

## CHEMICAL KINETICS OF HIGH TEMPERATURE AIR

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### ABSTRACT

When a hypersonic object enters Earth's atmosphere, a shock wave is formed in front of it, and the air passing through this shock wave is heated to high temperatures. The shock heated molecules equilibrate their translational and rotational degrees of freedom within a distance of a few mean free paths. To achieve equilibrium, it is necessary to excite vibration, dissociate molecules, produce new molecules and produce ions and electrons. The problem is complex, since all these phenomena occur simultaneously and because the reaction rates depend on the temperature, density and composition which are changing during the relaxation toward equilibrium.

The experimental techniques used to investigate these reactions are briefly discussed along with the resulting rate expressions obtained by the various investigators. A compilation of the rate expressions for these reactions representing the author's evaluation of all the available data is presented. Several pertinent problems which are not yet completely understood and which still require theoretical and experimental investigation are outlined. Computed concentration, temperature and density time histories are shown for three different shock speeds in air. The time rate of change of concentration for each chemical reaction is also shown and regimes of importance for the various processes are discussed.

### INTRODUCTION

Much progress has been made over the past ten years in  
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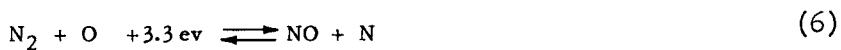
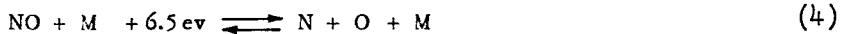
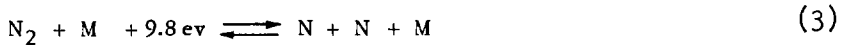
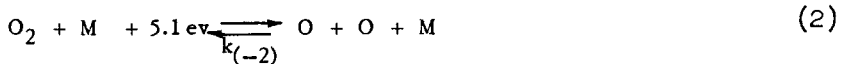
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HYPERSONIC FLOW RESEARCH

understanding the chemistry of high temperature air, due to the efforts of many researchers. Although the author does attempt to include in this paper a fairly comprehensive review of the literature of pertinent chemical rates, he realizes that his effort is not exhaustive. However, it is felt that the rate constants presented in Table 4 represent a reasonable evaluation of the available data.

For the purpose of the present paper, air will be considered as a simple oxygen-nitrogen mixture. In general, in the temperature range to be considered (3000 to 8000 K), triatomic species such as O<sub>3</sub>, NO<sub>2</sub> and other polyatomic oxides of nitrogen play no role. Furthermore, reactions leading to the production of electronically excited species will not be considered here.

With these limitations, the significant reactions occurring in high temperature air are as follows



In this paper, all rate constants will be given in units of cm<sup>3</sup>/mole-sec unless otherwise noted, and activation energies will be given in cal/mole. A chemical subscript on a rate constant identifies the catalytic species "M."

Use is often made of equilibrium constants in comparing

HYPERSONIC FLOW RESEARCH

forward and backward rate constants, and it is convenient to have these in a simple analytic form. For this purpose the equilibrium constants calculated from the partition functions for reactions 2 to 6 have been fitted with an equation of the form  $K = AT^n \exp(-D/RT)$ ,  $n = 0 \pm 1/2$ . The best fits over the temperature range 3000 to 8000 K were chosen and are given next.  $K_{(7)}$  was obtained from  $K_{(7)} = K_{(6)}/K_{(5)}$  and  $K_{(8)}$  was approximated from the partition functions directly.

$$K_{(2)} = 1.2 \times 10^3 T^{-1/2} \exp(-118,000/RT) \text{ moles/cm}^3$$

$$K_{(3)} = 18 \exp(-224,900/RT) \text{ moles/cm}^3$$

$$K_{(4)} = 4.0 \exp(-150,000/RT) \text{ moles/cm}^3$$

$$K_{(5)} = 0.24 \exp(-32,020/RT)$$

$$K_{(6)} = 4.5 \exp(-75,000/RT)$$

$$K_{(7)} = 19 \exp(-42,980/RT)$$

$$K_{(8)} = 3.6 \times 10^{-10} T^{1.5} \exp(-63,300/RT)$$

All the previously given equations yield the correct equilibrium constants to within 10% over the specified temperature range.

Reaction 1 indicates the vibrational relaxation of the diatomic molecules. At the lower temperatures under consideration, this reaction goes to equilibrium before the molecules dissociate to a significant extent. Reactions 2, 3 and 4 lead to the formation of atoms by the direct dissociation of the molecules. At higher temperatures these reactions are coupled to reaction 1 since the dissociation rate constant is a function of the vibrational state of the gas. The NO is formed by the exchange reactions 5 and 6 which are fast and tend toward local equilibrium early in the time history when there still is a high concentration of diatomic molecules. This results in a large overshoot in NO concentration during the relaxation period. Reaction 7 also contributes to the production of NO. Reaction 8 is the dominant mechanism by which electrons are produced in shock heated air in the temperature range being considered.

## HYPERSONIC FLOW RESEARCH

Many of the rate constants to be quoted in this paper will be the case M argon. Although it is not a major component of air, it does make an ideal collision partner in reactions 1 to 4. Also, of course, it offers the advantages of carrying out reactions under essentially isothermal and isobaric conditions and increases the test time in shock tube experiments.

### VIBRATIONAL RELAXATION, REACTION 1

The relaxation equation given by theory (Refs. 1 and 2) is

$$\frac{E_v - E_f}{E_i - E_f} = e^{-t/\tau}$$

where  $E_i$  and  $E_f$  are the vibrational energies corresponding to the initial and final conditions;  $E_v$  is the vibrational energy at time  $t$ ; and  $\tau$  is the relaxation time. This relaxation time is related to a transition probability by the equation

$$\frac{1}{\tau} = Z P_{10} (1 - e^{-\theta/T})$$

where  $P_{10}$  is the transition probability for transition between vibrational levels 1 and 0,  $Z$  is the number of collisions encountered by a single oscillator molecule per sec with catalyst particles, and  $\theta$  is the vibrational energy level spacing.

Theoretical formulas for  $P_{10}$  have been proposed by Landau and Teller (Ref. 3) and by Schwarz, Slawsky and Herzfeld (Ref. 4).

### Oxygen

Blackman (Ref. 5) has used an interferometer with a  $0.3\mu$  sec duration light source to study the vibrational relaxation of shock heated  $O_2$ ,  $N_2$  and  $O_2-N_2$  mixtures. The  $O_2$  relaxation was investigated over the temperature range 800-3000 K; some results are given in Table 1. He also found that  $N_2-O_2$  collisions at about 2000 K are 40% as effective in transferring energy to oxygen as  $O_2-O_2$  collisions assuming in the data analysis that no energy had gone into the excitation of  $N_2$ .

The relaxation of  $O_2$  by  $O_2$  and Ar has been studied by Camac (Ref. 6) over the temperature range 1200-7000 K. He monitored the vibrational temperature of the shock heated gas by its absorption of 1470A radiation. He gives the following results

$$\frac{1}{\tau} = n C_1 T^{1/6} [1 - \exp(-2228/T)] \exp[-(C/T)^{1/3}]$$

HYPERSONIC FLOW RESEARCH

where  $n$  is the number of particles/cc. For  $M=Ar$ ,  $C_1 = 1.2 \times 10^{-7}$ ; for  $M=O_2$ ,  $C_1 = 6.0 \times 10^{-7}$  cc/part-sec- $(K)^{1/6}$  and in both cases,  $C = 1.04 (\pm 30\%) \times 10^7$  K. These constants are in good agreement with those given by the SSH theory.

The transition probabilities obtained by Camac and by Blackman are tabulated at several temperatures in Table 1.

Table 1  $P_{10} \times 10^4$

T (deg Kelvin)	1200	1800	2400	3000	4000	6000
Camac, M = Ar	0.016	0.12	0.5	1.6	6.3	35
Camac, M = O <sub>2</sub>	0.072	0.54	2.3	7.2	30	170
Blackman, M = O <sub>2</sub>	0.24	0.98	3.7	12	...	...

Nitrogen

Blackman, as already noted, has studied the vibrational relaxation of nitrogen using an interferometric technique. The temperature range covered was 3500-5500 K. Values of  $P_{10}$  are given for several temperatures in Table 2.

Table 2  $P_{10} \times 10^5$ ; M = N<sub>2</sub>.

T (deg Kelvin)	3000	4000	5000
Blackman	3.1	9.7	25

Nitric Oxide

Robben (Ref. 7) has measured the vibrational relaxation rate of shock heated NO by NO over the temperature range 400-1500 K. Addition of Ar up to 99% did not have any measurable effect on the relaxation time. The technique employed by Robben was monitoring of the concentration of NO in the  $v=1$  level by absorption of 2260A radiation. His results are inconsistent with those predicted by the SSH theory (Ref. 4), the measured rate at 400 K being  $10^4$  times larger than theory.

By following the vibrational temperature of shock heated NO-Ar mixtures by absorption of 1270A radiation, Wray (Ref. 8) has measured the vibrational relaxation of NO by NO and Ar. The temperature range covered was 1500-7000 K. He finds  $P_{NO-Ar} \approx \frac{1}{50} P_{NO-NO}$  Wray has compared his data to two different theories,

HYPERSONIC FLOW RESEARCH

i.e., the adiabatic theory of SSH and the nonadiabatic theory of Kikitin (Ref. 9), and finds that the sum of the transition probabilities given by both theories agrees well with the data. The transition probabilities for the vibrational relaxation of NO are given in Table 3.

Table 3  $P_{10} \times 10^3; M = \text{NO}.$

T (deg Kelvin)	500	1000	1500	3000	5000	7000
Wray	...	...	1.0	3.2	12	28
Robben	0.40	1.6	3.2	...	...	...

THE DISSOCIATION REACTIONS 2, 3 AND 4.

Oxygen:  $D = 118,000$

Matthews (Ref. 10) has used an interferometer and spark light source of  $0.1\mu$  sec duration to measure the dissociation rate of shock heated oxygen between 3000 and 5000 K. He fit his data with

$$k_{(2)O_2} = 5.2 \times 10^{10} T^{1/2} (D/RT)^3 \exp(-D/RT)$$

Due to the small degree of dissociation, he was not able to measure the rate for  $M = 0.$

Using a long duration spark interferometer with a drum camera providing time resolution, Byron (Ref. 11) has studied oxygen dissociation from 2800-5000 K. By studying both 100%  $O_2$  and lean  $O_2$ -Ar mixtures, Byron was able to obtain rate expressions for  $M = O_2, O$  and Ar. They are

$$k_{(2)O_2} = 5.5 \times 10^{11} T^{1/2} (D/RT)^2 \exp(-D/RT)$$

$$k_{(2)Ar} = 8.6 \times 10^{11} T^{1/2} (D/RT) \exp(-D/RT)$$

$$k_{(2)O} = 1.9 \times 10^{13} T^{1/2} (D/RT) \exp(-D/RT)$$

By experiments with shock heated air, Byron also finds  $k_{(2)N_2} \approx \frac{1}{4} k_{(2)O_2}.$

Using the absorption of 1470A radiation to monitor the  $O_2$

HYPERSONIC FLOW RESEARCH

concentration behind shock heated  $O_2$ -Ar mixtures, Camac and Vaughan (Ref. 12) have measured dissociation rates from 3400-7500 K. Their results are

$$k_{(2)Ar} = 2.5 \times 10^{11} T^{1/2} (D/RT)^{1.5} \exp(-D/RT)$$

$$k_{(2)O} = 7.4 \times 10^{11} T^{1/2} (D/RT)^{2.5} \exp(-D/RT)$$

The  $k_{(2)O}$  was evaluated from data at temperature above 5000 K. They also state that  $k_{O_2} \leq 3k_{Ar}$  at  $T \approx 7000$  K.

Duff (Ref. 13) and co-workers have used an X-ray beam as a means of following the density change behind shock heated  $O_2$ - $X_e$  mixture. The  $X_e$  was used because its large atomic number was required for absorption of the X-ray beam. At 3500 K they find  $k_{(2)O}$  equal to  $1/2 k_{(2)O}$  given by extrapolating Camac results to the lower temperature.

For Table 4 Camac's  $M = Ar$  rate has been chosen, which is in good agreement with Byron. For the cases  $M = N, NO$ , the same rate is chosen for lack of any other evidence. For the cases  $M = N_2, O_2$  and  $O$  one may use  $k_{(2)N_2} = 2k_{(2)Ar}$ ,  $k_{(2)O_2} = 9k_{(2)Ar}$ ,

and  $k_{(2)O} = 25k_{(2)Ar}$  which are reasonable composite values considering the disagreement on pre-exponential temperature dependences reported by the various workers.

Nitrogen:  $D = 224,900$

By monitoring the  $N_2$  (first positive) radiation intensity ( $5500 < \lambda < 10,000 \text{ \AA}$ ) with a photomultiplier in shock heated  $N_2$ , Allen, Keck and Camm (Ref. 14) have investigated the approach to equilibrium at temperatures between about 6200 and 6800 K. (See Hammerling, Teare and Kivel in Ref. 15 for details of the approach to equilibrium in  $N_2$  shocks.) They give their results in terms of a recombination rate

$$k_{(-3)N} = 6.5 \times 10^{15} \text{ cm}^6/\text{mole}^2\text{-sec}$$

which, at 6500 K yields a dissociation rate of  $k_{(3)N} = 3.2 \times 10^9$ . They can only state an upper bound for the case  $M = N_2$ , that is,  $k_{N_2} \leq 1/20 k_N$ .

Byron (Ref. 16), by techniques already mentioned, has measured  $N_2$  dissociation rates in  $N_2$ -Ar mixtures covering a temperature range of approximately 6000-9000 K. He finds

HYPERSONIC FLOW RESEARCH

$$k_{(3)N_2} = 4.2 \times 10^{12} T^{1/2} (D/RT) \exp(-D/RT)$$

$$k_{(3)Ar} = 1.7 \times 10^{12} T^{1/2} (D/RT) \exp(-D/RT)$$

$$k_{(3)N} = 3.2 \times 10^{12} T^{1/2} (D/RT)^2 \exp(-D/RT)$$

Evaluating Byron's  $k_{(3)N}$  at  $T = 6500$  K, it is found that  $k_{(3)N} = 2.1 \times 10^9$ , which compares very favorably with Allen's value.

Byron's  $N_2$  dissociation rates in Table 4 are used, setting  $k_{(3)O}, O_2, NO = k_{(3)Ar}$  for lack of other evidence.

Nitric Oxide:  $D = 150,000$

Freedman and Daiber (Ref. 17) have studied the decomposition of lean NO-Ar mixtures in a reflected shock by monitoring the absorption of radiation at 2283A, where vibrationally excited  $O_2$  absorbs strongly, and at 2465A, the bandhead of the (0,2) band of the  $\gamma$  sequence of NO. The temperature range covered was 3000-4300 K. In this temperature regime the early decomposition of NO (diluted with Ar) is dominated by the dissociation reaction 4 with  $M = Ar$  and the bimolecular reaction (-7). The rate constant for the two processes could be separated because they are first and second order, respectively, in NO. These workers found for reaction 4

$$k_{(4)Ar} = 7 \times 10^{15} \exp(-D/RT)$$

By techniques already outlined, Wray and Teare (Ref. 18) have monitored the NO concentration behind shock waves in air, air-Ar, NO-Ar and NO- $O_2$ -Ar mixtures. The temperature range covered was 3000-8000 K. The various mixtures used were chosen to emphasize the relative contribution of particular reactions. In this temperature regime reactions 1 to 7 all can play an important role (with the exception of reaction 3 which is important only at the highest temperatures). Their data analysis was carried out with the aid of an electronic computer; the rate constants for reactions 4 to 7 were varied in a systematic trial and error process which yielded a set of rate constants which satisfactorily fit all the measurements. The lean NO-Ar mixtures emphasized reaction 4 with  $M = Ar$ . Wray and Teare find

$$k_{(4)Ar} = 7.0 \times 10^{10} T^{1/2} (D/RT)^2 \exp(-D/RT)$$



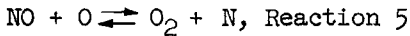
HYPERSONIC FLOW RESEARCH

which, at 4000 K where the data overlap, is about one-fourth the value obtained by Freedman; and from the rich NO-Ar mixtures, they estimate

$$k_{(4)\text{NO}} \approx 20k_{(4)\text{Ar}}$$

One may use Wray's results in Table 4 and set  $k_{(4)\text{O}_2}$ ,  $N_2 = k_{(4)\text{Ar}}$  and  $k_{(4)\text{O, N}} = k_{(4)\text{NO}}$ , which seem most consistent with his data but are by no means very well determined.

THE NO REACTIONS 5, 6 AND 7



Kaufman and Decker (Ref. 19) have measured the rate of decomposition of NO in NO-O<sub>2</sub> mixtures at temperatures around 1600 K. The reaction was carried out statically in porcelain reaction flasks, and the extent of reaction was determined by spectrophotometric analysis. By assuming the equilibrium O<sub>2</sub>  $\rightleftharpoons$  2O, that N is in a steady state by reactions 5, (-5) and (-6), that reaction 6 is negligibly slow in the temperature range investigated and finally using a known rate for reaction (-7) (Ref. 20), they arrived at a rate constant for reaction 5

$$k_{(5)} = 3.6 \times 10^{12} \exp(-39,500/RT)$$

which yields

$$k_{(-5)} = 1.5 \times 10^{13} \exp(-7,500/RT)$$

Using a low pressure flow system and a mass spectrometer to determine steady state concentrations, Kistiakowsky and Volpi (Ref. 21) have measured the rate constant for reaction (-5). The nitrogen atoms were produced in an electrodeless discharge. Over the temperature range 394-516 K, they fit their data with

$$k_{(-5)} = 2 \times 10^{12} \exp(-6,200/RT)$$

which gives

$$k_{(5)} = 5 \times 10^{11} \exp(-38,200/RT)$$

In similar work, Clyne and Thrush (Ref. 22) have measured

HYPERSONIC FLOW RESEARCH

$k_{(-5)}$  over the temperature range 412-755 K. They monitored the decay of N atoms along a tube by titrating with NO. They find

$$k_{(-5)} = 8.3 \times 10^{12} \exp(-7,100/RT)$$

yielding

$$k_{(5)} = 2.0 \times 10^{12} \exp(-39,100/RT)$$

Recently Mavroyannis and Winkler (Ref. 23) have also studied this reaction by similar techniques and find for  $448 \leq T \leq 623$  K

$$k_{(-5)} = 2.3 \times 10^{12} \exp(-5,900/RT)$$

so that

$$k_{(5)} = 5.5 \times 10^{11} \exp(-37,900/RT)$$

By shocking NO-O<sub>2</sub>-Ar mixtures, Wray and Teare (Ref. 18) were able to emphasize reaction 5 in the neighborhood of 5000 K where the O<sub>2</sub> dissociated rapidly compared to the NO. At this temperature, they found that  $k_{(5)}$  had to be increased by a factor of 10 over that given by the extrapolation of the rate expression of Kistiakowsky and Volpi, even after putting in an additional T<sup>1/2</sup> temperature dependence as suggested by Davidson (Ref. 24). Wray has fitted a single rate constant expression to the  $k_{(5)}$  reported in the foregoing, treating each as a single point at a temperature midway in the range covered by each investigation. The resulting equation, covering the temperature range 450-5000 K is

$$k_{(5)} = 3.2 \times 10^9 T \exp(-39,100/RT)$$

Though the numerical value of  $k_{(5)}$  varies by more than 10<sup>18</sup> over the applicable temperature range, this rate constant expression yields the results of the five independent investigations exceedingly well. This result has been used in Table 4.

N<sub>2</sub> + O  $\rightleftharpoons$  NO + N, Reaction 6

Glick, Klein and Squire (Ref. 25) used a single pulse shock tube (tailored interface technique) to study the formation of NO from N<sub>2</sub>-O<sub>2</sub>-inert gas mixtures over the temperature range 2000-3000 K. Data were obtained by chemical analysis of the

HYPERSONIC FLOW RESEARCH

shock heated gases. They found that the rate of formation of NO depended linearly on  $(O_2)^{1/2}$ . Assuming stationary concentrations for atomic species, they found

$$k_{(6)} = 5 \times 10^{13} \exp(-75,500/RT)$$

which yields

$$k_{(-6)} = 1.1 \times 10^{13}$$

Duff and Davidson (Ref. 26) have carried out a computed time history for conditions similar to those used in the experiments of Glick et al. They conclude that the rate constant given previously should be increased by 35%, since that much error is introduced by the assumptions made in analyzing the data.

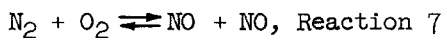
In the work by Wray and Teare, reaction 6 was not well determined. However, their data was satisfactorily fitted by the revised value obtained by Glick et al.

Clyne and Thrush (Ref. 22) have quoted a value of

$$k_{(-6)} = 3 \times 10^{13}$$

from their N atom experiments at temperatures between 412 and 755 K.

In Table 4 the results of Glick et al. have been used, increased by 35% as indicated in the foregoing.



The rate constants given next for reaction (-7) are defined without a factor of 2 in front of the rate constant.

Yuan et al. (Ref. 27) have studied the decomposition of NO in packed Alundum vessels using a flow method and photometric analyses. The temperature range covered was 1673-2073 K. They found no rate dependence on diluent gas. They give

$$k_{(-7)} = 1.9 \times 10^8 \exp(-63,100/RT) \text{ atm}^{-1} \text{ sec}^{-1}$$

which in the temperature range investigated becomes (in the units of the present paper)

## HYPERSONIC FLOW RESEARCH

$$k_{(-7)} = 2.9 \times 10^{13} \exp(-63,100/RT)$$

Kaufman and Kelso (Ref. 20) have made static measurements in quartz vessels over the temperature range 1400-1530 K using spectrophotometric analysis techniques. They find the decomposition rate of NO to be independent of diluent gas and diluent gas pressure. They give

$$k_{(-7)} = 2.6 \times 10^{12} \exp(-63,800/RT)$$

Freedman (Ref. 17) has measured the rate of reaction (-7) by techniques already described. The temperature range was 3000-4300 K. He found over this temperature range

$$k_{(-7)} = 8.2 \times 10^{12} \exp(-57,000/RT)$$

However, the rate given by Kaufman and Kelso when extrapolated to the higher temperatures had to be multiplied by a factor of 10 to agree with this result. Freedman combined his data with that of Kaufman and fit it all to a rate constant expression which covered a temperature range of 3000 deg. He gives for this combined result

$$k_{(-7)} = 4.8 \times 10^{23} T^{-5/2} \exp(-85,500/RT)$$

Wray's data in Ref. 18 describing NO rich NO-Ar mixtures which covered the temperature range 3000-8000 K could not be satisfactorily fitted with Kaufman's results for  $k_{(-7)}$ , the data demanding about a factor of 10 increase in the rate constant. Use of Freedman's composite rate expression fit the data well.

Other workers, including Wise and Frech (Ref. 28), Zeldovich (Ref. 29) and Frank-Kamenetsky (Ref. 30) have reported activation energies for reaction (-7) of about 80 kcal/mole. Freedman's composite rate expression is used in Table 4.

### THE IONIZATION REACTION 8

The rate of reaction 8 has been measured by Lin (Ref. 31) by simultaneously monitoring the d-c conductivity and microwave attenuation in shock heated 1/4% O<sub>2</sub>-99 3/4% N<sub>2</sub> mixtures. The temperature range covered was 4000-5000 K. Under these conditions, the O<sub>2</sub> dissociates rapidly and a steady state N

## HYPERSONIC FLOW RESEARCH

concentration is rapidly obtained due to reactions 5 and 6. He obtains a rate constant of<sup>2</sup>

$$k_{(8)} = 6.4 \times 10^9 T^{1/2} \exp(-63,290/RT)$$

The activation energy was arbitrarily set equal to the reaction energy--but this seems to fit the data well. In more recent work, Line (Ref. 32) utilizes a 2-ft diam shock tube permitting the use of initial pressures as low as  $20\mu$ . This slows down the chemistry allowing resolution of the electron production in air shocks. The rate expression given in the foregoing fits the air data adequately, and the result obtained is shown in Table 4.

### REMAINING PROBLEMS

The vibrational relaxation of the diatomic molecules in high temperature air has been fairly comprehensively investigated. There are, however, a few problems remaining. The catalytic efficiency of  $N_2$  in exciting  $O_2$  has not been unambiguously established, and likewise the related question of the exchange of vibrational energy between excited  $O_2$  and unexcited  $N_2$ . At temperatures around 8000 K and above, where a finite amount of O is produced before the  $O_2$  goes to vibrational equilibrium, knowledge of the efficiency of O in exciting  $O_2$  (and  $N_2$ ) vibration is of importance.

The rates for the dissociation reactions are now fairly well known. However, the catalytic efficiency of the important species  $N_2$  in the dissociation of  $O_2$  has not been well determined. Similarly, the efficiency of O (and  $O_2$ ) in the  $N_2$  dissociation has not been investigated, nor that of  $N_2$ ,  $O_2$  and O in the NO dissociation.

At low temperatures, the vibrational relaxation of  $O_2$  and the dissociation of  $O_2$  are essentially separated in time, the former process occurring first. As the temperature increases, both rates increase, but the dissociation rate increases faster, and by 8000 K, the dissociation has proceeded to a significant

<sup>2</sup>In a former report, "Relaxation Processes and Reaction Rates Behind Shock Fronts in Air and Component Gases," Avco-Everett Research Lab., Research Rep. 83, Dec. 1959, by Wray, Teare, Kivel and Hammerling, a rate constant of  $k_{(-8)} = 1.8 \times 10^{21} T^{-3/2}$  is quoted. This was obtained from Lin's results with the use of the equilibrium constant  $K_8 = 3.6 \times 10^{-12} T^2 \exp(-63,300/RT)$ . This analytical form of the equilibrium constant (which differs from the low temperature form given earlier in this paper) is applicable at temperatures above 10,000 K.

## HYPERSONIC FLOW RESEARCH

extent before vibrational equilibrium is established. Camac (Ref. 12) has given some evidence that under these conditions the dissociation rate is significantly reduced. Several workers including Ross (Ref. 33) and Widom (Ref. 34) have been seeking theoretical models of the dissociation process which would indicate how the dissociation rate couples to the vibrational state of the gas. Much experimental and theoretical work remains to be done on this problem.

A related problem is the recombination of atoms at high temperatures, that is, reactions (-2), (-3) and (-4). It is not at all certain that these recombination rates are correctly given by the ratio of the dissociation rate constant to the equilibrium constant. Furthermore, the temperature dependence of the recombination rate is uncertain. There is a great need for experimental recombination studies at intermediate temperatures, for example, O atoms at 800-3000 K.

There is some evidence that the exchange reactions produce molecules in excited vibrational states (Ref. 35) when proceeding in the exothermic direction. This certainly needs further clarification.

At sufficiently high temperatures, free electrons become a significant component of air. These electrons undoubtedly become important as catalysts in the dissociation reactions.

### COMPUTED TIME HISTORIES

Time histories have been computed from the shock front to full equilibrium behind shock heated air for three cases, all at an initial pressure of  $P_1 = 1$  mm. The shock speeds  $U_s$  are: Case 1 = 3.00, Case 2 = 4.62 and Case 3 = 6.55 mm/ $\mu$  sec. The results are shown in Figs. 1 to 9, all of which have as the abscissa the time measured in the particle coordinate system. The first figure for each case shows the temperature and density ratio (dashed curve); three temperatures are shown, the translational temperature and the  $N_2$  and  $O_2$  vibrational temperatures. The second figure shows the concentration profiles. The third figure of each case shows the time rate of change (in units of moles/original mole per sec) for each of the reactions 2 to 7.

The computer program includes a postulated mechanism for coupling the dissociation reactions to the vibrational temperature of the dissociating species (see Ref. 15). Due to the lack of any evidence to the contrary, this mechanism postulated that the rate constants for all vibrational levels are equal. This has the effect of slowing down the dissociation rate at

## HYPERSONIC FLOW RESEARCH

early times until the vibrational temperature has equilibrated. No such mechanism has been used for the other reactions.

Case 1: The disappearance of  $O_2$  is dominated by reaction 2, but reaction 7 is responsible for converting a significant amount of it into NO. Indeed, at early times reaction 7 is dominant in NO production, but by  $1 \times 10^{-4}$  sec the exchange reactions take over. At  $2.5 \times 10^{-3}$  sec all three NO producing reactions (-5), 6 and 7 reverse themselves, and thereafter, the net flux through these reactions is to remove NO--although reaction (-7) is not very important. The direct dissociation of NO and  $N_2$  plays no role. There is a very slight NO overshoot.

Case 2: The direct dissociation dominates at all times in getting rid of  $O_2$ . Reaction 7 dominates in NO production at very early times--actually getting NO up about its ultimate equilibrium value. But at about  $7 \times 10^{-7}$  sec the exchange reactions take over and bring the NO to its peak of  $(NO)_{\max} = 8.9 (NO)_{\text{eq}}$  at  $3.0 \times 10^{-6}$  sec. Up to this peak, reaction 7 has produced just about the same amount of NO as have the exchange reactions. Both exchange reactions reverse at the peak, and along with reaction 4 are responsible for the NO disappearance. The direct dissociation of  $N_2$  plays no role; most of the N atoms produced come from the net flux through the exchange reactions and by the direct dissociation of NO. An interesting phenomenon is the second reversal of reaction 6 so that it ends up producing NO and removing  $N_2$ .

Case 3: The  $O_2$  disappears by reaction 2. Reaction 7 plays no role except at very early times where it does get the NO up above its final equilibrium value. But reaction 6 rapidly becomes dominant in producing NO and it continues to do so until equilibrium. The NO maximum occurs at  $2.5 \times 10^{-7}$  sec where  $NO_{\max} = 14NO_{\text{eq}}$ . The other exchange reaction reverses itself at the NO peak but does not play an important role in depleting the excess NO--this is done by direct dissociation. The direct dissociation of  $N_2$  plays a minor role at very early and late times, the bulk of the  $N_2$  disappearing by exchange reaction 6.

### ACKNOWLEDGMENT

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Table 4 Rate constants for chemical processes

#	Reaction	Catalyst M	Rate Constant Expression
(2)	$O_2 + M + 5.1 \text{ ev} \rightleftharpoons 2 O + M$ D = 118,000	Ar, N, NO N <sub>2</sub> O <sub>2</sub> O	$k_{(2)} = 2.5 \times 10^{11} T^{1/2} \exp(-D/RT)$ $k_{(2)} = 2 k_{(2)} \text{ Ar}$ $k_{(2)} = 9 k_{(2)} \text{ Ar}$ $k_{(2)} = 25 k_{(2)} \text{ Ar}$
(3)	$N_2 + M + 9.8 \text{ ev} \rightleftharpoons 2 N + M$ D = 224,900	Ar, O, O <sub>2</sub> , NO N <sub>2</sub> N	$k_{(3)} = 1.7 \times 10^{12} T^{1/2} \exp(-D/RT)$ $k_{(3)} = 4.2 \times 10^{12} T^{1/2} \exp(-D/RT)$ $k_{(3)} = 3.2 \times 10^{12} T^{1/2} \exp(-D/RT)$
(4)	$NO + M + 6.5 \text{ ev} \rightleftharpoons N + O + M$ D = 150,000	Ar, O <sub>2</sub> , N <sub>2</sub> NO, O, N	$k_{(4)} = 7.0 \times 10^{10} T^{1/2} \exp(-D/RT)$ $k_{(4)} = 20 k_{(4)} \text{ Ar}$
(5)	$NO + O + 1.4 \text{ ev} \rightleftharpoons O_2 + N$	--	$k_{(5)} = 3.2 \times 10^9 T \exp(-39,100/RT)$
(6)	$N_2 + O + 3.3 \text{ ev} \rightleftharpoons NO + N$	--	$k_{(6)} = 7 \times 10^{13} \exp(-75,500/RT)$
(7)	$N_2 + O_2 + 1.9 \text{ ev} \rightleftharpoons 2 NO$	--	$k_{(7)} = 9.1 \times 10^{24} T^{-5/2} \exp(-128,500/RT)$
(8)	$N + O + 2.8 \text{ ev} \rightleftharpoons NO^+ + e$	--	$k_{(8)} = 6.4 \times 10^9 T^{1/2} \exp(-63,290/RT)$

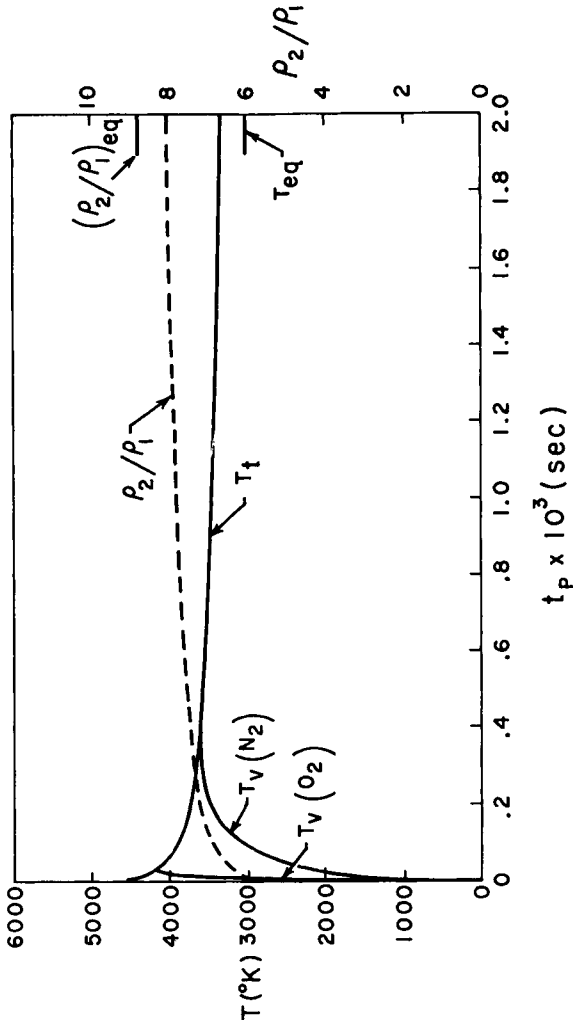


Fig. 1 Temperature and density ratio profiles for Case 1:  
 $U_s = 3.00 \text{ mm}/\mu \text{ sec}$ ,  $P_1 = 1 \text{ mm}$  of air.

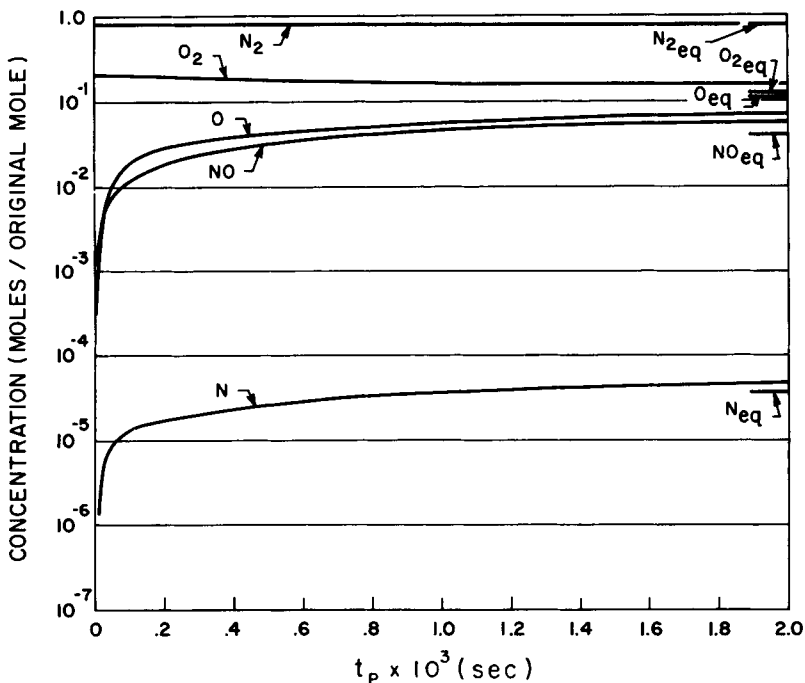


Fig. 2 Concentration profiles for Case 1:  $U_s = 3.00 \text{ mm}/\mu \text{ sec}$ ,  $P_s = 1 \text{ mm}$  of air.

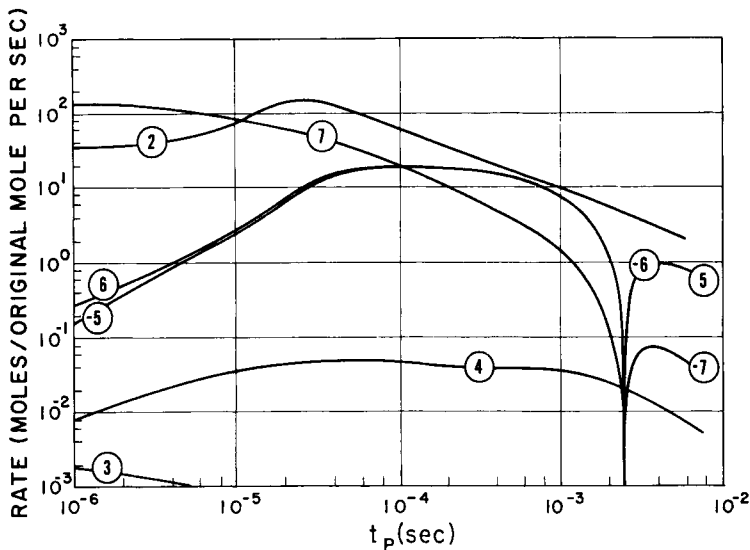


Fig. 3 The rate of reactions 2 to 7 plotted as a function of particle time for Case 1:  $U_s = 3.00 \text{ mm}/\mu \text{ sec}$ ,  $P_1 = 1 \text{ mm}$  of air.

HYPERSONIC FLOW RESEARCH

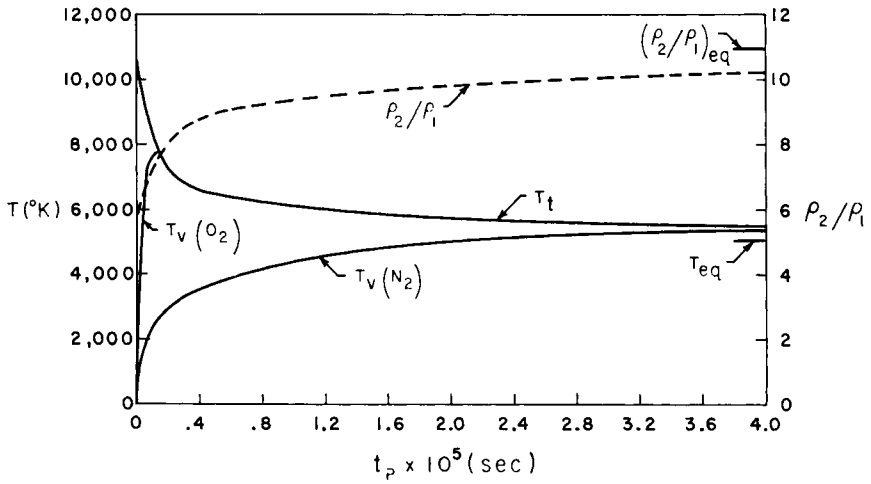


Fig. 4 Temperature and density ratio profiles for Case 2:  $U_s = 4.62$  mm/ $\mu$  sec,  $P_1 = 1$  mm of air.

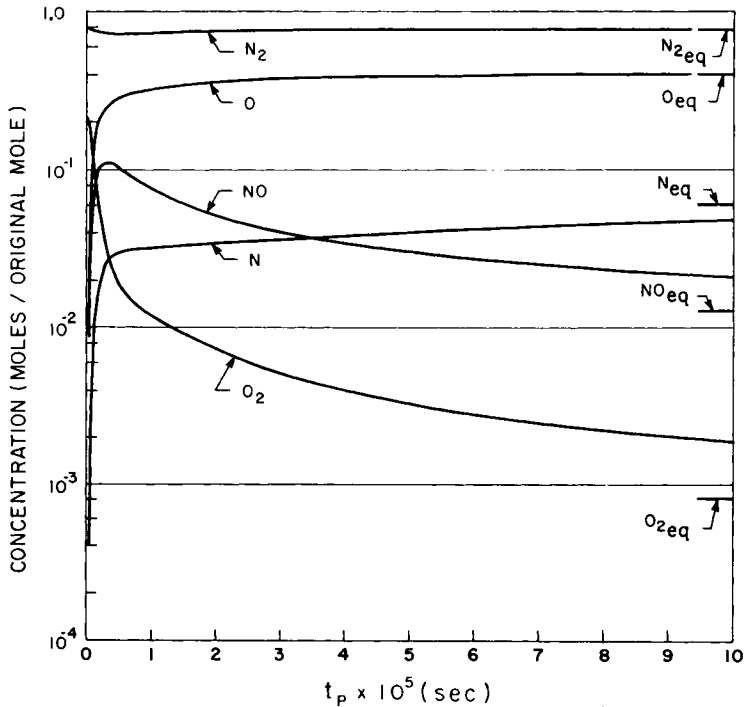


Fig. 5 Concentration profiles for Case 2:  $U_s = 4.62$  mm/ $\mu$  sec,  $P_1 = 1$  mm of air.

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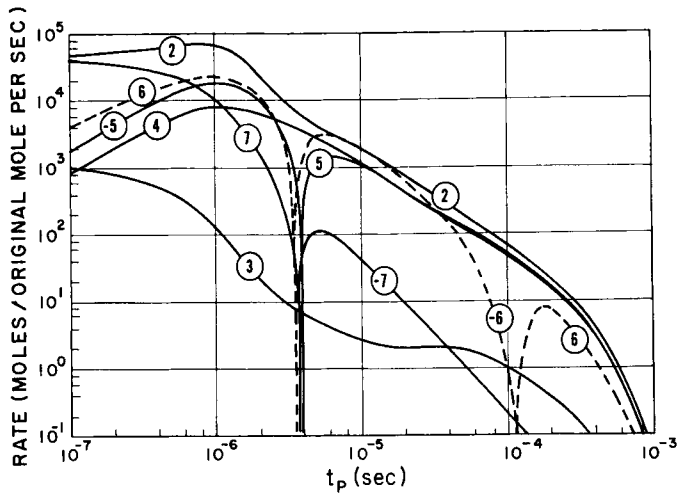


Fig. 6 The rate of reactions 2 to 7 plotted as a function of particle time for Case 2:  $U_s = 4.62 \text{ mm}/\mu \text{ sec}$ ,  $P_1 = 1 \text{ mm}$  of air.

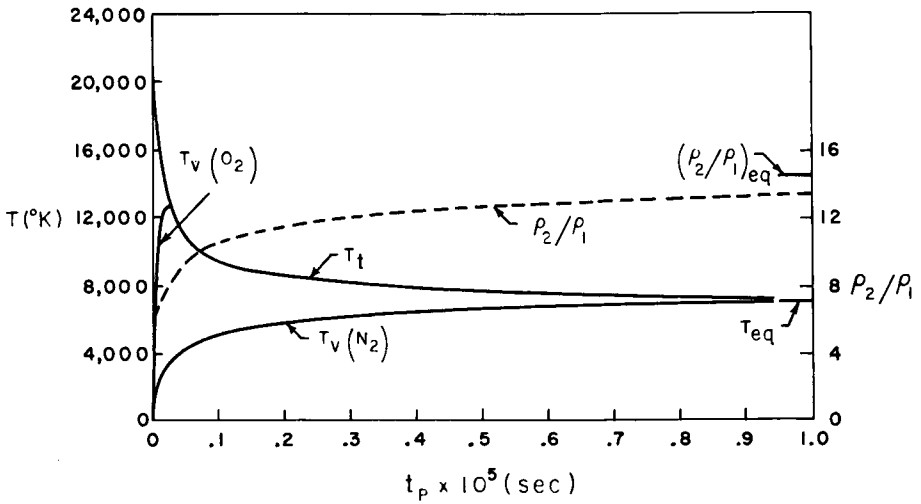


Fig. 7 Temperature and density ratio profiles for Case 3:  $U_s = 6.55 \text{ mm}/\mu \text{ sec}$ ,  $P_1 = 1 \text{ mm}$  of air.

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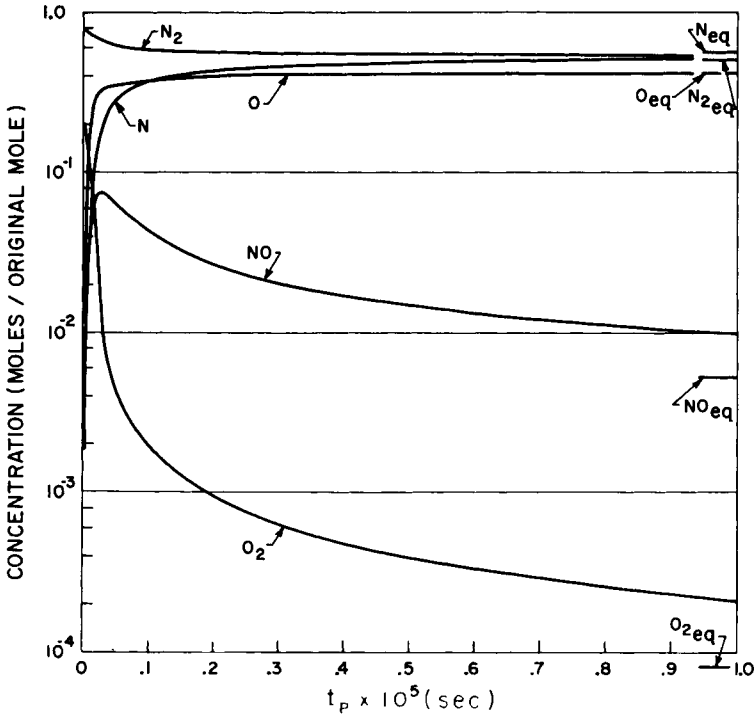


Fig. 8 Concentration profiles for Case 3:  $U_s = 6.55$  mm/ $\mu$  sec,  $P_1 = 1$  mm of air.

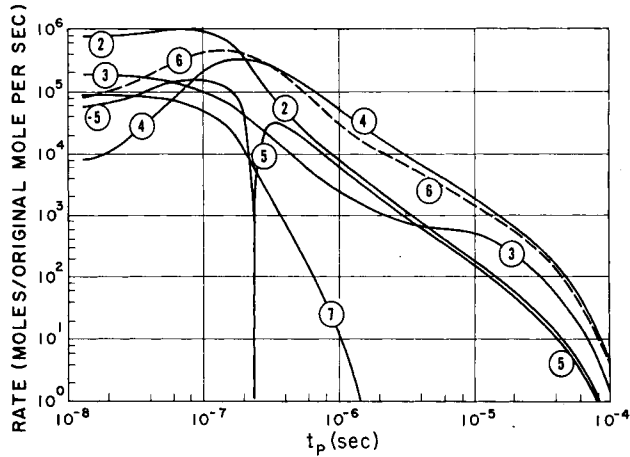


Fig. 9 The rate of reactions 2 to 7 plotted as a function of particle time for Case 3:  $U_s = 6.55$  mm/ $\mu$  sec,  $P_1 = 1$  mm of air.