contaminants from this source should have been less than 2×10^{-3} torr. At Ames, the tube was evacuated to an ultimate pressure level of about 0.2×10^{-3} torr before filling, but the apparent leak rate was less than 0.05×10^{-3} torr/min (owing primarily to a much longer pumping period between experiments), so that the final contamination level should have corresponded to a partial pressure of less than 1×10^{-3} torr.

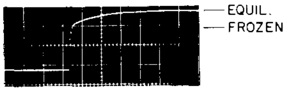
The capacitive-type pressure gage employed on the end wall as the primary diagnostic tool has been described elsewhere.[5,10,11] In brief, it was a larger (3-in. diam) modified version of the gage developed earlier by Baganoff;[12] the useful recording time of the gage was 10 μsec in the Stanford shock tube and 13 μsec in the Ames facility.

Results

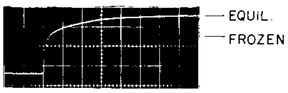
Typical pressure records are shown in Fig. 1. Time increases from left to right on the oscillograms and the sharp rise in pressure (poorly shown here because of insufficient film exposure) corresponds to the arrival of the shock wave at the end wall. For the present conditions, we expect nearly an instantaneous change in pressure (to the frozen value) upon shock arrival, but finite gage response time smears this out. The more gradual variation in pressure which follows is due to the influence of relaxation behind the incident shock wave. The small oscillations barely visible in the early stages of the transient signal are caused by wave reflections within the gage.

The records each indicate a final asymptotic value for the pressure which can be checked (using an appropriate gage calibration constant) against the theoretical equilibrium pressure level based on the initial pressure and incident-shock speed. These pressure levels generally agreed to within a few percent, thus providing confidence in the theoretical model and the experimental procedure. The few experimental records obtained with final pressures differing from theory by more than about 5% were not used in the data analysis. The fact that the pressure typically remained sensibly constant beyond the onset of equilibrium provides evidence that nonideal shock-tube effects were not significantly disturbing chemical relaxation in the center of the shock-tube flow where the measurements were made. It must be noted, however, that some decay of pressure level was recorded, after the onset of equilibrium, for the strongest shocks at low pressures. This effect was probably associated with the increase in shock-wave attenuation (to about 2%/ft) also observed at these conditions. (The fact that a pressure decay was observed, rather than an increase, suggests that imperfect burning of the driver gas and not side-wall boundary-layer effects was chiefly responsible for the shock attenuation.)

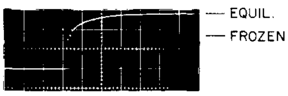
The records exhibited in Fig. 1 illustrate the strong dependence of the over-all relaxation time on the incident-shock speed for a fixed initial pressure. Also note that the proportion of the pressure signal owing to relaxation effects (i.e., that fraction of the total



a) V = 4.6 km/sec; 2 μsec/div



b) V = 5.1 km/sec; 1 μsec/div



c) V = 5.5 km/sec; 1 μsec/div

Fig. 1 Pressure-gage data for N_2 at 2.1 torr.

pressure change which occurs between the calculated frozen and measured equilibrium values marked in Fig. 1) increases slightly with the strength of the wave, in agreement with theory.

The first step in the data-reduction process consisted of replotting experimental records in the dimensionless form P/P_{final}. This form is more suitable for comparison with theoretical calculations and tends to reduce the influence of small errors in calibration. Next, a small, approximate instrument correction factor was applied to the pressure readings within the first microsecond after reflection. This factor was taken to be the ratio of the ideal response and the response actually recorded, at a given instant after shock reflection, when a step in pressure was applied to the gage (using a low Mach number shock and high-initial pressures so that nonequilibrium effects were negligible). Distortion of the data owing to imperfect instrument response was thus minimized.

The next step in the analysis consisted of a systematic comparison of measured and predicted pressure histories. The dissociation rates used in the theoretical computations were of the form

$$k_{d,N_2} = AT^{-C}\exp(-\theta/T) \tag{3}$$

and

$$k_{d,N} = BT^{-D}\exp(-\theta/T) \tag{4}$$

where θ is the characteristic temperature corresponding to the dissociation energy for N_2 (1.131×10^5 °K). Thus four adjustable rate parameters were available to fit the experimental data. For purposes of emphasizing the relative influence of the molecular and atomic rate contributions, it is convenient to rewrite Eq. (2) in the form

$$(\rho/W)(D\alpha/Dt) = k_{d,N_2}[N_2][1+2\alpha R/(1-\alpha)]([N_2]-[N]^2/K) \tag{5}$$

where R, the so-called relative collision efficiency, is given by

$$R = k_{d,N}/k_{d,N_2} = k_{r,N}/k_{r,N_2} \tag{6}$$

The total reaction rate is thus seen to be determined by the molecular rate coefficient when $2\alpha R/(1-\alpha) \ll 1$ (and not simply when $\alpha \ll 1$) and by the atomic rate coefficient when $2\alpha R/(1-\alpha) \gg 1$. We suspected from previous work that $2 \lesssim R \lesssim 10$, so that molecular rate parameters (A and C) were obviously best inferred from weak-shock records or from the initial stages of the relaxation histories of strong shocks. The atomic rate parameters (B and D) were best ascertained from records of strong shocks causing significant dissociation. The suitability of rate parameters obtained in this manner was further tested by comparing measured and predicted pressure histories at shock conditions where all four rate parameters were important.

The values for the rate coefficients finally selected (on the basis of data from 24 shock-tube runs) after several iterations on all four parameters were

$$k_{d,N} = 2.2 \times 10^{26} T^{-2.5} \exp(-\theta/T)(\text{cm}^3\text{-mole}^{-1}\text{-sec}^{-1}) \tag{7}$$

and

$$k_{d,N_2} = 3.9 \times 10^{33} T^{-4.5} \exp(-\theta/T) \quad (\text{cm}^3\text{-mole}^{-1}\text{-sec}^{-1}) \tag{8}$$

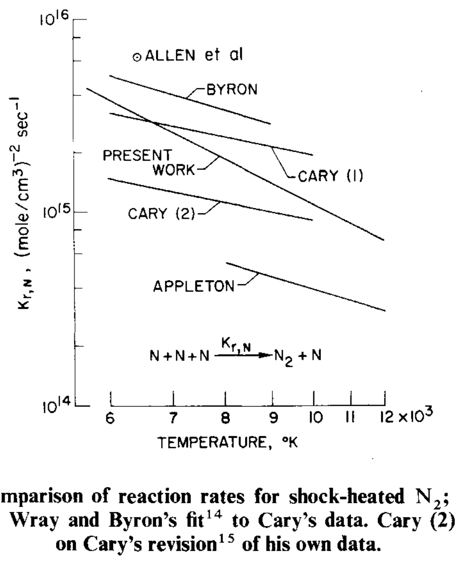


Fig. 2 Comparison of reaction rates for shock-heated N_2; Cary (1) is based on Wray and Byron's fit[14] to Cary's data. Cary (2) is based on Cary's revision[15] of his own data.

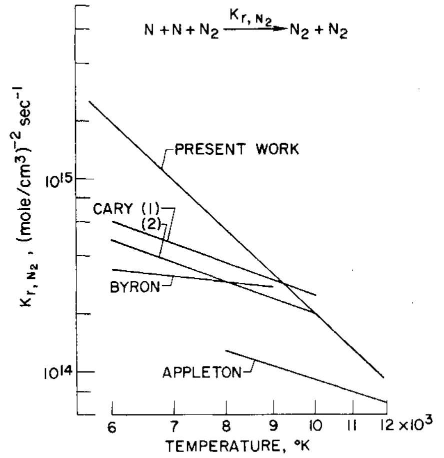


Fig. 3 Comparison of reaction rates for shock-heated N_2.

These coefficients were found to apply equally well to the data obtained in both shock-tube facilities. The range of temperature over which these coefficients were measured was about 5700–12,000°K. The lower limit was determined by the equilibrium temperature levels behind the weakest shocks studied. The upper limit was fixed by the temperatures which occurred near the fronts of the strongest shocks and within the resolution time of the instrument. That is, a comparison between measured and predicted pressures was only possible after a gage response time of about 0.1 μsec, and the incident-shock temperature corresponding to the pressure observed at that instant was the maximum temperature for which a rate measurement could be claimed for a given shock-tube run.

It is worth noting that the temperature exponents suggested for these rate coefficients are larger than those generally allowed in classical collision theory (e.g., Vincenti and Kruger[13]), and that extrapolation of these rate coefficients provides poor agreement with room-temperature recombination-rate data. The present results thus suggest that a more realistic kinetics model is needed, and that the present rate coefficients can only be considered as empirical fits which provide effective rate constants over the temperature range investigated.

For purposes of comparison with previous work, it is convenient to put these rate coefficients in recombination-rate form. Over the temperature range of interest, $K \simeq 20\exp(-\theta/T)$ moles/cm^3‡, so the rate coefficients in Eqs. (7) and (8) are equivalent to

$$k_{r,N} = 1.1 \times 10^{25} T^{-2.5} \quad (\text{cm}^6\text{-mole}^{-2}\text{-sec}^{-1}) \tag{9}$$

and

$$k_{r,N_2} = 2.0 \times 10^{32} T^{-4.5} \quad (\text{cm}^6\text{-mole}^{-2}\text{-sec}^{-1}) \tag{10}$$

These rate coefficients are compared with previously published results in Figs. 2 and 3.

Recombination rates for an atomic third body are plotted in Fig. 2. Note that two curves are used to represent Cary's results. His initial data evaluation[2] was criticized by Wray and Byron, and they suggested an improved fit to his data, labeled here Cary (1).[14] Subsequently, Cary reanalyzed his data and suggested the rate coefficient labeled Cary (2).[15] Also shown are the results of Byron[1] and Appleton et al.[4] and the single data point of Allen et al.[3] (at 6400°K).

Allen, Byron and Cary's rate coefficients were probably only

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‡ From a simplified statistical mechanics model; accurate to within about 10% in the temperature range of present interest.

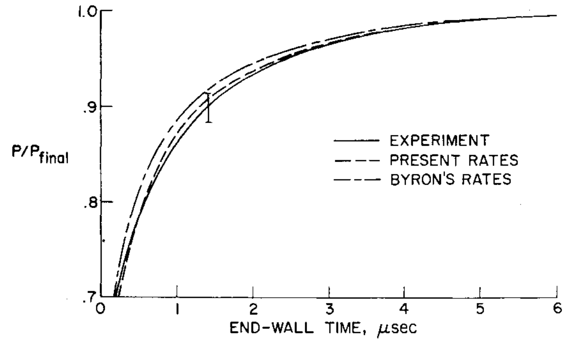

Fig. 4 Comparison of predicted and observed pressure histories in N_2; $V = 5.4$ km/sec, $P_1 = 2.1$ torr, $T_1 = 298°K$.

determined within a factor of about 2, so the present rate coefficient is in reasonable agreement with this previous work. The best agreement is found with the results presented by Byron and Cary, as one would hope since the measurement techniques were sensitive to the same macroscopic feature of the incident-shock flowfield (density). The scatter in Appleton's data was small ($\pm 37\%$) but his rate-coefficient curve falls significantly below all other plotted results, perhaps as an obscure result of his measurement scheme or the assumptions in his data analysis relating the parameter measured to the rate coefficients. However, the difference between Appleton's results and the present work decreases at high temperatures; e.g., at 12,000°K the present coefficient is only 2.3 times that of Appleton. Perhaps the most striking feature exhibited in Fig. 2 is the strength of the temperature dependence found in the present work.

The method of data reduction employed here and by Byron and Cary consisted of visual comparisons between measured relaxation profiles and profiles calculated using hypothesized rate coefficients [of the form shown in Eqs. (3) and (4)]. A strong element of individual interpretation is to be expected in their work since it was necessary to infer six rate parameters (two additional parameters because of the diluent) from a rather narrow range of shock conditions. The discrepancy between the rate coefficients labeled Cary (1) and Cary (2) is some measure of the subjectivity and uncertainty involved in that work. The present study can claim reduced subjectivity and uncertainty because: a) experiments were conducted over a much wider range of shock conditions (possible because of the instrument sensitivity and temporal resolution); and b) fewer rate parameters were available for adjustment in fitting the experimental data. The pressure-gage technique has one further advantage which should be noted. The location of the gage sensor on the tube axis permits sampling of gas which has been processed entirely within the core of the flow, thus minimizing effects associated with shock-wave curvature and side-wall boundary layers. (The observation times are short enough that shock-wave bifurcation is not a problem since there is insufficient time during the observations for a disturbance to travel from the side of the tube to the sensor.)

Figure 3 presents a similar comparison of recombination rates with a molecular third body. The present work is seen to agree with that of Byron and Cary at the high-temperature end of the experiments, but at low temperatures the present rate coefficient is larger than previously reported. Appleton's rate curve again falls below all other plotted results, with the difference between the present work and Appleton's curve decreasing rapidly at high temperatures. The temperature dependence of our rate coefficient is again larger than that of the other plotted results, but this finding is not entirely unexpected. Similar temperature dependences have been observed in tests of other undiluted gases (e.g., p. 154 of Stupochenko et al.[16]).

From the curves plotted in Figs. 2 and 3 one can see that the relative collision efficiency R found in the present work decreases from 8 at 12,000°K to 2 at 6000°K, which indicates that molecular N_2 is increasingly effective, relative to atomic N, in promoting dissociation at lower temperatures. Cary's results are comparable, in that R diminishes with decreasing temperature, although the variations with temperature are smaller. On the other hand, Appleton's results indicate a value of R which is independent of temperature ($R \simeq 4$), and Byron's results suggest that R increases from about 10 at 9000°K to 15 at 6000°K. We feel that the present results are more accurate and that differences with other work are due primarily to the difficulties inherent in inferring proper rate parameters for pure gases from dilute gas systems. In fact, both Byron[1] and Cary[2,15] noted that they were unable to fit Cary's pure gas runs satisfactorily with the best rate coefficients extracted from mixture cases.

It is difficult to make a precise estimate of the error involved in our rate coefficients, but a systematic study of the influence of varying each adjustable rate parameter suggests that C and D in Eqs. (3) and (4) have been chosen with ± 1 of their best possible values (for fitting the present data) and that the over-all magnitudes of the individual rate coefficients have been selected to better than a factor of 2. These estimated error limits apply at the extremes of the temperature range investigated, where the uncertainties are largest. At intermediate temperatures, the uncertainties in rate-coefficient magnitude are roughly half as large.

In order to illustrate the difficulties of sorting out a correct set of rate parameters, it is convenient to compare some actual measured pressure histories with those computed using the present rate coefficients and, for example, those of Byron. Figure 4 presents such a comparison for a moderate-strength shock wave. The temperature, during the portion of the incident-shock relaxation zone corresponding to the useful pressure-gage recording period, varied from about 9500°K near the incident-shock front to about 6200°K at equilibrium; $\alpha_{eq} = 0.2$. This is a case where both atomic and molecular rate coefficients are important in the profile calculations, and Byron's larger atomic rate and smaller molecular rate (smaller for most of the profile) combine to yield a fit which is nearly as good as that produced by the present rate coefficients. The results in Fig. 4 thus emphasize that a single shock profile can be fit with many combinations of rate-coefficient parameters, and that only by working with profiles for a wide range of shock conditions can one determine the proper individual rate coefficients. The error bar ($\pm 1\frac{1}{2}\%$) on the experimental curve represents the estimated maximum uncertainty due principally to the potential errors in shock-speed measurement and oscillogram reading.

Figure 5 presents similar comparisons for a low-speed shock. In this case, the useful temperature variation was from about 7700–5900°K, $\alpha_{eq} = 0.09$, and the pressure history depended strongly on the molecular rate coefficient. A larger rate coefficient than Byron's was necessary to fit this experimental record (and others like it). Experiments with high-speed shocks causing significant production of atoms early in the relaxation zone were equally effective in isolating the atomic rate coefficient, and the coefficient required to fit the present data was smaller in magnitude than Byron's. A typical example is shown in Fig. 6.

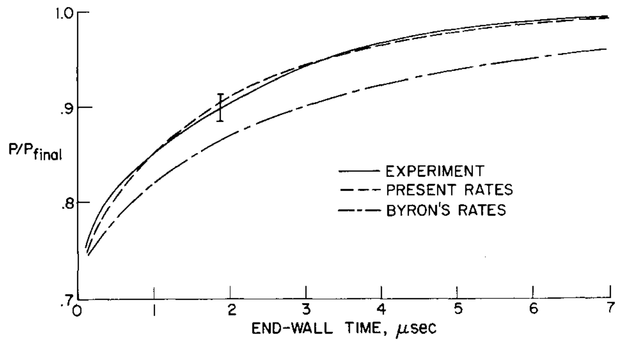

Fig. 5 Comparison of predicted and observed pressure histories in N_2; $V = 4.5$ km/sec, $P_1 = 5.1$ torr, $T_1 = 298°K$.

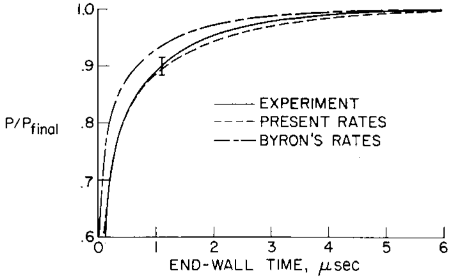

Fig. 6 Comparison of predicted and observed pressure histories in N_2; $V = 7.1$ km/sec, $P_1 = 0.53$ torr, $T_1 = 298$°K.

In this case, the temperature varied from about 12,000°K (the highest temperature reached in this study), at the point where useful pressure data were first available, to about 6650°K at equilibrium, and $\alpha_{eq} = 0.47$. We conclude from such comparisons that the use of a wider range of experimental data has permitted selection of more accurate individual rate coefficients than previously reported.

Conclusions

The thermal dissociation rate of undiluted nitrogen has been studied in a shock tube over a temperature range from 5700–12,000°K. Improved rate coefficients for the dissociation of N_2 by impact with N_2 and N were inferred from comparisons of measured and predicted end-wall pressure histories. The results are in reasonable agreement with most previous work based on the same kinetics scheme, although the temperature dependences of the coefficients found here are stronger than previously reported.

The ratio of the dissociation rates with N and N_2 as collision partners was found to decrease from 8 at 12,000°K to 2 at 6000°K, thus indicating an increasing collision efficiency for molecular N_2, relative to atomic N, in promoting dissociation at lower temperatures.

Discrepancies between the rate-coefficient magnitudes and temperature dependences inferred in the present work and those found in previous studies can be partly attributed to experimental inaccuracies and partly to inherent differences between results inferred (with the present kinetics model) from observations of different quantities and different gas systems. The multiplicity of rate-coefficient parameters of course adds to the uncertainty with which each parameter can be specified. Clearly, experiments of increased accuracy are still needed to reduce uncertainties, and a more realistic kinetics scheme is needed to properly correlate rate coefficients measured with different gas mixtures and experimental techniques.

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