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Monograph

REACTION RATES FOR HIGH-TEMPERATURE AIR

Mina L. Carnicom

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IN NUCLEAR SCIENCE ABSTRACTS

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By

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May 1966

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ABSTRACT

The reaction rate values used by a number of investigators in the field of high-temperature ($\geq 1000^\circ\text{K}$) reactions of nitrogen and oxygen species have been compiled and are presented in tabular forms for comparison. Included are radiative processes and reactions involving neutral and/or charged particles. An attempt was made to trace the rate values to their origin publications. Also included is a list of the air models considered by several investigators.

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REACTION RATES FOR HIGH-TEMPERATURE AIR

INTRODUCTION

This report lists the different values used by various investigators for the forward and reverse rates of reactions involving high-temperature air species. The reactions included are those considered to be the most important in estimating flow-field parameters in reentry atmospheres. Some of the listed values were determined experimentally; others were obtained from equilibrium constants; and still a third group of rates was inferred. These are discussed in some detail later.

In many instances the reaction rates are duplicated in the tables, since the suggestion of one investigator with regard to a rate value is frequently used by another investigator. Although this practice may lend a certain amount of authority and popularity to some values, it does not guarantee the validity of a reaction rate value.

Whenever possible, the original publication of a particular reaction rate value was consulted and referenced in the tables along with the works of other investigators who used the same value. In those cases where the original publications were not available, the works of other investigators had to be taken as representing correctly the rate values and sources.

Values for reaction rate constants that are known to be based on experimental evidence are underlined in the tables. These include:

1. Reaction rates determined experimentally by a referenced author;
2. Rates which were calculated by one author using experimental data reported by another investigator who did not publish a rate constant expression; and
3. Rates which are versions of previously reported values, but modified to correct for experimental oversights included in the earlier values.

Not underlined in the tables are:

1. Reaction rate values derived from equilibrium constants;
2. Estimations of values;
3. Extrapolations of values;
4. Other theoretical values based on nonexperimental considerations; and
5. Values whose bases are not fully known. (This may cause some valid, experimentally determined, reaction rate values to appear without an underline.)

The tables of published reaction rates used in this report are divided into, at most, nine columns. These are:

M	Reference	a	b	c	a	b	c	Applicable Range
1	2	3	4	5	6	7	8	9

Columns 1, 2, and 9 apply to both the forward and the reverse reaction rates. Columns 3, 4, and 5 are the values of a, b, and c, respectively, for the forward rates, k_f ; and Columns 6, 7, and 8 are the values of a, b, and c, respectively, for the reverse rates, k_r . The orders of the reactions are given by (n + 1) at the tops of the tables.

Column 1 lists the third body for which a group of reaction rates is thought to be applicable. Column 2 gives the reference number of the source for each reaction rate. Within each subgroup in the tables, the entries are listed chronologically, with the most recently published rates listed last. Column 9 gives the temperature limits, in °K, for which a particular reaction rate is applicable, according to the source. No rates known to be limited to temperatures of less than 1000°K are considered here. Where no applicable temperature range has been given in a source, no applicable range was included in the tables.

The rates given in this report are in the form

$$k = aT^b \exp\left(\frac{-c}{T}\right) \quad (1)$$

with units for a of $(\text{cm}^3 \text{ mole}^{-1})^n \text{ sec}^{-1}$, where n is 0, 1, or 2, depending on whether the reaction is, respectively, first, second, or third order. To convert the units into particles per cubic centimeter, the listed values for a should be divided by $(6.02 \times 10^{23})^n$. The unit for c is °K. To obtain the activation energy in calories per mole, the listed values of c should be multiplied by 1.9872. To get the activation energy in electron volts, the listed values of c should be divided by 11,606. These were the values used in converting other forms of the reaction rates encountered in the literature search to the units adopted in this report. Temperature (T) is expressed in degrees Kelvin throughout.

Air models of similar reactions under different conditions are included in this report in an attempt to show the importance of particular reactions under differing conditions. These air models are listed chronologically, with the most recent ones first.

REACTION RATE TABLES FOR HIGH-TEMPERATURE AIR

$$k = aT^b \exp\left(\frac{-c}{T}\right)$$

I. Neutral Species

A. Dissociation, Three-Body Recombination

M	Ref.	$k_f(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
		a	b	c	a	b	c	
Nonspecific	1, 2				7.2×10^{15}	0	0	
	3				3×10^{14}	0	0	
	4	5.4×10^{15}	0	113,000	3.0×10^{14}	0	0	
	5				5×10^{19}	-1.5	0	
	6				1.8×10^{16}	-1.0	0	
N ₂	7				1.6×10^{20}	-1.5	0	
	8				2.0×10^{20}	-1.5	0	
	9	9.4×10^{17}	-0.5	113,200				T = 6000-9000
	10				1.5×10^{20}	-1.5	0	
	11	2.97×10^{21}	-1.5	113,260				
	12	3.0×10^{21}	-1.5	113,260				T = 5000-18,000
	13	2.97×10^{21}	-1.5	113,260				
	14				2.7×10^{16}	-0.5	0	T = 300-30,000
	5				1.5×10^{20}	-1.5	0	
	15	5.6×10^{22}	-1.7	113,260				T = 6000-8500
	16	3.8×10^{19}	-1.0	113,200	2×10^{18}	-1.0	0	
	17			116,000	2.76×10^{16}	-0.5	0	
	18	5.6×10^{22}	-1.7	113,310				T = 6000-10,000
	19	1.0×10^{22}	-1.5	113,000	9.55×10^{20}	-1.57	0	
	20	3.0×10^{21}	-1.5	113,260				
	21	5.02×10^{17}	-0.5	113,000	2.76×10^{16}	-0.5	0	
	22	3.0×10^{21}	-1.5	113,260				
	23	3.0×10^{21}	-1.5	113,260				
	24	4.8×10^{17}	-0.5	133,200	2.6×10^{16}	-0.5	0	T = 6000-9000

M	Ref.	$k_f(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
		a	b	c	a	b	c	
N	7				8.0×10^{20}	-1.5	0	
	8				5.5×10^{20}	-1.5	0	
	25	$\leq 3.2 \times 10^9$	0	0	6.5×10^{15}	0	0	T = 6200-6800
	9	4.1×10^{22}	-1.5	113,200				T = 6000-9000
	10				7.5×10^{20}	-1.5	0	
	12	1.5×10^{22}	-1.5	113,260				T = 5000-18,000
	14				2.4×10^{21}	-1.5	0	T = 300-30,000
	5				7.5×10^{20}	-1.5	0	
	15	7.1×10^{19}	-1.0	113,260				T = 6000-8500
	16	1.3×10^{20}	-1.0	113,200	7×10^{18}	-1.0	0	
	17			116,000	2.36×10^{21}	-1.5	0	
	18	7.1×10^{19}	-1.0	113,310				T = 6000-10,000
	19	6×10^{21}	-1.5	113,000	5.73×10^{20}	-1.57	0	
	20	1.5×10^{22}	-1.5	113,260				
	21	4.29×10^{22}	-1.5	113,000	2.36×10^{21}	-1.5	0	
	22	1.5×10^{22}	-1.5	113,260				
O ₂	23	1.5×10^{21}	-1.5	113,260				
	24	4.3×10^{22}	-1.5	133,200	2.4×10^{21}	-1.5	0	T = 6000-9000
	8				6.0×10^{15}	-0.5	0	
	9	1.97×10^{19}	-0.5	113,200				T = 6000-9000
	10				5×10^{19}	-1.5	0	
	11	9.2×10^{20}	-1.5	113,260				T ≤ 6000
	12	9.9×10^{20}	-1.5	113,260				T = 5000-18,000
	14				1.1×10^{16}	-0.5	0	T = 300-30,000
	16	1.9×10^{19}	-1.0	113,200	1×10^{18}	-1.0	0	
	17			116,000	1.09×10^{16}	-0.5	0	
	19	4×10^{21}	-1.5	113,000	3.82×10^{20}	-1.57	0	
	20	9.9×10^{20}	-1.5	113,260				
	21	1.98×10^{17}	-0.5	113,000	1.09×10^{16}	-0.5	0	
	22	1.0×10^{21}	-1.5	113,260				
	23	9.9×10^{20}	-1.5	113,260				

M	Ref.	$k_f(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
		a	b	c	a	b	c	
O	8				6.0×10^{15}	-0.5	0	T = 6000-9000
	9	1.97×10^{19}	-0.5	113,200				
	10				5×10^{19}	-1.5	0	
	11	9.2×10^{20}	-1.5	113,260				T ≤ 6000
	12	9.9×10^{20}	-1.5	113,260				T = 5000-18,000
	14				1.1×10^{16}	-0.5	0	T = 300-30,000
	16	1.9×10^{19}	-1.0	113,200	1×10^{18}	-1.0	0	
	17			116,000	1.09×10^{16}	-0.5	0	
	19	1.0×10^{22}	-1.5	113,000	9.55×10^{20}	-1.57	0	
	20	9.9×10^{20}	-1.5	113,260				
	21	1.98×10^{17}	-0.5	113,000	1.09×10^{16}	-0.5	0	
	22	1.0×10^{21}	-1.5	113,260				
	23	9.9×10^{20}	-1.5	113,260				
NO	8				6.0×10^{15}	-0.5	0	T = 6000-9000
	9	1.97×10^{19}	-0.5	113,200				
	10				5×10^{19}	-1.5	0	
	12	9.9×10^{20}	-1.5	113,260				T = 5000-18,000
	14				1.1×10^{16}	-0.5	0	T = 300-30,000
	16	1.9×10^{19}	-1.0	113,200	1×10^{18}	-1.0	0	
	17			116,000	1.09×10^{16}	-0.5	0	
	19	4×10^{21}	-1.5	113,000	3.82×10^{20}	-1.57	0	
	20	9.9×10^{20}	-1.5	113,260				
	21	1.98×10^{17}	-1.5	113,000	1.09×10^{16}	-0.5	0	
	23	9.9×10^{20}	-1.5	113,260				
NO ⁺	16	1.9×10^{19}	-1.0	113,200	1×10^{18}	-1.0	0

M	Ref.	$k_f(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
		a	b	c	a	b	c	
Nonspecific	26				1.1×10^{15}	0	0	
	27	7×10^{16}	0	59,360	1×10^{15}	0	0	T = 6000
	3				3×10^{14}	0	0	
	4	5.4×10^{15}	0	59,380	3.0×10^{14}	0	0	
	28				1.85×10^{17}	-0.5	0	T = 1000-3300
	29				2×10^{18}	-1.0	0	T = 3000
	5	1.19×10^{21}	-1.5	59,380				T = 7200
	6	1.2×10^{19}	-1.0	59,400	1.1×10^{16}	-0.5	0	
	30				2.5×10^{15}	-0.5	0	T = 3300-6000
	31	2.9×10^{19}	-1.0	60,600	3×10^{14}	0	0	T = 1000-3000
	32				1.85×10^{17}	-0.5	0	
O ₂	33	3.5×10^{16}	0	58,900				T ≤ at least 1100
	34	<u>1.1×10^{25}</u>	<u>-2.5</u>	<u>59,380</u>		-2.0		T = 3000-5000
	34				8.4×10^{14}	0	0	T = 3500
	35	<u>1.8×10^{14}</u>	<u>-1.0</u>					
		<u>$\times 59,380^{1.0 \pm 2}$</u>	<u>± 0.2</u>	<u>59,380</u>				T = 6000-7000
	36	<u>1.9×10^{21}</u>	<u>-1.5</u>	<u>59,380</u>				T = 2800-5000
	8				8.0×10^{19}	-1.5	0	
	37				<u>1.6×10^{18}</u>	<u>-1.0</u>	<u>0</u>	T = 3000-6000
	9	3.26×10^{19}	-1.0	59,380				T = 3400-7500
	10				6×10^{19}	-1.5	0	
	38				<u>$1.4 \times 10^{18} (\pm 15\%)$</u>	<u>-1.0</u>	<u>0</u>	T = 4360-5325
	11	<u>3.56×10^{21}</u>	<u>-1.5</u>	<u>59,380</u>				T ≤ 6000
	39			59,350	<u>$2.5 \pm 0.5 \times 10^{18}$</u>	<u>-1.0</u>	<u>0</u>	T = 2700
	12	3.6×10^{21}	-1.5	59,380				T = 5000-18,000
	13	1.14×10^{25}	-2.5	59,380				
	40				$\sim 7 \times 10^{14}$	0	0	T = 2000
	14				8.0×10^{19}	-1.5	0	T = 300-30,000
	5	3.6×10^{21}	-1.5	59,380				T = 7200
	16	2.3×10^{19}	-1.0	59,400	1.9×10^{16}	-0.5	0	

M	Ref.	$k_f(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
		a	b	c	a	b	c	
O ₂ (continued)	41	<u>$4.6(\pm 14\%) \times 10^{17}$</u>	<u>-0.5</u>	<u>59,400</u>				T = 5000-18,000
	41				<u>4.6×10^{14}</u>	<u>0</u>	<u>0</u>	T = 2000
	17			61,000	8.0×10^{19}	-1.5	0	
	19	1.2×10^{17}	-0.5	59,353	4.4×10^{15}	-0.44	0	
	20	3.2×10^{21}	-1.5	59,380				
	42				<u>$6.81 \pm 0.54 \times 10^{14}$</u>	<u>-1.22</u>		
					<u>$\times 2200^{1.22 \pm .53}$</u>	<u>± 0.53</u>	<u>0</u>	T = 1500-2800
	21	1.33×10^{21}	-1.5	59,400	7.99×10^{19}	-1.5	0	
	22	3.6×10^{21}	-1.5	59,380				
	23	3.6×10^{21}	-1.5	59,380				
O	35	<u>1.5×10^{15}</u>	<u>-1.0</u>					T = 5000-7500
		<u>$\times 59,380^{1.0 \pm .2}$</u>	<u>± 0.2</u>	<u>59,380</u>				T = 2800-5000
	36	<u>1.1×10^{18}</u>	<u>-0.5</u>	<u>59,380</u>				
	4				3.6×10^{11}	0	0	
	8				2.2×10^{20}	-1.5	0	
	37				<u>4.8×10^{18}</u>	<u>-1.0</u>	<u>0</u>	T = 3000-6000
	9	1.12×10^{20}	-1.0	59,380				T = 3400-7500
	10				3×10^{20}	-1.5	0	
	38				<u>$4.7 \times 10^{18}(\pm 15\%)$</u>	<u>-1.0</u>	<u>0</u>	T = 4360-5325
	11	<u>2.1×10^{18}</u>	<u>-0.5</u>	<u>59,380</u>				T ≤ 6000
	12	2.1×10^{18}	-0.5	59,380				T = 5000-18,000
	14				2.2×10^{20}	-1.5	0	T = 300-30,000
	5	2.1×10^{18}	-0.5	59,380				
	6				7.2×10^{16}	-0.5	0	
	16	8.5×10^{19}	-1.0	59,400	7.1×10^{16}	-0.5	0	
	41	<u>$1.3(\pm 14\%) \times 10^{18}$</u>	<u>-0.5</u>	<u>59,400</u>				T = 5000-18,000
	41				<u>1.3×10^{15}</u>	<u>0</u>	<u>0</u>	T = 2000
	17			61,000	2.25×10^{20}	-1.5	0	
	19	6.25×10^{17}	-0.5	59,353	2.2×10^{16}	-0.44	0	
	20	2.1×10^{18}	-0.5	59,380				
	21	3.75×10^{21}	-1.5	59,400	2.25×10^{20}	-1.5	0	
	22	2.1×10^{18}	-0.5	59,380				
	23	2.1×10^{18}	-0.5	59,380				

M	Ref.	$k_F(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
		a	b	c	a	b	c	
N ₂	36	4.9×10^{20}	-1.5	59,380				T = 2800-5000
	8				2.5×10^{15}	-0.5	0	
	9	7.2×10^{18}	-1.0	59,380				T = 3400-7500
	10				2×10^{19}	-1.5	0	
	11	1.19×10^{21}	-1.5	59,380				T ≤ 6000
	12	1.2×10^{21}	-1.5	59,380				T = 5000-18,000
	14				6.2×10^{15}	-0.5	0	T = 300-30,000
	16	3.0×10^{18}	-1.0	59,400	2.5×10^{15}	-0.5	0	
	17			61,000	6.19×10^{15}	-0.5	0	
	19	5.0×10^{16}	-0.5	59,353	1.8×10^{15}	-0.44	0	
	20	1.2×10^{21}	-1.5	59,380				
	21	1.03×10^{17}	-0.5	59,400	6.17×10^{15}	-0.5	0	
	22	1.2×10^{21}	-1.5	59,380				
	23	1.2×10^{21}	-1.5	59,380				
N or NO	8				2.5×10^{15}	-0.5	0	
	9	3.6×10^{18}	-1.0	59,380				T = 3400-7500
	10				2×10^{19}	-1.5	0	
	12	1.2×10^{21}	-1.5	59,380				T = 5000-18,000
	14				3.0×10^{15}	-0.5	0	T = 300-30,000
	16	3.0×10^{18}	-1.0	59,400	2.5×10^{15}	-0.5	0	
	17			61,000	3.02×10^{15}	-0.5	0	
	19	5.0×10^{16}	-0.5	59,353	1.8×10^{15}	-0.44	0	
	20	1.2×10^{21}	-1.5	59,380				
	21	5.02×10^{16}	-0.5	59,400	3.01×10^{15}	-0.5	0	
	22	1.2×10^{21}	-1.5	59,380				
	23	1.2×10^{21}	-1.5	59,380				
NO ⁺	16	3.0×10^{18}	-1.0	59,400	2.5×10^{15}	-0.5	0

M	Ref.	$k_f(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
		a	b	c	a	b	c	
Nonspecific	3				6×10^{14}	0	0	T = 3000-4300 T ≤ 6000
	4	2.0×10^{15}	0	75,500	5.8×10^{14}	0	0	
	43	7×10^{15}	0	75,500	1×10^{17}	-0.5	0	
	11	5.18×10^{21}	-1.5	75,490				
	13	5.18×10^{21}	-1.5	75,490				
	28				4.3×10^{20}	-1.5	0	T = 1000-3300
	5	5.18×10^{21}	-1.5	75,490				T = 3300-6000
	6				6.2×10^{16}	-0.5	0	
	30				1×10^{20}	-1.5	0	
	20	5.2×10^{21}	-1.5	75,490				
	32	1.06×10^{25}	-2.5	77,500	4.3×10^{20}	-1.5	0	
	22	5.18×10^{21}	-1.5	75,490				
	23	5.2×10^{21}	-1.5	75,490				
N ₂ or O ₂	8				1.0×10^{20}	-1.5	0	T = 3000-8000
	9	4.0×10^{20}	-1.5	75,480				
	10				6×10^{20}	-1.5	0	
	12	5.2×10^{21}	-1.5	75,490				T = 5000-18,000
	14				1.0×10^{20}	-1.5	0	T = 300-30,000
	16	2.4×10^{17}	-0.5	75,500	6×10^{16}	-0.5	0	
	17				1.02×10^{20}	-1.5	0	
	19	1.1×10^{21}	-1.5	75,483	3.3×10^{20}	-1.52	0	
	21	4.08×10^{20}	-1.5	75,500	1.02×10^{20}	-1.5	0	
N or O	8				2.0×10^{21}	-1.5	0	T = 3000-8000
	9	8.0×10^{21}	-1.5	75,480				
	10				6×10^{20}	-1.5	0	
	12	5.2×10^{21}	-1.5	75,490				T = 5000-18,000
	14				1.0×10^{20}	-1.5	0	T = 300-30,000
	16	2.4×10^{17}	-0.5	75,500	6×10^{16}	-0.5	0	
	17				1.02×10^{20}	-1.5	0	
	19	2.8×10^{21}	-1.5	75,483	8.3×10^{20}	-1.52	0	
	21	4.08×10^{20}	-1.5	75,500	1.02×10^{20}	-1.5	0	

M	Ref.	$k_f(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
		a	b	c	a	b	c	
NO	8				2.0×10^{21}	-1.5	0	T = 3000-8000
	9	8.0×10^{21}	-1.5	75,480				
	10				6×10^{20}	-1.5	0	T = 5000-18,000
	12	5.2×10^{21}	-1.5	75,490				
	14				2.0×10^{21}	-1.5	0	T = 300-30,000
	17				2×10^{21}	-1.5	0	
	19	1.1×10^{21}	-1.5	75,483	3.3×10^{20}	-1.52	0	
	21	8.0×10^{21}	-1.5	75,500	2.00×10^{21}	-1.5	0	
NO ⁺	16	2.4×10^{17}	-0.5	75,500	6×10^{16}	-0.5	0

M	Ref.	$k_f(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
		a	b	c	a	b	c	
Nonspecific	27	2.03×10^{15}	0	12,100				T = 6000
	4	4.6×10^{15}	0	12,400	5.8×10^{13}	0	0	
	44	$5.8 \pm 0.6 \times 10^{14}$	0	11,650				T = 1300-3000
				± 150				
	13	4.6×10^{15}	0	12,380				T < 6000
	45				1.1×10^{14}	0	0	
O ₂	33	$2.03 \pm 0.11 \times 10^{15}$	0	12,100	$2.64 \pm 0.14 \times 10^{13}$	0	-302	
	46				$2.65 \pm 0.14 \times 10^{13}$	0	3,020	
N ₂	33	$1.89 \pm 0.10 \times 10^{15}$	0	12,100	$2.46 \pm 0.14 \times 10^{13}$	0	-302	
O ₃	33	$4.61 \pm 0.25 \times 10^{15}$	0	12,100	$6.00 \pm 0.33 \times 10^{13}$	0	-302	

B. Rearrangement

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
47				2.6×10^{12}	0	32,100	T = 1400-1530
48				2.4×10^{12}	0	32,100	T = 1500-1700
49				2.9×10^{13}	0	31,800	T = 1673-2073
4	2.7×10^{13}	0	53,800	1.3×10^{12}	0	31,700	
43				8.2×10^{12}	0	28,700	T = 3000-4300
43				4.79×10^{23}	-2.5	43,000	T = 1500-4300
9	9.1×10^{24}	-2.5	64,660				T = 3000-8000
9				4.8×10^{23}	-2.5	43,000	T = 1400-4300
12	9.1×10^{24}	-2.5	65,000				T = 5000-18,000
13	9.1×10^{24}	-2.5	64,660				T = 1400-4300
28	2.7×10^{13}	0	53,800				T = 1000-3300
14				2.4×10^{23}	-2.5	43,000	T = 300-30,000
5	9.1×10^{24}	-2.5	65,000				
19	6.69×10^{24}	-2.54	64,641	2.4×10^{23}	-2.5	43,000	T = 1400-4300
20	9.1×10^{24}	-2.5	65,000				
21	4.56×10^{24}	-2.5	64,600	2.41×10^{23}	-2.5	43,000	
23	9.1×10^{24}	-2.5	65,000				

*Nawrocki⁴ reports 1.8 ev for this reaction.

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
47				$\leq 1.9 \times 10^{15}$	0	4,000	T = 1600
50	5×10^{13}	0	38,000	1.1×10^{13}	0	0	T = 2000-3000
48, 51				$6.0 \times 10^{12 \pm 1}$	0	0	
3	6.75×10^{13}	0	38,000				

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
52				9.0×10^{12}	0.5	0	
4	5.0×10^{13}	0	37,700	1.3×10^{13}	0	0	
8				1.3×10^{13}	0	0	
43	5×10^{13}	0	37,700				T = 2000-3000
9	7×10^{13}	0	38,000				T = 2000-3000
10				1.3×10^{13}	0	0	
11	5×10^{13}	0	38,016				
12	5.0×10^{13}	0	38,000				T = 5000-18,000
13	5.5×10^{11}	0.5	36,245				T = 2000-6000
28	1.01×10^{12}	0.5	38,000				T = 1000-3300
53	7×10^{13}	0	37,700				T = 10,000
14				1.6×10^{13}	0	0	T = 300-30,000
5	5×10^{13}	0	38,016				
45				$1.3 \times 10^{12 \pm .5}$	0	0	
30	5×10^{13}	0	38,000				T = 3300-6000
16	6.8×10^{13}	0	37,750	1.5×10^{13}	0	0	
17				1.62×10^{13}	0	0	
19	6.8×10^{13}	0	37,748	2.1×10^{13}	-0.04	0	
20	5.0×10^{13}	0	38,000				
21	7.41×10^{13}	0	37,800	1.63×10^{13}	0	0	
32	1.01×10^{12}	0.5	38,000				
22	4.5×10^{13}	0	38,016				
23	5.0×10^{13}	0	38,000

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
47	8.3×10^{12}	0	20,400	3.8×10^{13}	0	4,000	T = 1600-1800
48,54				$6.0 \times 10^{9 \pm 2}$	0	0	
48	3.6×10^{12}	0	19,900	1.5×10^{13}	0	3,770	T = 1500-1700

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
3				1×10^{11}	0.5	3,120	
52				9.0×10^{10}	0.5	3,120	
4	2.1×10^{10}	0.5	19,300	1×10^{11}	0.5	3,120	
55				1.02×10^{11}	0.5	3,120	T = 1000-3300
8				1.0×10^{12}	0.5	3,120	
56	<u>3.2×10^9</u>	<u>1.0</u>	<u>19,700</u>				T = 450-5000
10				1×10^{12}	0.5	3,120	
11				1×10^{12}	0.5	3,120	
12				1.0×10^{12}	0.5	3,120	T = 5000-18,000
13	3.2×10^9	1.0	19,700				T = 450-5000
28				1.02×10^{11}	0.5	3,120	T = 1000-3300
14				1.3×10^{10}	1.0	3,560	T = 300-30,000
5				1×10^{12}	0.5	3,120	
45				$2.4 \times 10^{11 \pm .5}$	0.5	3,320	
30				1×10^{12}	0.5	3,120	T = 3300-6000
16	4.3×10^7	1.5	19,100	1.8×10^8	1.5	3,020	
19	3.2×10^9	1.0	19,700	2.67×10^{10}	0.92	3,544	T = 450-5000
20				1.0×10^{12}	0.5	3,120	
21	3.19×10^9	1.0	19,700	1.33×10^{10}	1.0	3,560	
32				1.02×10^{11}	0.5	3,120	
22				1.0×10^{12}	0.5	3,120	
23				1.0×10^{12}	0.5	3,120

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
33	6.7×10^{12}	0	49,900	$2.96 \pm 0.21 \times 10^{13}$	0	3,020	T ≤ at least 1100
27	1.37×10^{13}	0	49,900				T = 6000
4	6.6×10^{12}	0	46,300	$3 \times 10^{13 \pm 1}$	0	3,020	
44				<u>$2.4 \pm 0.5 \times 10^{13}$</u>	<u>0</u>	<u>2,820</u>	
						<u>±250</u>	T = 1300-3000

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
13 45	6.7×10^{12}	0	49,900	$4.3 \times 10^{12 \pm .5}$	0	1,600	$T < 6000$

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
53	1×10^{14}	0	33,250				$T = 2000$

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
53	1×10^{14}	0	4,030				$T = 2000$

II. Charged Species

A. Charge Exchange

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
7 4 10 13	6×10^{11}	0.5	0	6×10^{10} 7.8×10^{11} 7.8×10^{11}	0 0.5 0.5	0 0 0

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
4				6×10^{10}	0	0	
45				$6 \times 10^{12 \pm 2}$	0	0

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
4				6×10^{10}	0	0	
45				$3 \times 10^{13 \pm 1}$	0	0	
57				$2.4 \pm 1.2 \times 10^{11}$	0	0	

*Hartecck and Reeves⁵⁸ give 3.4 ev for this reaction.

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
4				6×10^{10}	0	0	
45				$3 \times 10^{12 \pm 2}$	0	0

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
4				6×10^{12}	0	0	
10				7.8×10^{11}	0.5	0	
13				7.8×10^{11}	0.5	0	
45				$6 \times 10^{12 \pm 1}$	0	0	

*Hartek and Reeves⁵⁸ give 1.4 ev for this reaction.

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
59				$6 \times 10^{14 \pm 2}$	0	0	
45				$6 \times 10^{12 \pm 2}$	0	0	
21	2.08×10^{12}	0.5	16,200	1.22×10^{12}	0.5	5,330	

*Nawrocki⁴ gives 1.32 ev for this reaction.

B. Ion-Pair Formation, Mutual Neutralization

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
4				$6 \times 10^{15.5 \pm .5}$	0	0	
45				$1.2 \times 10^{17 \pm 1}$	-0.5	0	
21	6.53×10^{18}	-1.0	91,800	1×10^{18}	-0.5	0

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
4				$6 \times 10^{15.5 \pm .5}$	0	0	
45				$1.2 \times 10^{17 \pm 1}$	-0.5	0	
21	1.11×10^{19}	-1.0	103,000	1×10^{18}	-0.5	0

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
60				6×10^{16}	0	0	
45				$1.2 \times 10^{17 \pm 1}$	-0.5	0

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
60				6×10^{16}	0	0	
45				$6 \times 10^{17 \pm 1}$	-0.5	0

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
4				$6 \times 10^{15 \pm 1}$	0	0	
45				$2.2 \times 10^{17 \pm .5}$	-0.5	0	

C. Rearrangement

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
45				$6 \times 10^{11 \pm 2}$	0	3,000	

*Nawrocki⁴ gives 0.9 ev for this reaction.

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
45				$6 \times 10^{11 \pm 2}$	0	3,500

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
45				$6 \times 10^{11 \pm 2}$	0	0	
57				$1.8 \pm 0.6 \times 10^{12}$	0	0

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
4				$6 \times 10^{12 \pm 1}$	0	0	
45				$6 \times 10^{12 \pm 2}$	0	500	

*Nawrocki⁴ gives 2.8 ev for this reaction, while Harteck and Reeves⁵⁸ give 3.0 ev.

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
4				6×10^{14}	0	0	
45				$6 \times 10^{12 \pm 2}$	0	500	

*Harteck and Reeves⁵⁸ give 4.3 ev for this reaction.

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
4				$6 \times 10^{13 \pm 1}$	0	0	
45				$6 \times 10^{12 \pm 2}$	0	500	
57				$3.0 \pm 1.2 \times 10^{14}$	0	0	

*Nawrocki⁴ gives 7.6 ev for this reaction.

III. Reactions Involving Free Electrons

A. Detachment, Three-Body Recombination

M	Ref.	$k_f(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
		a	b	c	a	b	c	
Nonspecific	4	$< 6 \times 10^{-27}$	0	0				T = 1000
	4				1.8×10^{27}	0	0	

*Nawrocki⁴ suggests 12.0 ev for this reaction.

M	Ref.	$k_f(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
		a	b	c	a	b	c	
O ₂	14	6.6×10^{-10}	4.5	141,000				$T \leq 5000^*$
N ₂	14	2.7×10^{-1}	2.5	141,000				$T \leq 5000^*$

*See discussion for equations for temperatures up to 30,000°K.

M	Ref.	$k_f(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
		a	b	c	a	b	c	
Nonspecific	4	$< 6 \times 10^{-27}$	0	0				$T = 1000$
	4				3.6×10^{20}	0	0	
	13	2.77×10^{12}	0.5	157,500				$T = 2000-6000$
	45				$4.7 \times 10^{23 \pm 2}$	-1.5	0	
N ₂	20				2.0×10^{26}	-2.5	0	
O ₂	20				9.0×10^{26}	-2.5	0	
N or O	20				6.0×10^{24}	-2.5	0	
NO	20				1.0×10^{28}	-2.5	0	
e	20	1.63×10^{13}	0.5	157,800

M	Ref.	$k_f(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
		a	b	c	a	b	c	
Nonspecific	4	$< 6 \times 10^{-27}$	0	0				$T = 1000$
	4				1.8×10^{27}	0	0	

M	Ref.	$k_f(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
		a	b	c	a	b	c	
N ₂	14	1.7×10^{-4}	3.5	181,000				$T \leq 5000^*$

*See discussion for equation for temperatures up to 30,000°K.

M	Ref.	$k_f(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
		a	b	c	a	b	c	
Nonspecific	4	$< 6 \times 10^{-27}$	0	0				$T = 1000$
	4				3.6×10^{20}	0	0	
	13	2.93×10^{12}	0.5	167,600				$T = 2000-6000$
N ₂	20				2.0×10^{26}	-2.5	0	
O ₂	20				9.0×10^{26}	-2.5	0	
N or O	20				6.0×10^{24}	-2.5	0	
NO	20				1.0×10^{28}	-2.5	0	
e	20	2.7×10^{13}	0.5	168,800

M	Ref.	$k_f(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
		a	b	c	a	b	c	
Nonspecific	6	3.0×10^{11}	1.0	5,100	3.6×10^{19}	-0.5	0	

*Nawrocki⁴ suggests 0.9 ev for this reaction.

M	Ref.	$k_f(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
		a	b	c	a	b	c	
O_2	4				1.8×10^{18}	0	0	
	45	$4.8 \times 10^{13 \pm 1}$	0	5,100	1.1×10^{18}	0	0	
	19	4.7×10^{11}	0.9	5,100	5×10^{19}	-0.5	0	
	21	6×10^9	1.5	5,330	1×10^{18}	0	0	
O	45	$4.8 \times 10^{13 \pm 1}$	0	5,100				
	21	6×10^7	1.5	5,330	1×10^{16}	0	0	
N_2	45	$4.8 \times 10^{13 \pm 1}$	0	5,100	3.6×10^{16}	0	0	
	19	1.87×10^{10}	0.9	5,100	2×10^{18}	-0.5	0	
	21	6×10^7	1.5	5,330	1×10^{16}	0	0	
N or NO	21	6×10^7	1.5	5,330	1×10^{16}	0	0

M	Ref.	$k_f(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
		a	b	c	a	b	c	
O_2	4	6×10^8	0	0	3.6×10^{16}	0	0	
	6	6×10^{12}	1.0	17,000	3.6×10^{20}	-0.5	0	
	16	1.4×10^{12}	1.0	17,000	8.5×10^{19}	-0.5	0	
	19	3.7×10^{12}	1.05	16,998	5×10^{20}	-0.5	0	
	21	1.12×10^{11}	0.5	16,200	1.10×10^{19}	-1.0	0	
N_2	4	6×10^8	0	0	3.6×10^{16}	0	0	
	6	1.8×10^{11}	1.0	17,000	1.1×10^{19}	-0.5	0	
	16	1.4×10^{12}	1.0	17,000	8.5×10^{19}	-0.5	0	
	19	1.48×10^{11}	1.05	16,998	2×10^{19}	-0.5	0	
	21	1.12×10^{11}	0.5	16,200	1.10×10^{19}	-1.0	0	
N, O, or NO	16	1.4×10^{12}	1.0	17,000	8.5×10^{19}	-0.5	0	
	21	1.12×10^{11}	0.5	16,200	1.10×10^{19}	-1.0	0

M	Ref.	$k_f(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
		a	b	c	a	b	c	
Nonspecific	6	6.0×10^{11}	0	35,000	3.6×10^{19}	-0.5	0	
N ₂	4				3.6×10^{16}	0	0	

B. Associative Detachment, Dissociative Recombination

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
61	6.4×10^9	0.5	31,850				T = 4000-5000
62				1.8×10^{21}	-1.5	0	T > 10,000
63				1.8×10^{15}	0	0	
4	6.0×10^{-2}	0	0				T = 1000
9	6.4×10^9	0.5	31,850				T = 4000-5000
12				1.8×10^{21}	-1.5	0	T = 5000-18,000
13	1.86×10^{12}	0.5	31,800				T = 2000-6000
14	3.0×10^{13}	-0.5	32,500	1.8×10^{21}	-1.5	0	T ≤ 3000
5				1.8×10^{21}	-1.5	0	
45				$1.8 \times 10^{19 \pm 1}$	-1.0	0	
16	1.3×10^8	1.0	31,900	2×10^{19}	-1.0	0	
64				3×10^{19}	-0.5	0	T = 5100-7750
19	6.4×10^9	0.5	32,386	7×10^{18}	-0.9	0	
20				7.22×10^{19}	-1.0	0	T ≤ 3000
20				3.98×10^{21}	-1.5	0	T > 3000
21	3.02×10^{13}	-0.5	32,500	1.81×10^{21}	-1.5	0

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
7				9.6×10^{21}	-1.5	0	
63				8.4×10^{17}	0	0	
4				8.4×10^{16}	0	0	T = 2500
10				9.6×10^{21}	-1.5	0	
13				9.6×10^{21}	-1.5	0	
14	3.0×10^{13}	-0.5	32,500	1.8×10^{21}	-1.5	0	T ≤ 3000
45				$5.4 \times 10^{18 \pm .5}$	-0.5	0	
20				1.8×10^{21}	-1.5	0

Ref.	$k_f(n = 1)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
4				1.2×10^{17}	0	0	T = 2500
10				1.9×10^{21}	-1.5	0	
13				1.92×10^{21}	-1.5	0	
14				1.2×10^{21}	-1.5	0	T ≤ 3000
45				$5.4 \times 10^{19 \pm .5}$	-1.0	0	

*Nawrocki⁴ gives 7.0 ev for this reaction.

C. Photodetachment, Radiative Attachment

Ref.	$k_f(n = 0)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
65				$6 \times 10^{6 \pm 2}$	0	0	T = 3000
4				6×10^4	0	0	
6				6.0×10^5	0	0	
66				6×10^5	0	0	

*Nawrocki⁴ suggests 0.9 ev for this reaction.

Ref.	$k_f(n = 0)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
4				7.2×10^8	0	0	T = 2000
6				7.2×10^8	0	0	
16				7.2×10^8	0	0	
66				7.2×10^8	0	0	T = 3000

Ref.	$k_f(n = 0)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
4				7.8×10^{11}	0	0	T = 1000
4				4.8×10^{11}	0	0	T = 2000
45				$1.35 \times 10^{14 \pm 1}$	-0.75	0

Ref.	$k_f(n=0)$			$k_r(n=1)$			Applicable Range (°K)
	a	b	c	a	b	c	
4				6×10^{11}	0	0	

*Nawrocki⁴ suggests 12.0 ev for this reaction.

Ref.	$k_f(n=0)$			$k_r(n=1)$			Applicable Range (°K)
	a	b	c	a	b	c	
4				$6 \times 10^{11 \pm 2}$	0	0

Ref.	$k_f(n=0)$			$k_r(n=1)$			Applicable Range (°K)
	a	b	c	a	b	c	
4				6×10^{11}	0	0

Ref.	$k_f(n=0)$			$k_r(n=1)$			Applicable Range (°K)
	a	b	c	a	b	c	
6				6×10^8	0	0	

IV. Miscellaneous Reactions

A. Nonradiative Processes

Ref.	$k_f(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
	a	b	c	a	b	c	
4				$3.6 \times 10^{14 \pm 3}$	0	0	
45				$3.6 \times 10^{16 \pm 1}$	0	0

Ref.	$k_f(n = 1)$			$k_r(n = 2)$			Applicable Range (°K)
	a	b	c	a	b	c	
14	2.7×10^{-1}	2.5	141,000				$T \leq 5000^*$

*See discussion for equation for temperatures up to 30,000°K.

B. Radiative Processes

Ref.	$k_f(n = 0)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
14				$6 \times 10^{3 \pm 2}$	0	0

Ref.	$k_f(n = 0)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
45				$6 \times 10^{1 \pm 2}$	0	0

Ref.	$k_f(n = 0)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
45				$6 \times 10^{8 \pm 3}$	0	0

Ref.	$k_f(n = 0)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
45				$6 \times 10^{10 \pm 2}$	0	0

Ref.	$k_f(n = 0)$			$k_r(n = 1)$			Applicable Range (°K)
	a	b	c	a	b	c	
45				$6 \times 10^{3 \pm 2}$	0	0	
67				1.07×10^{11}	-1.59	-337	T = 200-4000

DISCUSSION

In the following section, the various factors which have gone into measuring or calculating the reaction rate tables are discussed in some detail. The important parameters considered are test environment, range of applicability, and the reasons given for accepting or rejecting the products of other work. The discussion is divided into groups arranged in the same order as are the reactions in the tables, except for the "General" category, which applies to all the reactions considered by the investigators mentioned here.

General

Wray, et al.¹⁰ chose the recombination rate constant expressions of Matthews,³⁴ Camac and Vaughan,³⁵ Byron,³⁶ and Camac, et al.⁶⁸ Lenard¹⁶ got his reaction rates from Bortner.^{6,70} Chung¹⁷ accepted the rates of Lin and Teare.⁷¹ Vinokur, et al.²⁰ accepted the rates of Hall, et al.¹² and Bortner⁷⁰ and assumed ambient air to be 21 parts O₂ molecules and 79 parts N₂ molecules. Webb and Hromas²¹ chose from among the reaction rates given by Nawrocki,⁴ Hall, et al.,¹² Lin and Teare,⁷¹ and Chanin, et al.⁷² Reinhardt and Baldwin²² and Dushin and Lun'kin⁶⁹ used the rate constants of Hall, et al.¹² Spurk, et al.²³ used the rates of Marrone⁵ and Wray.⁹ Anisimov, et al.³⁰ applied the reaction rates of Lin and Fyfe⁸ in calculating species concentrations behind shock fronts for temperatures ranging from 3300 to 6000°K. Lezberg, et al.³² used the rates accepted by Momtchiloff, et al.²⁸ for calculations at 1.8 and 3.6 atmospheres pressure and for temperatures of about 1700 to 1900°K. Sotter⁷³ accepted the rate-constant expressions of Ellis and Bahn.¹³ Marrone⁵ stated that his air model has possible application for flight velocities of less than 23,000 ft/sec. Eschenroeder, et al.¹¹ considered pressures of 100 to 1000 atmospheres. Lin and Teare¹⁴ performed their calculations for 21% O₂ - 79% N₂ by partial pressure, at initial pressures of from 0.02 to 0.2 mm Hg and shock velocities of from 4.5 to 7 km/sec. Momtchiloff, et al.²⁸ used their rates for calculations at 1-atm pressure.

I. Neutral Species

A. Dissociation, Three-Body Recombination

M = Nonspecific. The reverse value given for Harteck, et al.¹ and Herron, et al.² was reported by Nawrocki.⁴ Duff and Davidson³ assumed a reverse rate of $3 \times 10^{14} \text{ cm}^6 \text{ mole}^{-2} \text{ sec}^{-1}$, which, they said, is in line with the investigations of Byron⁷⁴ and of Bunker and Davidson.⁷⁵

M = N₂. Hammerling, et al.⁷ and Lin and Fyfe⁸ calculated reverse rates from O₂ recombination rates according to Keck's⁷⁶ statistical theory for three-body recombination. The value derived by Hammerling, et al.,⁷ along with the rate determined by Wray, et al.⁶²

was used by Eschenroeder, et al.¹¹ and Hall, et al.¹² to calculate the forward reaction rate. Wray⁹ accepted Byron's⁷⁷ forward rate, which is based on experiments in N₂-argon mixtures. Ellis and Bahn¹³ accepted the forward reaction rate derived by Eschenroeder, et al.¹¹ Cary's¹⁵ value was reported by Langan, et al.¹⁹ from experiments with nitrogen. Cary's¹⁸ dissociation rate constant, said to be within ± 50 percent correct, was based on studies of pure nitrogen and mixtures of nitrogen and argon or helium at initial pressures of 9 to 43 mm Hg. He found the dissociation zone to be at least six times longer than the vibrational zone; therefore the coupling could be ignored, at least within the temperature range of 6000 to 10,000°K. Langan, et al.¹⁹ assumed that the efficiency of N₂ as a third body is equal to that of O and five times larger than that of argon. Byron's²⁴ forward value was based on experiments of 5% N₂ in argon to 100% N₂, at pressures of 5 to 50 mm Hg and shock speeds of Mach 9 to 13. The temperature range covered was 6000 to 9000°K. The temperature exponent in the equation is within ± 1 . Byron's²⁴ reverse rate expression was obtained through use of the equilibrium constant.

M = N. Hammerling, et al.⁷ assumed the efficiency of N as being five times that of N₂ for the reverse reaction rate, while Langan, et al.¹⁹ chose an N efficiency equal to three times that of argon. Lin and Fyfe⁸ extrapolated their reverse rate from oxygen values according to Keck.⁷⁶ Wray⁹ again accepted Byron's⁷⁷ reverse rate, which is based on experiments with N₂-argon mixtures. Hall, et al.¹² set the efficiency of N equal to five times the efficiency of N₂, based on Wray, et al.⁶² The value listed for Cary¹⁵ was reported by Langan, et al.¹⁹ and is based on experiments in nitrogen. The values listed for Allen, et al.²⁵ were based on experiments in pure nitrogen and were given by Wray.⁹ Cary's¹⁸ value was stated to be within ± 100 percent correct. Byron's²⁴ power of T was stated to be within ± 1 . See above for the experimental conditions used by Cary¹⁸ and Byron.²⁴

M = O₂, O, NO, or NO⁺. Marrone⁵ equated the efficiencies of all non-N or N₂ third bodies. From Keck,⁷⁶ Lin and Fyfe⁸ equated the efficiencies of O₂, O, NO, and argon, as did Wray⁹ for lack of other evidence. Wray⁹ based his value on Byron's⁷⁷ experiments in N₂-argon mixtures. Eschenroeder, et al.¹¹ considered the efficiencies of O and O₂ to be the same and equal to one-third the efficiency of N₂, based on Wray, et al.⁶² Hall, et al.¹² also based their value on Wray, et al.⁶² and equated the efficiency of NO to it. Lin and Teare¹⁴ said also that the efficiencies of O₂, O, and NO are the same, as did Vinokur, et al.,²⁰ Webb and Hromas;²¹ and Spurk, et al.²³ Lenard¹⁶ equated the efficiencies of O, O₂, NO, and NO⁺. Langan, et al.,¹⁹ however, said that the efficiencies of O₂ and NO are equal to twice that of argon, and the efficiencies of N₂ and O are equal to five times that of argon.

M = Nonspecific. The reverse rate of Duff and Davidson³ was assumed and said to be in line with Byron⁷⁴ and Bunker and Davidson.⁷⁵ The reverse rate listed for Golden and Myerson²⁶ is from Nawrocki.⁴ Duff²⁷ modified the forward rate of Benson and Axworthy³³ to account for the nature of the third body, while his reverse rate was suggested by Davidson⁷⁸ from halogen studies. Duff²⁷ used these in calculating shock profiles at initial pressure of 5 cm Hg and shock velocity of 3.77 mm/ μ sec. Momtchiloff, et al.²⁸ used the same reverse

rate for general third bodies and for temperatures between 1000 and 3300°K that Matthews³⁴ calculated for O₂ as the third body at temperatures below 1000°K. Lezberg, et al.,³² as mentioned earlier, accepted the reaction rates as given by Momtchiloff, et al.²⁸ Westenberg and Favin²⁹ took the reverse rate that Rink, et al.³⁷ found for O₂ as the third body, and applied it to calculations involving pressures of 0.1 to 100 atmospheres at 3000°K.

M = O₂. Byron's³⁶ forward rate value was given by Wray.⁹ Eschenroeder, et al.,¹¹ and Hall, et al.¹² calculated their forward reaction rates from Byron's³⁶ data from experiments with shock-heated oxygen, oxygen-argon mixtures, and air. The reason for the discrepancy in these calculated values is unknown. Lin and Fyfe⁸ and Wray⁹ based their rates on the O₂-argon experiments of Camac and Vaughan.³⁵ Wray⁹ assumed the efficiency of O₂ to be nine times that of argon. Ellis and Bahn¹³ based their dissociation rate on the work of Matthews.³⁴ Langan, et al.¹⁹ assumed the efficiency of O₂ to be five times as great as that of argon. Benson and Axworthy³³ gave a probable forward rate constant, based on their experiments with ozone. Matthews³⁴ based his values on experiments in pure oxygen at initial pressures of 1 to 2 cm Hg and shock velocities of Mach 8 to 10. Camac and Vaughan³⁵ and Rink, et al.³⁷ stated their values to be good to ±20 percent. Rink, et al.³⁷ studied O₂-xenon mixtures at initial pressures of 9 to 30 mm Hg. Rink³⁸ set the efficiency of O₂ equal to three times that of xenon, based on earlier experiments.³⁷ The T exponent was assumed. Wilson³⁹ studied O₂-argon mixtures at an initial pressure of 2 cm. Rink, et al.³⁷ and Wilson³⁹ assumed a T⁻¹ dependence for the reverse reaction, since it is somewhere between -1/2 and -2. Wise and Rosser⁴⁰ took their approximate recombination rate constant expression from Kaufman and Kelso⁷⁹ and stated that the dissociation energy for O₂ used by Benson and Axworthy³³ is too low. Wray⁴¹ studied dilute mixtures of O₂ in argon in a shock tube to get his expression for the dissociation of O₂. He set the efficiency of O₂ equal to 18 times that of argon. To determine the recombination rate constant, Wray⁴¹ studied dilute mixtures of ozone in argon at temperatures of 1500 to 3000°K. He gave both rate constant expressions as being within 14 percent correct at the temperatures considered. Kiefer and Lutz⁴² studied oxygen-ozone-argon/krypton mixtures at initial pressures of 4.18 to 12.89 cm Hg and shock velocities of 0.958 to 1.785 mm/μsec. Schexnayder and Evans⁸⁰ studied oxygen and oxygen-argon mixtures at pressures of 0.5 to 4 mm Hg and temperatures of 4,000 to 10,000°K. A rate expression for their work was given by Greene and Toennies.⁸¹

M = O. Refer to the above paragraph for the experimental conditions used by the various investigators. Hall, et al.¹² calculated their forward rate from Byron's³⁶ work, and Lin and Fyfe⁸ based their reverse rate on the experiments of Camac and Vaughan.³⁵ Wray⁹ and Langan, et al.¹⁹ assumed the efficiency of O as being 25 times as great as that of argon; but after further experiments, Wray⁴¹ accepted an O efficiency of 50 times that of argon and slightly under 3 times that of O₂. Camac and Vaughan³⁵ and Rink, et al.³⁷ stated that their values are good to ±20 percent. Byron's³⁶ value was given by Wray.⁹ Rink, et al.³⁷ derived, and Kiefer and Lutz⁴² accepted, an O efficiency equal to 3 times that of O₂. Rink³⁸ found the efficiency of O to be 10 times that of xenon.

M = N₂. Lin and Fyfe⁸ based their reverse rate on the experiments of Camac and Vaughan.³⁵ Wray⁹ gave N₂ an efficiency twice that of argon. Eschenroeder, et al.¹¹ and Hall, et al.¹² set the efficiency of N₂ as one-third that of O₂. Byron's³⁶ value was given by Wray.⁹

M = N, NO, or NO⁺. Wray⁹ set the efficiencies of N and NO as equal to argon, for lack of further evidence. From Wray, et al.,⁶² Hall, et al.¹² set the efficiencies of N and NO equal to that of N₂. Vinokur, et al.²⁰ and Spurr, et al.²³ also equated the efficiencies of N, NO, and N₂. Lenard¹⁶ added NO⁺ to this series of equal efficiencies. Based on Camac and Vaughan's³⁵ experiments, Lin and Fyfe⁸ set the efficiencies of N, NO, and N₂ equal to that of argon, but Langan, et al.¹⁹ set them equal to twice that of argon.

M = Nonspecific. Duff and Davidson³ assumed their reverse rate and stated it as being in line with Byron⁷⁴ and Bunker and Davidson.⁷⁵ Eschenroeder, et al.¹¹ stated that the efficiency of argon as a third body is generally considered to be one-sixth that of the other species, but that the lumped third-body dependence will have little effect because of the low concentration of argon. They calculated their forward rate from the Wray, et al.⁶² reverse rate and the equilibrium constant. Hall, et al.¹² calculated their forward rate from the reverse rate of Wray, et al.⁶² and the equilibrium constant, and assumed equal efficiencies for O₂, N₂, O, N, and NO. Ellis and Bahn¹³ chose a forward rate based on the recombination rate given by Wray, et al.^{10,62} Momtchiloff, et al.²⁸ and, in turn, Lezberg, et al.³² accepted the rates of Wray, et al.¹⁰ Freedman and Daiber⁴³ obtained their forward rate by studying nitric oxide-argon mixtures at initial pressures of 10 to 40 cm Hg. Their reverse rate was obtained from their forward rate and the equilibrium constant.

M = N₂ or O₂. Lin and Fyfe⁸ based their reverse rate value on the experiments of Wray and Teare⁸² and set the efficiencies of N₂ and O₂ equal to that of argon. Wray⁹ accepted the value given by Wray and Teare⁵⁶ based on studies of air and mixtures of air and argon, nitric oxide and argon, and nitric oxide, oxygen, and argon. Here he set the efficiency of argon equal to that of N₂ and O₂, but elsewhere¹⁰ argon is given an efficiency of only one-sixth that of N₂, O₂, N, O, or NO. Langan, et al.¹⁹ set the efficiencies of N₂ and O₂ as equal to twice that of argon, the value of which they chose as intermediate between the values of Wray and Teare⁵⁶ and Freedman and Daiber.⁴³

M = N, O, NO, or NO⁺. Lin and Fyfe⁸ equated the efficiencies of N, O, and NO and based this on the experiments of Wray and Teare.⁸² Wray⁹ also assumed the equivalence of the efficiencies of N, O, and NO and set them equal to 20 times the efficiency of argon, but Langan, et al.¹⁹ equated the efficiencies of NO, N₂ and O₂ and set them equal to twice that of argon. Lin and Teare¹⁴ and Webb and Hromas²¹ set the efficiencies of N and O equal to that of N₂ and O₂. Lenard¹⁶ added to this series the efficiency of NO⁺. Langan, et al.¹⁹ assumed the efficiencies of O and N to be the same and equal to 5 times that of argon.

M = Nonspecific. Ellis and Bahn¹³ accepted the forward rate of Davidson.⁸³ Duff's²⁷ value for the forward rate constant was taken from Benson and Axworthy,³³ but was modified slightly to account for the nature of the third body. The value is for a shock wave in oxygen with an initial pressure of 5 cm Hg, a velocity of 3.77 mm/ μ sec, and a temperature of 6000°K after vibrational equilibrium but before any dissociation has occurred. Duff's²⁷ calculations showed that the ozone mechanism of Benson and Axworthy³³ contributes less than 1/2 percent of the total dissociation rate of oxygen, and can be neglected. The value listed for Jones and Davidson⁴⁴ was given by Kiefer and Lutz⁴² and is based on studies of ozone decomposition at high temperatures.

M = O₂, N₂, or O₃. Benson and Axworthy³³ experimented with mixtures of ozone and oxygen at about 373°K to get a forward reaction rate constant with O₃ as the third body. They announced efficiencies of 0.44 and 0.41 for O₂ and N₂, respectively, as third bodies compared to ozone. They calculated the reverse rate from the forward rate and thermochemical data. Kondratiev⁴⁶ used the reverse rate of Benson and Axworthy³³ for oxygen as the third body, but the reason for the difference in both sign and magnitude of the activation energy given is unknown.

B. Rearrangement

Kaufman and Kelso⁴⁷ determined their reverse rate value by studying the decomposition of nitric oxide in pure nitric oxide, and in nitric oxide and nitrogen or helium mixtures. They defined their reverse rate with a factor of 1 in their calculations. Freedman and Daiber⁴³ also used a factor of 1 for their reverse rate, and determined it by studying shock-heated mixtures of nitric oxide and argon at pressures ranging from 10 to 40 cm Hg. Kaufman and Decker⁴⁸ accepted a slightly smaller preexponential factor than did Kaufman and Kelso,⁴⁷ and defined it with a factor of 1. Freedman and Daiber⁴³ combined Kaufman and Kelso's⁴⁷ data with their own data to give an expression covering a wider temperature range than either value individually. This composite value is defined with a factor of 1. Wray⁹ accepted this composite value, since it agreed with his own data, and calculated the forward reaction rate from it and the equilibrium constant. Langan, et al.¹⁹ also used the Freedman-Daiber-Kaufman-Kelso composite reverse reaction rate value, but defined it with a factor of 2. The reverse rate value listed for Yuan, et al.⁴⁹ was given by Wray,⁹ and is with a factor of 1. It is based on experimental studies of the decomposition of NO. Momtchiloff, et al.²⁸ and apparently Nawrocki⁴ got their forward reaction rate values from Kaufman and Kelso,⁴⁷ while Hall, et al.,¹² Ellis and Bahn,¹³ and apparently Marrone⁵ accepted Wray's⁹ calculated value. Duff and Davidson³ stated that, using the reverse reaction rate value of Kaufman and Kelso,⁴⁷ at a shock temperature of 7000°K this reaction contributes less than 4 percent of the NO produced.

Glick, et al.⁵⁰ studied the formation of nitric oxide by experimenting with diluted air and mixtures of oxygen and nitrogen of various proportions. The air diluents used were argon, krypton, and mixtures of argon and helium. They found the Zel'dovich⁸⁴ chain mechanism to dominate the formation of nitric oxide in the temperature range 2000 to 3000°K, with the reaction $\text{N}_2 + \text{O} \rightarrow \text{NO} + \text{N}$ being the rate-determining step in the chain. From the data of Glick, et al.,⁵⁰ many investigators, among them Davidson,⁸³ Freedman and Daiber,⁴³ and Wray,⁹ calculated the rate values listed as those of Glick, et al.⁵⁰ Duff and Davidson³ show by calculation that the Zel'dovich mechanism is not descriptive of the reactions of high-temperature undiluted air, and that the forward rate value from the data of Glick, et al.⁵⁰ is too low by 35 percent at 3000°K. Ellis and Bahn¹³ accepted a forward reaction rate constant expression from Marrone.⁸⁵ Bauer and Tsang⁵³ accepted the value of Wray⁸⁶ for their calculations. Lin and Fyfe,⁸ Wray, et al.,¹⁰ Eschenroeder, et al.,¹¹ Hall, et al.,¹² Freedman and Daiber,⁴³ and apparently, Nawrocki⁴ and Marrone⁵ accepted the values of Glick, et al.⁵⁰ Wray,⁹ Lenard¹⁶ (through Bortner⁷⁰), and Langan, et al.¹⁹ chose the modified forward value suggested by Duff and Davidson.³ Momtchiloff, et al.²⁸ used the value of Davidson.⁸³ The reverse rate values listed for Kaufman and Decker,⁴⁸ Kistiakowsky and Volpi,⁵¹ and ARF⁵² are from Nawrocki.⁴ Kaufman and Kelso⁴⁷ estimated their reverse rate from the rate of the reaction $\text{N} + \text{O}_2 \rightarrow \text{NO} + \text{O}$. Langan, et al.¹⁹ calculated their reverse rate from their chosen forward rate and the equilibrium constant.

Duff and Davidson³ used the reverse rate that Davidson⁸³ determined from the experiments of Glick, et al.⁵⁰ and Kistiakowsky and Volpi,⁵⁴ extrapolated from low temperatures. Lin and Fyfe,⁸ Wray, et al.,¹⁰ Eschenroeder, et al.,¹¹ and Hall, et al.¹² increased by a factor of 10 the value determined by Davidson⁸³ so that it would fall in line with the data of Wray, et al.⁶² and Wray and Teare.⁸² Kaufman and Kelso⁴⁷ determined their forward rate constant from Vetter's⁸⁷ data, and stated that this is the rate-controlling reaction in the nitric oxide decomposition chain above about 1800 to 1900°K and in the presence of excess oxygen. Their reverse rate was calculated from their forward rate and the equilibrium constant. The reverse rate values listed for ARF,⁵² Kaufman and Decker,⁴⁸ and Kistiakowsky and Volpi⁵⁴ are from Nawrocki.⁴ Kaufman and Decker⁴⁸ calculated their forward rate value from the reaction $\text{NO} + \text{NO} \rightarrow \text{N}_2 + \text{O}_2$, and their reverse rate value, given by Wray,⁹ from the forward rate and the equilibrium constant. Wray and Teare⁵⁶ studied mixtures of nitric oxide, oxygen, and argon. They combined their data with those of other investigators to produce the value listed for Wray and Teare,⁵⁶ as given by Wray.⁹ This forward rate value was accepted by Langan, et al.¹⁹ and used to calculate their reverse rate value. Ellis and Bahn¹³ also accepted the forward rate value determined by Wray and Teare.⁵⁶ Momtchiloff, et al.²⁸ accepted the reverse rate value of Vincenti.⁵⁵

Ellis and Bahn¹³ got their value from Davidson.⁸³ Benson and Axworthy³³ based their values on the dissociation rate of ozone and thermochemical data. Duff's²⁷ forward reaction rate value was taken from Benson and Axworthy,³³ but modified slightly. The reverse rate of Jones and Davidson⁴⁴ was given by Kiefer and Lutz,⁴² and is based on studies of high-temperature ozone decomposition.

The rates given for these last two reactions by Bauer and Tsang⁵³ were assumed.

II. Charged Species

A. Charge Exchange

The reaction rate used by Hammerling, et al.⁷ for the reaction $\text{N}_2 + \text{N}^+ + 1.0 \text{ ev} \rightarrow \text{N}_2^+ + \text{N}$ was extrapolated from Sayers'⁸⁸ work with oxygen. The reverse rate listed for Wray, et al.¹⁰ and accepted by Ellis and Bahn¹³ is also based on Sayers'⁸⁹ work with oxygen. Fehsenfeld, et al.⁵⁷ added oxygen or nitrogen to fast-flowing streams of weakly ionized helium to get an expression for the rate of the reaction $\text{N}_2^+ + \text{O}_2 \rightarrow \text{N}_2 + \text{O}_2^+ + 3.5 \text{ ev}$. Bortner's⁴⁵ rate for the reaction $\text{O}_2^+ + \text{NO} \rightarrow \text{O}_2 + \text{NO}^+ + 2.8 \text{ ev}$ was taken from Fite, et al.⁹⁰ The rate for the reaction $\text{O}_2 + \text{O}^+ \rightarrow \text{O}_2^+ + \text{O} + 1.6 \text{ ev}$ listed for Wray, et al.¹⁰ and accepted by Ellis and Bahn¹³ is based on the work of Sayers.⁸⁹ The value for the rate of the reaction $\text{O}_2^- + \text{O} \rightarrow \text{O}_2 + \text{O}^- + 1.0 \text{ ev}$ listed for Haaland⁵⁹ was given by Nawrocki.⁴

B. Ion-Pair Formation, Mutual Neutralization

The values for the rates of the reactions $\text{O}_2^+ + \text{O}^- \rightarrow \text{O}_2 + \text{O} + 10.7 \text{ ev}$ and $\text{O}_2^+ + \text{O}_2^- \rightarrow \text{O}_2 + \text{O}_2 + 11.4 \text{ ev}$ listed for Mitra⁶⁰ were given by Nawrocki.⁴

C. Rearrangement

For the reactions $\text{N}_2 + \text{O}^+ \rightarrow \text{NO}^+ + \text{N} + 1.1 \text{ ev}$ and $\text{N}^+ + \text{O}_2 \rightarrow \text{NO}^+ + \text{O} + 6.7 \text{ ev}$, Fehsenfeld, et al.⁵⁷ studied the effects of O_2 or N_2 on weakly ionized helium afterglows, as mentioned above.

III. Reactions Involving Free Electrons

A. Detachment, Three-Body Recombination

Lin and Teare¹⁴ extrapolated ionization cross section graphs to get forward rate expressions good to ± 30 percent for temperatures up to 30,000°K. Their expression with O_2 as the third body is:

$$k_f = 6.6 \times 10^{-10} T^{9/2} (1 + 4 \times 10^{-5} T) e^{-141,000/T} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}.$$

For N_2 as the third body, their expression is:

$$k_f = 2.71 \times 10^{-1} T^{5/2} (1 + 3 \times 10^{-5} T) e^{-141,000/T} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}.$$

Nawrocki⁴ and Bortner⁴⁵ both obtained their reverse rate values from Massey and Burhop.⁹¹ Ellis and Bahn¹³ took their forward reaction rate value from Atallah.⁹² Vinokur, et al.²⁰ assumed that the recombination of an electron with positively charged oxygen and nitrogen atoms has the same rate with the same third bodies in their calculations of the reverse rates.

Lin and Teare¹⁴ again extrapolated ionization cross section graphs to obtain an expression for the forward reaction rate said to be valid to ± 30 percent for temperatures up to 30,000°K. For N_2 as the third body, the derived expression is:

$$k_f = 1.7 \times 10^{-4} T^{7/2} (1 + 3 \times 10^{-5} T) e^{-181,000/T} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}.$$

Vinokur, et al.²⁰ again assumed that the recombination of an electron with O^+ and with N^+ has the same rate with the same third-body species. Ellis and Bahn¹³ took their forward reaction rate value from Atallah.⁹²

Bortner,⁴⁵ from Chanin, et al.⁷² and Phelps and Pack,⁹³ set the efficiencies of N₂, O₂, and O to be equal for the forward reaction rate, but accepted an efficiency of O₂ as being 30 times as large as that of N₂ for the reverse reaction. Later, Bortner⁶ accepted a general third-body efficiency and introduced a T factor. Webb and Hromas²¹ accepted an oxygen efficiency 100 times greater than other third-body efficiencies for both forward and reverse reactions. Langan, et al.,¹⁹ from Bortner,⁷⁰ accepted an O₂ efficiency equal to 25 times that of N₂ or argon.

Nawrocki⁴ accepted a forward reaction rate at 25 ev from Branscomb and Smith.⁹⁴ Lenard¹⁶ and Webb and Hromas²¹ set the efficiencies of N₂, O₂, N, O, and NO as being equal. Langan, et al.¹⁹ accepted rate values from Bortner,⁷⁰ which are based on Bailey and Branscomb,⁹⁵ and set the efficiency of O₂ equal to 25 times that of N₂ or argon.

B. Associative Detachment; Dissociative Recombination

The reverse rate value listed for ARF⁶³ was given by Nawrocki.⁴ Lin and Teare¹⁴ reported their values as being valid within ± 20 percent. Hall, et al.¹² got their reverse rate value from Teare, et al.,⁹⁶ Lin, et al.,⁹⁷ and Eschenroeder.⁹⁸ The forward rate value listed for Lin⁶¹ was reported by Langan, et al.¹⁹ who modified the activation energy value given by Lin. Wray, et al.⁶² accepted the value of Lin,⁶¹ and used it with the equilibrium constant for T > 10,000°K to calculate the reverse reaction rate. Ellis and Bahn¹³ also accepted the results of Lin's⁶¹ studies, but the vastly differing preexponential factor remains unexplained. Myers⁶⁴ studied various ratios of O₂ and N₂ in 98-percent neon in a shock tube at temperatures of 5100 to 7750°K.

The reverse rate value listed for ARF⁶³ was given by Nawrocki.⁴ Wray, et al.¹⁰ based their reverse reaction rates on the work of Sayers⁸⁹ with oxygen. Ellis and Bahn¹³ accepted these values given by Wray, et al.¹⁰

C. Photodetachment, Radiative Attachment

Phelps and Pack⁶⁶ got their rates for the radiative attachment of electrons to O_2 and O from Branscomb.⁹⁹ The value listed for ARF⁶⁵ was given by Nawrocki.⁴ Nawrocki⁴ took his value for the reaction $O + e \rightarrow O^- + h\nu + 1.46 \text{ ev}$ from Branscomb, et al.¹⁰⁰ Bortner⁴⁵ based his rate for the reaction $O^+ + e \rightarrow O + h\nu + 13.6 \text{ ev}$ on the work of Bates, et al.,¹⁰¹ Breene,¹⁰² and Bates and Dalgarno.¹⁰³ Nawrocki⁴ obtained his rate for the reaction $N^+ + e \rightarrow N + h\nu + 14.5 \text{ ev}$ by analogy.

IV. Miscellaneous Reactions

A. Nonradiative Processes

Lin and Teare¹⁴ extrapolated ionization cross section graphs to get a rate expression for the reaction $N_2 + O_2 + 11.2 \text{ ev} \rightarrow NO + NO^+ + e$. They claimed an accuracy of ± 30 percent for temperatures up to $30,000^\circ K$ for their expression:

$$k_f = 2.71 \times 10^{-1} T^{5/2} (1 + 3 \times 10^{-5} T) e^{-141,000/T} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}.$$

B. Radiative Processes

For the reaction $O + O \rightarrow O_2 + h\nu + 5.1 \text{ ev}$, Bortner⁴⁵ based his value on the studies of Nicolet¹⁰⁴ and Nicolet and Mange.¹⁰⁵ He used the works of Bates¹⁰⁶ and Danilov¹⁰⁷ as the basis for his value for the rate of the reaction $O + O^+ \rightarrow O_2^+ + h\nu + 6.5 \text{ ev}$, and the studies of Fite, et al.⁹⁰ for a rate expression for the reaction $N_2^+ + N_2 \rightarrow N_4^+ + h\nu$. Bortner⁴⁵ obtained his rate constant expression for the reaction $NO + O \rightarrow NO_2 + h\nu + 3.2 \text{ ev}$ from Clyne and Thrush.¹⁰⁸ Levitt⁶⁷ analyzed the works of Clyne and Thrush¹⁰⁹ and Fontijn, et al.¹¹⁰ to produce an expression for this reaction. Broida, et al.,¹¹¹ however, believed that excited states of NO_2 are involved and that several steps are involved in this over-all reaction.

AIR MODELS CHOSEN BY VARIOUS INVESTIGATORS*

Dushin and Lun'kin (1966), Reference 69

These reactions were chosen for a study of a flow of a supersonic stream of nonequilibrium-dissociating air around blunt bodies.

1. $O_2 + M \rightleftharpoons O + O + M$ (M = O_2 , N_2 , NO, O, N, Ar)
2. $N_2 + M \rightleftharpoons N + N + M$ (M = O_2 , N_2 , NO, O, N, Ar)
3. $NO + M \rightleftharpoons N + O + M$ (M = O_2 , N_2 , NO, O, N, Ar)
4. $N + O_2 \rightleftharpoons NO + O$
5. $N_2 + O \rightleftharpoons NO + N$
6. $N_2 + O_2 \rightleftharpoons NO + NO$

Spurk, Gerber, and Sedney (1966), Reference 23

These reactions were chosen for a study of inviscid supersonic flow fields around pointed bodies.

1. $O_2 + M \rightleftharpoons O + O + M$ (M = N_2 , N, NO; O_2 ; O)
2. $N_2 + M \rightleftharpoons N + N + M$ (M = O_2 , O, NO; N_2 ; N)
3. $NO + M \rightleftharpoons N + O + M$ (M = O_2 , O, N_2 , N, NO)
4. $N_2 + O \rightleftharpoons NO + N$
5. $N + O_2 \rightleftharpoons NO + O$
6. $N_2 + O_2 \rightleftharpoons NO + NO$

Reinhardt and Baldwin (1965), Reference 22

These reactions were chosen for a study of nonequilibrium, chemically reacting airflows.

1. $N_2 + M \rightleftharpoons N + N + M$ (M = N_2 ; N; O, O_2)
2. $O_2 + M \rightleftharpoons O + O + M$ (M = O_2 ; O; N_2 , N)
3. $NO + M \rightleftharpoons N + O + M$ (M = Nonspecific)
4. $O_2 + N \rightleftharpoons NO + O$
5. $N_2 + O \rightleftharpoons NO + N$

*Note: Within the parentheses, the specified third bodies separated by commas are considered by the author(s) to have the same efficiencies. Those separated by semicolons are thought to have different efficiencies.

Webb and Hromas (1965), Reference 21

These reactions were chosen for a study of a reacting wake.

1. $N + N + M \rightleftharpoons N_2 + M$ (M = O₂, O, NO; N; N₂)
2. $O + O + M \rightleftharpoons O_2 + M$ (M = NO, N; N₂; O₂; O)
3. $N + O + M \rightleftharpoons NO + M$ (M = NO; N₂, O₂, N, O)
4. $N + O_2 \rightleftharpoons NO + O$
5. $NO + N \rightleftharpoons N_2 + O$
6. $NO + NO \rightleftharpoons N_2 + O_2$
7. $NO^+ + e \rightleftharpoons N + O$
8. $O_2 + e + M \rightleftharpoons O_2^- + M$ (M = N₂, NO, N, O; O₂)
9. $O + e + M \rightleftharpoons O^- + M$ (M = N₂, O₂, NO, N, O)
10. $O^- + NO^+ \rightleftharpoons O + NO$
11. $O_2^- + NO^+ \rightleftharpoons NO + O_2$
12. $O_2^- + O \rightleftharpoons O^- + O_2$

Vinokur, Nicolet, Buckingham, and Hoshizaki (1965), Reference 20

These reactions were chosen for a study of inviscid flow fields.

1. $O_2 + M \rightleftharpoons O + O + M$ (M = O₂; O; N₂, N, NO)
2. $N_2 + M \rightleftharpoons N + N + M$ (M = N₂; N; O₂, O, NO)
3. $NO + M \rightleftharpoons N + O + M$ (M = Nonspecific)
4. $O_2 + N \rightleftharpoons NO + O$
5. $N_2 + O \rightleftharpoons NO + N$
6. $N_2 + O_2 \rightleftharpoons NO + NO$
7. $NO^+ + e \rightleftharpoons N + O$
8. $N_2^+ + e \rightleftharpoons N + N$
9. $O + M \rightleftharpoons O^+ + e + M$ (M = N₂; O₂; NO; N, O; e)
10. $N + M \rightleftharpoons N^+ + e + M$ (M = N₂; O₂; NO; N, O; e)

Chung (1965), Reference 17

These reactions were listed as being the major neutral gas reactions in air boundary layers.

1. $O_2 + M \rightleftharpoons O + O + M$ (M = O; O₂; N₂; N, NO)
2. $N_2 + M \rightleftharpoons N + N + M$ (M = N; N₂; O₂, O, NO)
3. $NO + M \rightleftharpoons N + O + M$ (M = NO; N₂, O₂, N, O)
4. $N_2 + O \rightleftharpoons NO + N$

These reactions were chosen for a study of atmospheric deionization.

Well-characterized reactions important to atmospheric deionization:

1. $O + e \rightarrow O^- + h\nu$
2. $N_2^+ + e \rightarrow N + N$
3. $O_2^+ + e \rightarrow O + O$
4. $O_2 + e + M \rightarrow O_2^- + M$ (M = O_2)
5. $O + O + M \rightarrow O_2 + M$ (M = O_2 ; O; $\neq O_2$ or O)
6. $O + O_2 + M \rightarrow O_3 + M$ (M = Nonspecific)
7. $O + O_3 \rightarrow O_2 + O_2$
8. $N + NO \rightarrow N_2 + O$
9. $N + O_2 \rightarrow NO + O$

Important reactions most needing investigating:

1. $NO^+ + e \rightarrow N + O$
2. $N_2^+ + O \rightarrow N_2 + O^+$
3. $N_2^+ + O \rightarrow NO^+ + N$
4. $N_2^+ + O_2 \rightarrow N_2 + O_2^+$
5. $O^+ + N_2 \rightarrow NO^+ + N$
6. $O^+ + O_2 \rightarrow O + O_2^+$
7. $O_2 + e \rightarrow O_2^- + h\nu$
8. $O_2^- + M \rightarrow O_2 + e + M$ (M = N_2 , O_2 , O)

Possibly important reactions that are inaccurately known:

1. $O_2^+ + NO \rightarrow O_2 + NO^+$
2. $O_2^+ + N_2 \rightarrow NO^+ + NO$
3. $N_2^+ + O_2 \rightarrow NO^+ + NO$
4. $NO^+ + O^- \rightarrow NO + O$
5. $O_2^+ + O^- \rightarrow O_2 + O$
6. $O^+ + O \rightarrow O_2^+ + h\nu$
7. $O^+ + O + M \rightarrow O_2^+ + M$ (M = Nonspecific)
8. $N_2^+ + N_2 \rightarrow N_4^+ + h\nu$
9. $N_2^+ + N_2 + M \rightarrow N_4^+ + M$ (M = Nonspecific)
10. $O + O \rightarrow O_2 + h\nu$
11. $O + O_2 \rightarrow O_3 + h\nu$

Bortner (1963) - continued

12. $N^+ + O_2 \rightarrow NO^+ + O$
13. $O_2^+ + N \rightarrow NO^+ + O$
14. $NO^+ + O_2^- \rightarrow NO + O_2$
15. $O_2^+ + O_2^- \rightarrow O_2 + O_2$
16. $O^+ + O^- \rightarrow O + O$
17. $O^+ + e \rightarrow O + h\nu$
18. $O^+ + e + M \rightarrow O + M$ (M = Nonspecific)

Reactions which are of great importance to the normal atmosphere but of limited importance to the disturbed atmosphere include:

1. Photodissociation of O_2 , O_3 , O_2^+
2. Photoionization of NO , O_2 , O , N , N_2

Marrone (1963), Reference 5

These reactions were chosen for a study of inviscid, nonequilibrium flow behind bow and normal shock waves.

1. $O_2 + M \rightleftharpoons 2 O + M$ (M = O_2 ; O ; $\neq O_2$ or O)
2. $N_2 + M \rightleftharpoons 2 N + M$ (M = N_2 ; N ; $\neq N_2$ or N)
3. $NO + M \rightleftharpoons N + O + M$ (M = Nonspecific)
4. $N + O_2 \rightarrow NO + O$
5. $O + N_2 \rightarrow NO + N$
6. $N + O \rightarrow NO^+ + e$
7. $N_2 + O_2 \rightarrow NO + NO$

Lin and Teare (1963), Reference 14

These reactions were chosen for a study of ionization behind strong shock waves.

1. $O_2 + M \rightleftharpoons 2 O + M$ (M = O ; O_2 ; N_2 ; N , NO)
2. $N_2 + M \rightleftharpoons 2 N + M$ (M = N ; N_2 ; O_2 , O , NO)
3. $NO + M \rightleftharpoons N + O + M$ (M = NO ; O , N , O_2 , N_2)
4. $O + N_2 \rightleftharpoons NO + N$
5. $NO + O \rightleftharpoons N + O_2$
6. $N_2 + O_2 \rightleftharpoons NO + NO$
7. $N + O \rightleftharpoons NO^+ + e$
8. $N + N \rightleftharpoons N_2^+ + e$

Lin and Teare (1963) - continued

Hall, Eschenroeder and Marrone (1962), Reference 12

These reactions were chosen for a study of blunt-nose inviscid airflows with coupled nonequilibrium processes.

Eschenroeder, Boyer and Hall (1962), Reference 11

These reactions were chosen for a study of the expansion of reacting air in a hypersonic nozzle and in a stream tube typical of those near blunt hypersonic bodies.

Wray (1962), Reference 9

These reactions were chosen for a survey of the chemical kinetics of high-temperature air.

CONCLUSION

An attempt has been made to clarify the origins of many of the reaction rate constant values in use today. The rate values for many high-temperature air reactions determined or adopted by various investigators have been presented and discussed. No attempt has been made to pass judgment on the validity of the individual rates. More extensive general listings of air-reaction rates can be found in the works of Nawrocki,⁴ Bortner,⁴⁵ and especially Ellis and Bahn.¹³

The various air models used by some of the investigators in the field of air reactions have been presented to show the trend of thinking along these lines.

FUTURE PLANS

This report will be updated periodically and will include the reactions of contaminants with normal air species as well. So far, the alkali metals seem to be the contaminants investigated most extensively, with water and carbon running close behind. Data for other contaminants appear to be quite scarce.

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