N Atom Measurements in High-Temperature N_2 Dissociation Kinetics

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The dissociation of N_2 has been measured behind reflected shock waves in a temperature range of $3390 \leq T \leq 6435$ K. By use of the atomic resonance absorption spectroscopy (ARAS), the formation of N atoms could directly be observed in the postshock reaction zone. The experiments have been performed in mixtures of N_2 and Ar at pressures between 0.9 and 2.1 bar. The rate coefficient of the reaction, $N_2 + Ar \rightarrow N + N + Ar$ [$k_{N_2,Ar} = 1.71 \cdot 10^4 T^{-3.33} \exp(-113{,}220K/T) \mathrm{cm}^3/\mathrm{s} \pm 20\%$] could directly be determined from the measured N atom concentrations.

Introduction

THE N_2 molecule is known to be very stable up to very high temperatures. Nevertheless, the dissociation of N_2 can be of considerable interest in plasma reaction kinetics or in hypersonic wind tunnels. Because of the very high activation energy of the N_2 dissociation, experimental data are available only at temperatures higher than 6000 K.

Essentially, there are four experimental results of the N_2 dissociation that were evaluated by Baulch et al.[1] These investigations were performed in shock tubes using different detection techniques. Cary[2] and Byron[3] observed the reaction in N_2/Ar mixtures, recording the density profiles by interferometry. Hanson and Boganoff[4] measured pressure profiles in the reaction zone of pure N_2. A spectroscopic method was used by Appleton et al.[5] in mixtures of N_2 and Ar. They monitored the rate of N_2 dissociation more directly by the vacuum ultraviolet absorption of N_2 at 117.6 nm. Their expression of the rate coefficient was recommended by Baulch et al.[1] for use in the 6000-15,000 K temperature range. The proposed rate coefficients of Byron,[3] Cary,[2] and Hanson and Boganoff[4] were found to be higher than the recommended value of Baulch et al.[1]

It is the aim of the present study to determine the rate coefficient of the N_2 dissociation in N_2/Ar mixtures by measuring the N atoms as reaction products, mainly in the temperature region below the 6000 K limit.

Experimental

The experiments were conducted behind reflected shock waves in a stainless steel shock tube of 79 mm i.d. The tube is constructed as an ultrahigh vacuum apparatus and can be heated and evacuated down to pressures of about 10^{-8} mbar. Typical rates of leaks plus outgassing were 8.10^{-7} mbar/min. A detailed description of the equipment is given in Ref. 6. The test gases used in the experiments were supplied by Messer Griesheim, FRG. They were certificated to be of the purities $N_2 \geq 99.9995\%$ and $Ar \geq 99.9999\%$.

The atomic resonance absorption spectroscopy (ARAS) is the measurement technique applied in this investigation of the NI triplet at 119.9 nm. It is a very sensitive line-emission-line absorption method for measuring N atom concentrations in the range of 5.10^{11}-3.10^{13} atoms/cm^3. The spectral shape of the emitter line is not known in detail. It is supposed to be influenced by self-reversal. Hence, calibration measurements were necessary to obtain the required relation between the measured resonance absorption and the corresponding N atom concentrations. The calibration measurements were conducted in a temperature range of $4300 \leq T \leq 8200$ K and at pressures similar to those used in the present experiments. Although there was some scattering in the calibration data, a temperature or pressure dependence of the calibration curve could not be observed. The optical arrangement, the operating conditions of the resonance lamp, and the calibration procedure were described previously.[7]

The mean temperature behind the reflected shock wave was computed from the incident shock speed using one-dimensional gasdynamic equations. The optical windows were located 15 mm from the end plate of the shock tube. Under these conditions, cooling of the reaction volume by heat transfer in the temperature boundary layer can assumed to be small.

It is known that shock/boundary-layer effects can cause changes in the steadiness conditions behind the reflected shock. This was ignored in the data evaluation. The rate coefficient was determined from the N atom increase measured at short dissociation times. Therefore, any changes in the postshock conditions are assumed to have negligible effect on the results reported here.

Results

The dissociation of N_2 was studied in the temperature range $3390 \leq T \leq 6435$ K at pressures of 0.9-2.1 bar. In 34 shock tube experiments, the relative initial concentrations of N_2 were between 87 ppm and 100%. In each experiment, the measured incident shock speed served to calculate the temperature and pressure behind the reflected shock. The N atom resonance absorption signals were monitored from the reacting gas mixture. A representative absorption profile is shown in Fig. 1. Using the calibration curve given in Ref. 7, each absorption signal can be easily transformed to a N atom concentration profile. One example is shown in Fig. 2. In all cases, the N atom increase is nearly linear during the total experimental time. Only in some experiments, mainly at temperatures below 4000 K, an induction period of about 40-100 μs was observed after the arrival of the shock. This must be caused by the vibrational relaxation or reaction incubation processes. Acceptable agreement with predicted values based on the measurements of Millikan and White[8] and Appleton[9] was found.

A first rough reduction of the measured N atom concentration data was made by dividing the slope of the N atom

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increase d[N]/dt by the product 2[N_2][M]. As the maximum measurable value is about 3.10^{13} N atoms/cm^3, the N atom concentrations in the experiments were very low with respect to the initial concentrations of N_2. Therefore, the N_2 concentration can always assumed to be nearly constant over the experimental period of time. Consequently, $[M] = [\mathrm{Ar}] + [\mathrm{N_2}]$ is the quasitotal concentration of the reacting mixture. In Table 1, the experimental conditions and the reduced data of the experiments are summarized.

Discussion

The first step in data interpretation is made by considering a reaction with unspecified collision partner,

$$\mathrm{N_2} + M \xrightarrow{k_{\mathrm{N_2},M}} \mathrm{N} + \mathrm{N} + M \tag{1}$$

and evaluating the quantity

$$k_{\mathrm{N_2},M} = \frac{\mathrm{d[N]/d}t}{2[\mathrm{N_2}]\,[M]} \tag{2}$$

as a function of the reciprocal temperature. Equation (2) represents the rate coefficient of the N_2 dissociation if Ar and N_2 are assumed to have the same collision efficiency. The results are given in Table 1. If the values of $k_{\mathrm{N_2},M}$ were plotted in a Arrhenius diagram, a slight non-Arrhenius behavior could be found. For experiments with relative concentrations of $\mathrm{N_2} \leq 5\%$, the data points scatter around a straight line, whereas for $\mathrm{N_2} > 5\%$ (i.e., at the low temperature end of the Arrhenius plot), the experimental points appear to be systematically deviated from the straight line. This behavior can be explained by the more effective collision partner N_2.

A more detailed kinetic interpretation of the dissociation experiments was done by considering the reactions

$$\mathrm{N_2} + \mathrm{Ar} \xrightarrow{k_{\mathrm{N_2,Ar}}} \mathrm{N} + \mathrm{N} + \mathrm{Ar} \tag{3}$$

$$\mathrm{N_2} + \mathrm{N_2} \xrightarrow{k_{\mathrm{N_2,N_2}}} \mathrm{N} + \mathrm{N} + \mathrm{N_2} \tag{4}$$

The rate coefficient of Eq. (3) can therefore be described as

$$k_{\mathrm{N_2,Ar}} = \frac{\mathrm{d[N]/d}t}{2[\mathrm{N_2}]\,([\mathrm{Ar}] + \eta[\mathrm{N_2}])} \tag{5}$$

Table 1 **Experimental conditions and rate coefficients**

T, K	p, bar	N_2, %	N_2, cm^{-3}	Ar, cm^{-3}	$\frac{\mathrm{d[N]/d}t}{2[\mathrm{N_2}][M]}$, cm$^3\cdot$s^{-1}	$k_{\mathrm{N_2,Ar}}$, cm$^3\cdot$s^{-1}
3392	1.51	100	3.24×10^{18}	—	2.45×10^{-22}	—
3478	2.10		4.38×10^{18}	—	5.99×10^{-22}	—
3548	1.37		2.76×10^{18}	—	1.10×10^{-21}	—
3530	1.97	75	3.03×10^{18}	1.01×10^{18}	7.35×10^{-22}	3.46×10^{-22}
3421	2.26	50	2.39×10^{18}	2.39×10^{18}	3.00×10^{-22}	1.71×10^{-22}
3673	1.07		1.05×10^{18}	1.05×10^{18}	1.42×10^{-21}	8.11×10^{-22}
3675	2.12		2.09×10^{18}	2.09×10^{18}	1.66×10^{-21}	9.48×10^{-22}
3861	1.72		1.60×10^{18}	1.60×10^{18}	5.30×10^{-21}	3.03×10^{-21}
3953	1.99		1.81×10^{18}	1.81×10^{18}	7.60×10^{-21}	4.34×10^{-21}
3730	1.24	25	6.03×10^{17}	1.81×10^{18}	2.85×10^{-21}	2.07×10^{-21}
3805	1.13		5.38×10^{17}	1.61×10^{18}	4.40×10^{-21}	3.21×10^{-21}
4073	1.08		4.80×10^{17}	1.44×10^{18}	1.63×10^{-20}	1.18×10^{-20}
4142	1.07	5	9.37×10^{16}	1.78×10^{18}	1.67×10^{-20}	1.48×10^{-20}
4178	1.23		1.07×10^{17}	2.02×10^{18}	2.20×10^{-20}	1.93×10^{-20}
4240	1.20	2	4.12×10^{16}	2.02×10^{18}	5.26×10^{-20}	5.00×10^{-20}
4384	1.38		4.56×10^{16}	2.23×10^{18}	8.11×10^{-20}	7.72×10^{-20}
4510	1.17		3.75×10^{16}	1.84×10^{18}	1.48×10^{-19}	1.41×10^{-19}
4171	1.03	1	1.78×10^{16}	1.76×10^{18}	2.99×10^{-20}	2.93×10^{-20}
4238	1.17		1.99×10^{16}	1.97×10^{18}	4.34×10^{-20}	4.23×10^{-20}
4346	1.23		2.05×10^{16}	2.03×10^{18}	7.57×10^{-20}	7.38×10^{-20}
4526	1.16		1.85×10^{16}	1.83×10^{18}	2.04×10^{-19}	1.99×10^{-19}
4703	1.08		1.66×10^{16}	1.64×10^{18}	3.60×10^{-19}	3.51×10^{-19}
4894	1.04		1.54×10^{16}	1.53×10^{18}	6.37×10^{-19}	6.21×10^{-19}
4557	1.03	0.5	8.18×10^{15}	1.63×10^{18}	1.99×10^{-19}	1.96×10^{-19}
4806	0.95		7.17×10^{15}	1.43×10^{18}	6.10×10^{-19}	6.02×10^{-19}
5412	0.93		6.23×10^{15}	1.24×10^{18}	6.05×10^{-18}	5.96×10^{-18}
5243	1.06	0.25	3.65×10^{15}	1.46×10^{18}	2.33×10^{-18}	2.31×10^{-18}
5496	0.95		3.13×10^{15}	1.25×10^{18}	6.82×10^{-18}	6.77×10^{-18}
5385	0.91	0.20	2.44×10^{15}	1.22×10^{18}	4.33×10^{-18}	4.31×10^{-18}
5600	1.87	0.01	2.42×10^{14}	2.42×10^{18}	1.31×10^{-17}	1.31×10^{-17}
5835	1.91		2.37×10^{14}	2.37×10^{18}	2.05×10^{-17}	2.05×10^{-17}
6063	1.77		2.12×10^{14}	2.12×10^{18}	3.67×10^{-17}	3.67×10^{-17}
6434	1.70		1.92×10^{14}	1.92×10^{18}	9.04×10^{-17}	9.04×10^{-17}
5843	1.69	0.0087	1.83×10^{14}	2.10×10^{18}	1.87×10^{-17}	1.87×10^{-17}

where η is the dissociation efficiency of N_2 relative to Ar,

$$\eta = k_{N_2,N_2}/k_{N_2,Ar} \tag{6}$$

Normally, the efficiency η can assumed to be independent of temperature. With the assumption of $\eta = 2.5$, the rate coefficient $k_{N_2,Ar}$ was determined as given in the last column of Table 1.

It has been common practice to express dissociation rates in the form

$$k = A \cdot T^n \cdot \exp(-D/T) \tag{7}$$

with D as the dissociation temperature. A least squares fit of the $k_{N_2,Ar}$ data, presented in Table 1, leads to the expression

$$k_{N_2,Ar} = 1.71 \cdot 10^4 T^{-3.33} \exp(-113{,}200 K/T)\ \mathrm{cm^3/s} \pm 20\% \tag{8}$$

where $3390 \leq T \leq 6435$ K.

The given uncertainty is the percentage standard deviation. The absolute value of the temperature exponent seems to be too high from the theoretical point of view. It results from the used approximation method used to fit the data points.

A comparison between Eq. (8) and the rate coefficients obtained by several other investigators[2,3,5] is shown in Fig. 3. It is obvious that an extrapolation of our expression up to more elevated temperatures crosses the rate coefficient proposed by Appleton et al.[5]

For the temperature range of this experimental study, the presented value of $k_{N_2,Ar}$ [Eq. (8)] is in good agreement with estimates obtained from Troe's weak collision unimolecular reaction rate theory,[10] although it is known that this theory is normally valid only for molecules with more than one vibrational degree of freedom. According to this theory, the dissociation rate coefficient for the low-pressure region can be expressed as

$$k_{N_2,Ar} = k^{sc}_{N_2,Ar} \cdot \beta_c \tag{9}$$

where $k^{sc}_{N_2,Ar}$ denotes the strong collision rate coefficient and β_c the weak collision factor. The strong collision rate coefficient depends on several molecular quantities and can be calculated according to Ref. 10. The weak collision factor includes all of the uncertainties in the theory and experiments and will, in general, be fitted to the experimentally determined reaction coefficient. In the present case, the strong collision rate coefficient $k^{sc}_{N_2,Ar}$ was computed based on the equations given by Troe.[10] The weak collision factor β_c can be determined using Eq. (9). Results are given in Table 2. The values of β_c show the expected temperature behavior and the absolute quantity seems to be in agreement with the unimolecular reaction theory of Troe.[10]

Table 2 Measured and calculated rate coefficients for unimolecular low-pressure dissociation of N_2

T, K	$k_{N_2,Ar}$, cm^3/s	$k^{sc}_{N_2,Ar}$, cm^3/s	β_c
3330	5.49×10^{-23}	9.32×10^{-22}	5.89×10^{-2}
4000	8.86×10^{-21}	2.75×10^{-19}	3.22×10^{-2}
5000	1.21×10^{-18}	7.60×10^{-17}	1.59×10^{-2}
7000	2.54×10^{-16}	4.51×10^{-14}	5.64×10^{-3}

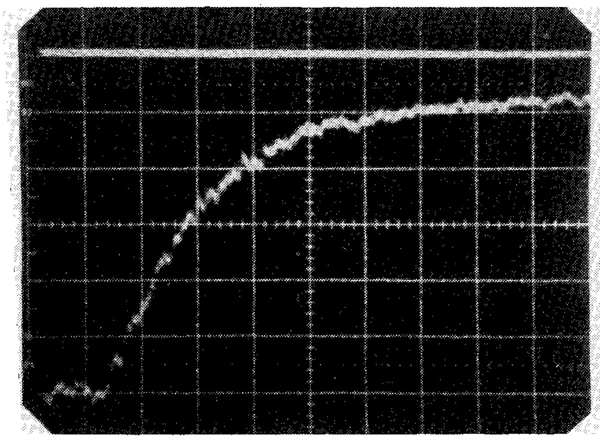

Fig. 1 Measured N atom absorption signal: $[N_2]_0 = 1.54 \times 10^{16}$ cm^{-3}, $[Ar] = 1.53 \times 10^{18}$ cm^{-3}, $T = 4894$ K, $p = 1.04$ bar, 100 μs/div.

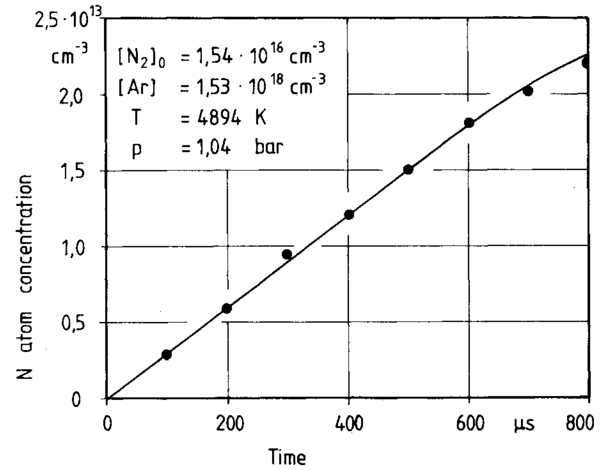

Fig. 2 Example of a measured N atom concentration profile in a shock heated N_2/Ar mixture.

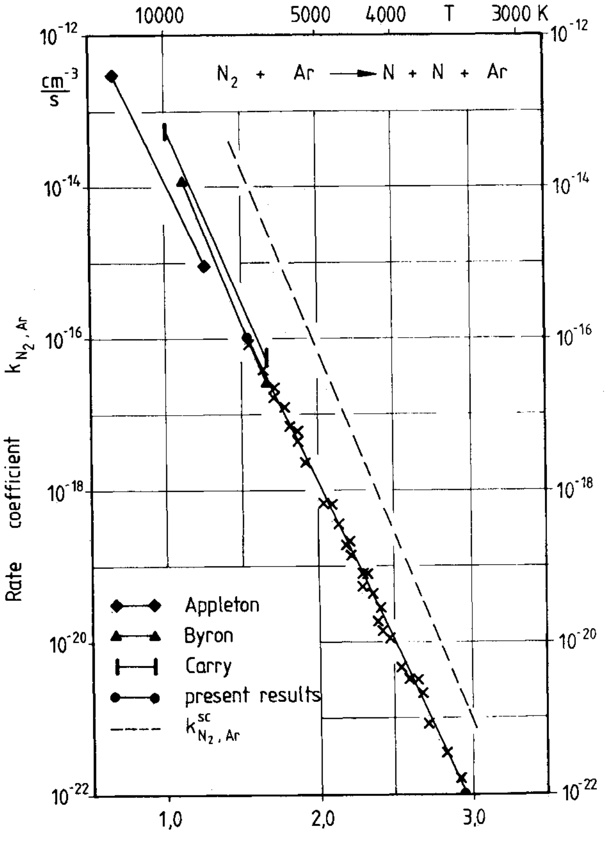

Fig. 3 Comparison of rate coefficients for $N_2 + Ar \rightarrow N + N + Ar$.

Conclusion

Resonance absorption measurements of N atoms was shown to be a sensitive method to study N_2 dissociation kinetics in the temperature range $3390 \leq T \leq 6435$ K behind reflected shock waves. It seems to be the first time in N_2 dissociation that the reaction product could be directly observed. The rate coefficient for N_2 dissociation with Ar as a collision partner was determined with acceptable uncertainties when the collision efficiency of the species N_2 relative to Ar is assumed to be $\eta = 2.5$. Comparison of the experimental data with the theoretical data obtained using the weak collision unimolecular rate theory of Troe[10] leads to reasonable weak collision factors β_c.

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