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A SURVEY OF THE REACTION RATE CONSTANTS FOR THE THERMAL DISSOCIATION AND RECOMBINATION OF NITROGEN AND OXYGEN

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ABSTRACT

The objective of the present report is to survey the various values of forward and backward reaction rate constants used up to date by investigators in the field of high temperature ($T > 2000°K$) gas reactions involving nitrogen and oxygen only. By comparing the various published rate constants, which were either estimated by the reference authors or adopted from the works of others, it is examined how closely these various values of reaction rate constants are reproduced. The objective is to find those values that correlate well so that they can be used for the studies of hypersonic flow and supersonic combustion with a reasonable confidence. The relatively good agreement among these various values is observed for the temperature lower than 10,000°K.

INTRODUCTION

The report lists various values of forward and backward reaction rate constants used up to date by investigators in the field of high temperature ($T \geq 2000°K$) gas reactions involving nitrogen and oxygen. The reactions considered in this paper are:

$$N_2 + N_2 \leftrightarrow N_2 + 2N \qquad 1(a)$$

$$N_2 + N \leftrightarrow N + 2N \qquad 1(b)$$

and

$$O_2 + O_2 \leftrightarrow O_2 + 2O \qquad 2(a)$$

$$O_2 + O \leftrightarrow O + 2O \qquad 2(b)$$

$$O_2 + N_2 \leftrightarrow N_2 + 2O \qquad 2(c)$$

A few of the reported values were determined experimentally. Some of the reported values were obtained by assuming a particular set of reactions and then modifying the rate constants until a satisfactory match could be made between predicted and experimentally determined concentration histories.

All reaction rate constants can be computed from:

$$k = aT^b e^{-c/T} \qquad (3)$$

where T is the absolute temperature in degrees Kelvin so that the units of k are $(cm^3/mole)^n sec^{-1}$. The values of a, b, and c are tabulated (Tables 1(a) to 2(c) with the forward reaction rate constant, k_f, on the left and the backward reaction rate constant, k_b, on the right. Above each set of a, b, and c values is the value of exponent n for that reaction. The applicable or used temperature ranges reported by the various investigators, and the reference number of the publication source of each listed value are also tabulated. All the listed values are plotted for easier visual comparison. Specifically, there are five sets of four figures. Each set corresponds to one of the above mentioned reactions and contains plots of $\log_{10}k_f$ vs. T, $\log_{10}k_b$ vs. T, K vs. T, and $\log_{10}$ K vs. T. Here, K are the equilibrium constants based on concentrations. They were computed as:

$$K = k_f/k_b \qquad (4)$$

Notice that in ref. 29:

$$K = \exp(A_1 + A_2Z + A_3Z^2 + A_4Z^3 + A_5Z^4) \qquad (5)$$

where

$$Z = 10{,}000/T \qquad (6)$$

One value for K was used for the reactions 1(a)-1(b) and another value for K was used for the reactions 2(a)-2(c). The corresponding values of the coefficients (ref. 29) are:

	A_1	A_2	A_3	A_4	A_5
1(a) or 1(b)	3.898	-12.611	0.683	-0.118	0.006
2(a), 2(b), or 2(c)	1.335	-4.127	-0.616	0.093	-0.005

The values of k_f for these reactions were given in ref. 29. We computed the corresponding values of k_b from the formulas (4), (5), and (6) with the help of the above table.

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CONCLUSION

An attempt has been made to correlate the published values for the reaction rate constants involving nitrogen and oxygen only. From the tabulated and plotted data it is possible to judge the validity of the individual rate constants in the temperature ranges considered here. It is obvious that there is a discrepancy of the published data for higher temperatures. Reliability of the published values for the backward reaction rates is highly questionable, thus, warranting a more accurate experimental and analytical verification of these parameters.

ACKNOWLEDGMENTS

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Table 1(a). Reaction Rate Constants

$N_2 + N_2 = N_2 + 2N$							
	k_f (n=1)			k_b (n=2)			Applicable Temp.
ref	a	b	c	a	b	c	Range (K)
1				2.2×10^{14}	0.5	0	
2				1.5×10^{20}	1.5	0	
3	3.0×10^{21}	-1.5	113,260				
4	2.8×10^{19}	-1.0	113,200	2.0×10^{18}	-1.0	0	7,400-23,000
5				2.8×10^{16}	-0.5	0	
6	3.0×10^{21}	-1.5	113,220				1,350-7,000
7	3.8×10^{19}	-1.0	113,200	2.0×10^{18}	-1.0	0	
8				2.0×10^{18}	-1.0	0	
9	4.8×10^{17}	-0.5	113,100	2.6×10^{16}	-0.5	0	high-temp.
10				1.78×10^{17}	-0.5	0	
11	4.8×10^{17}	-0.5	113,000				0-6,000
12	7.1×10^{19}	-1.0	113,225				6,000-10,000
13				1.5×10^{20}	-1.5	0	300-3,100
13	3.0×10^{21}	-1.5	132,600				300-4,500
14	4.75×10^{17}	-0.5	113,171				4,120-5,725
15	4.8×10^{17}	-1.5	113,100	2.6×10^{16}	-0.5	0	≥ 2,000
16	1.0×10^{22}	-1.5	113,232	9.55×10^{20}	-1.57	0	
17				1.5×10^{20}	-1.5	0	7,300-10,300
18				5.0×10^{14}	0	-503 ±151	90-6,400
19				1.4×10^{21}	-1.7	0	
20				1.5×10^{20}	-1.5	0	
26	3.7×10^{21} ±1.0	-1.6	113,200	2.2×10^{20} ±0.6	-1.6	0	8,000-15,000
27				3.0×10^{14}	0	-500	3,000-10,000
28	1.92×10^{17}	-0.5	113,100	1.09×10^{16}	-0.5	0	1,000-3,000
29	3.7×10^{21}	-1.6	113,200				500-50,000
30	3.0×10^{21}	-1.5	113,260	1.67×10^{20}	-1.5	810	
31	4.7×10^{17}	-0.5	113,200				

Table 1(b). Reaction Rate Constants

$N_2 + N = N + 2N$							
	k_f (n=1)			k_b (n=2)			Applicable Temp.
ref	a	b	c	a	b	c	Range (K)
2				7.5×10^{20}	-1.5	0	
3	1.5×10^{20}	-1.5	113,260				
4	1.3×10^{20}	-1.0	113,200	7.0×10^{18}	-1.0	0	7,400-23,000
5				2.4×10^{21}	-1.5	0	
6	1.5×10^{22}	-1.5	113,220				1,350-7,000
7	1.3×10^{21}	-1.0	113,200	7.0×10^{19}	-1.0	0	
8				7.0×10^{18}	-1.0	0	10,000
9	4.2×10^{22}	-1.5	113,100	2.3×10^{21}	-1.5	0	high-temp.
11	4.2×10^{22}	-1.5	113,000				0-6000
12				5.0×10^{15}	0	0	700-6,800
12	7.1×10^{19}	-1.0	113,225				6,000-10,000
13				7.5×10^{20}	-1.5	0	300-3,100
13	1.5×10^{22}	-1.5	132,600				300-4,500
14	4.1×10^{22}	-1.5	113,171				4,120-5,725
15	4.2×10^{22}	-1.5	113,100	2.3×10^{21}	-1.5	0	≥ 2,000
16	6.0×10^{21}	-1.5	113,232	5.73×10^{20}	-1.57	0	
17				7.5×10^{20}	-1.5	0	7,300-10,300
20				7.5×10^{20}	-1.5	0	
26	1.6×10^{22} ±0.6	-1.6	113,200	9.8×10^{20} ±3.6	-1.6	0	8,000-15,000
27				9.0×10^{14}	0	-500	3,000-10,000
28	4.15×10^{22}	-1.5	113,100	2.32×10^{21}	-1.5	0	1,000-3,000
29	1.11×10^{22}	-1.6	113,200				500-50,000
30	1.5×10^{22}	-1.5	113,260	8.33×10^{20}	-1.5	810	
31	4.1×10^{22}	-1.5	113,200				

Table 2(a). Reaction Rate Constants

$O_2 + O_2 = O_2 + 2O$							
	k_f (n=1)			k_b (n=2)			Applicable Temp.
ref	a	b	c	a	b	c	Range (K)
2	3.6×10^{21}	-1.5	59,380				
3	3.6×10^{21}	-1.5	59,380				
4	2.3×10^{19}	-1.0	59,400	1.9×10^{16}	-0.5	0	7,400-23,000
5				8.0×10^{19}	-1.5	0	
6	3.6×10^{21}	-1.5	59,360				1,350-7,000
7	2.3×10^{19}	-1.0	59,400	1.9×10^{16}	-0.5	0	
8				1.9×10^{16}	-0.5	0	10,000
9	3.3×10^{19}	-1.0	59,400	2.7×10^{16}	-0.5	0	high-temp.
11	3.3×10^{19}	-1.0	59,300				0-6,000
12	1.0×10^{16}	0	59,380				2,800-5,000
13	3.56×10^{21}	-1.5	59,380				300-3,100
14	3.26×10^{19}	-1.0	59,378				4,120-5,725
15	3.3×10^{19}	-1.0	59,400	2.7×10^{16}	-0.5	0	≥ 2000
16	1.3×10^{17}	-0.5	59,352	4.5×10^{15}	-0.44	0	
17	3.6×10^{21}	-1.5	59,380				
19				6.9×10^{22}	-2.5 ±0.5	0	2,500-5,000
20	3.56×10^{21}	-1.5	59,380				
21				2.5×10^{18} ±0.5	-1.0	0	
22	1.06×10^{25}	-2.5	59,395				
23	3.258×10^{19}	-1.0	59,395	2.715×10^{16}	-0.5	0	
24	1.1×10^{25}	-2.5	59,380				1,500-8,000
27				1.38×10^{18}	-1.0	171.5	3,000-10,000
29	2.75×10^{19}	-1.0	59,500				500-50,000
30	3.6×10^{21}	-1.5	59,380	3.0×10^{18}	-1.0	380	
31	3.2×10^{19}	-1.0	59,500				

Table 2(b). Reaction Rate Constants

$O_2 + O = O + 2O$							
	k_f (n=1)			k_b (n=2)			Applicable Temp.
ref	a	b	c	a	b	c	Range (K)
2	2.1×10^{18}	-0.5	59,380				
3	2.1×10^{18}	-0.5	59,380				
4	8.5×10^{19}	-1.0	59,400	7.1×10^{16}	-0.5	0	7,400-23,000
5				2.3×10^{20}	-1.5	0	
6	2.1×10^{18}	-0.5	59,360				1,350-7,000
7	8.5×10^{19}	-1.0	59,400	7.1×10^{16}	-0.5	0	
8				7.1×10^{16}	-0.5	0	10,000
9	9.0×10^{19}	-1.0	59,400	7.6×10^{16}	-0.5	0	high-temp
11	9.0×10^{19}	-1.0	59,300				0-6,000
12	3.0×10^{16}	0	59,380				2,800-5,000
13	2.1×10^{18}	-0.5	59,380				300-3,100
14	9.04×10^{19}	-1.0	59,378				4,120-5,725
15	9.0×10^{19}	-1.0	59,400	7.6×10^{17}	-0.5	0	≥ 2,000
16	6.3×10^{17}	-0.5	59,352	2.2×10^{16}	-0.44	0	
17	2.1×10^{18}	-0.5	59,380				
20	2.1×10^{18}	-0.5	59,380				
24	1.1×10^{25}	-2.5	59,380				1,500-8,000
27				4.14×10^{18}	-1.0	171.5	3,000-10,000
29	8.25×10^{19}	-1.0	59,500				500-50,000
30	2.1×10^{18}	-0.5	59,380	1.75×10^{15}	0	380	
31	2.0×10^{19}	-1.0	59,500				

Table 2(c). Reaction Rate Constants

$O_2 + N_2 = N_2 + 2O$							
	k_f (n=1)			k_b (n=2)			Applicable Temp.
ref	a	b	c	a	b	c	Range (K)
5				6.2×10^{15}	-0.5	0	
7				2.0×10^{16}	-0.5	0	
9	7.2×10^{18}	-1.0	59,400	6.2×10^{15}	-0.5	0	high-temp.
11	7.2×10^{18}	-1.0	59,300				0-6,000
14	7.23×10^{18}	-1.0	59,378				4,120-5,725
15	7.2×10^{18}	-1.0	59,400	6.2×10^{15}	-0.5	0	≥ 2,000
19				6.9×10^{22}	-2.5 ±0.5	0	2,500-5,000
23	7.24×10^{18}	-1.0	59,395	6.033×10^{15}	-0.5	0	
27				1.38×10^{18}	-1.0	171.5	3,000-10,000
29	2.75×10^{19}	-1.0	59,500				500-50,000
30	1.2×10^{21}	-1.5	59,380	1.0×10^{18}	-1.0	380	
31	7.2×10^{18}	-1.0	59,500				

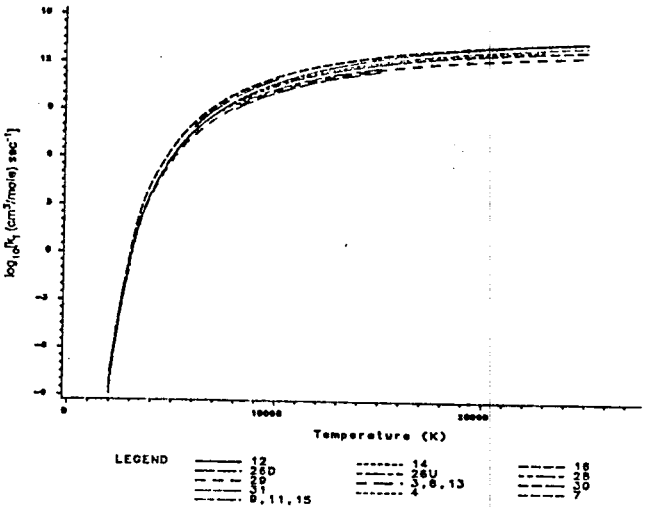

Fig. 1(a)–1 Forward Reaction Rate Kf $N_2 + N_2 = N_2 + 2N$

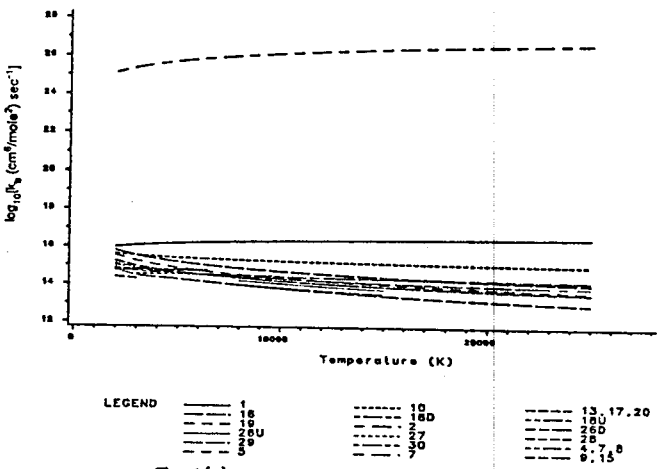

Fig. 1(a)–2 Backward Reaction Rate Kb $N_2 + N_2 = N_2 + 2N$

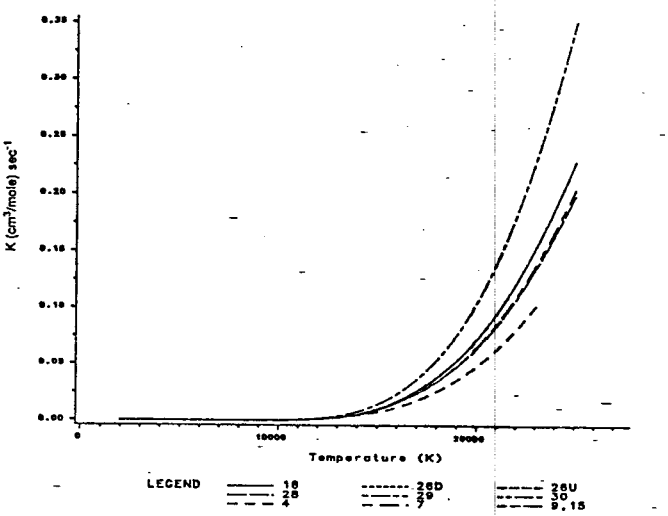

Fig. 1(a)–3 Equilibrium Constants K $N_2 + N_2 = N_2 + 2N$

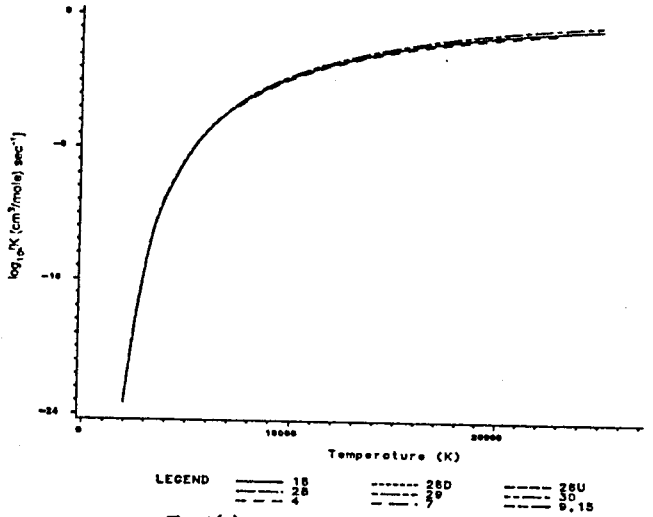

Fig. 1(a)–4 Equilibrium Constants K $N_2 + N_2 \rightleftharpoons N_2 + 2N$

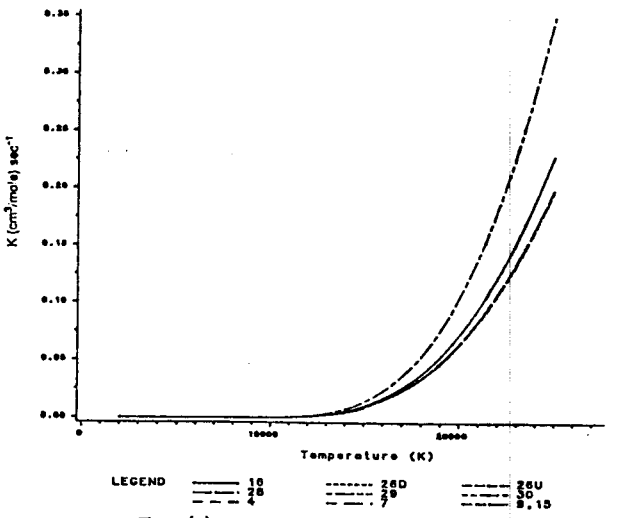

Fig. 1(b)–3 Equilibrium Constants K $N_2 + N \rightleftharpoons N + 2N$

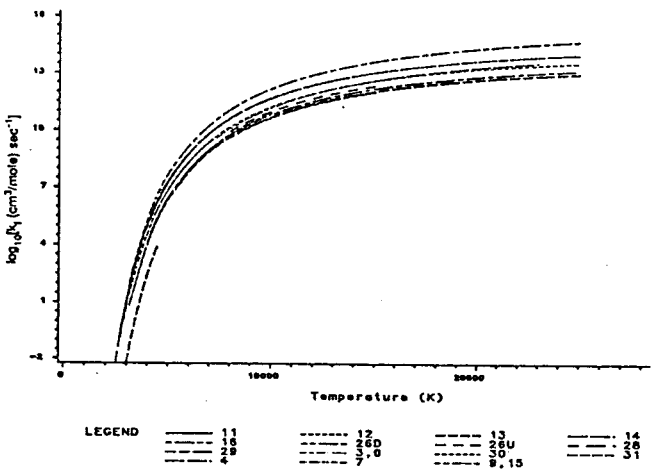

Fig. 1(b)–1 Forward Reaction Rate Kf $N_2 + N \rightleftharpoons N + 2N$

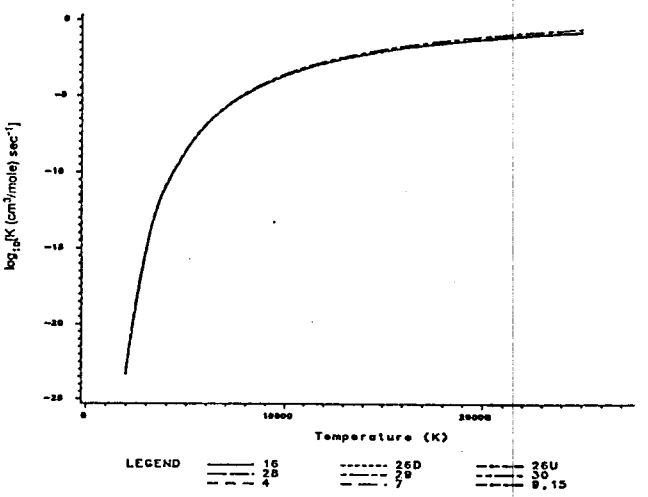

Fig. (1b)–4 Equilibrium Constants K $N_2 + N \rightleftharpoons N + 2N$

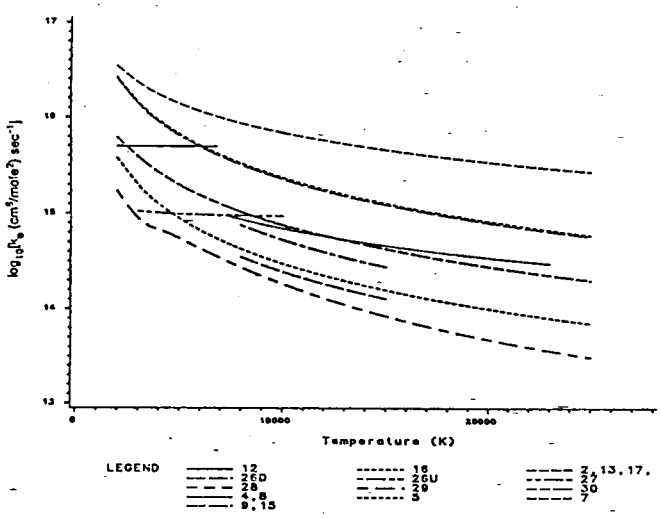

Fig. 1(b)–2 Backward Reaction Rate Kb $N_2 + N \rightleftharpoons N + 2N$

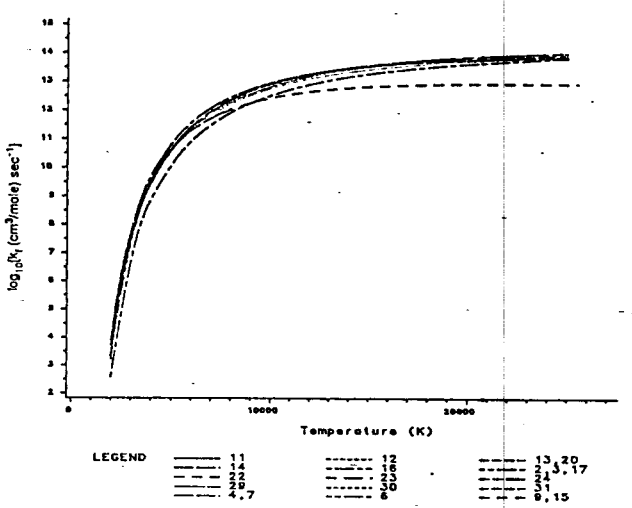

Fig. 2(a)–1 Forward Reaction Rate Kf $O_2 + O_2 \rightleftharpoons O_2 + 2O$

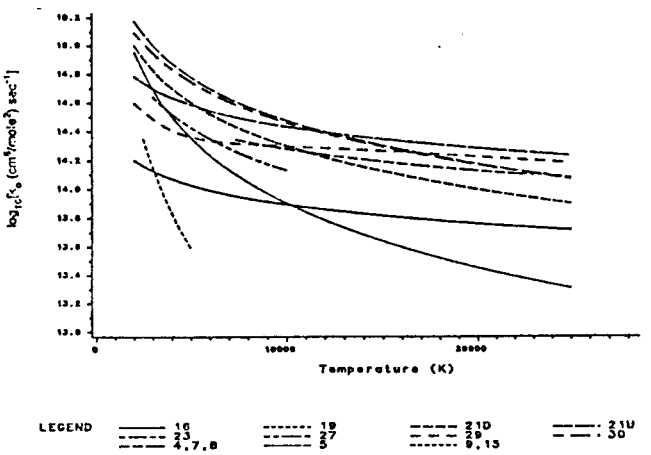

Fig. 2(a)–2 Backward Reaction Rate Kb $O_2 + O_2 \rightleftharpoons O_2 + 2O$

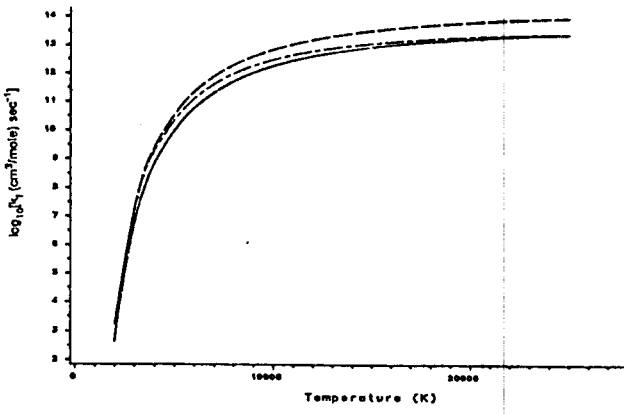

Fig. 2(c)–1 Forward Reaction Rate Kf $O_2 + N_2 \rightleftharpoons N_2 + 2O$

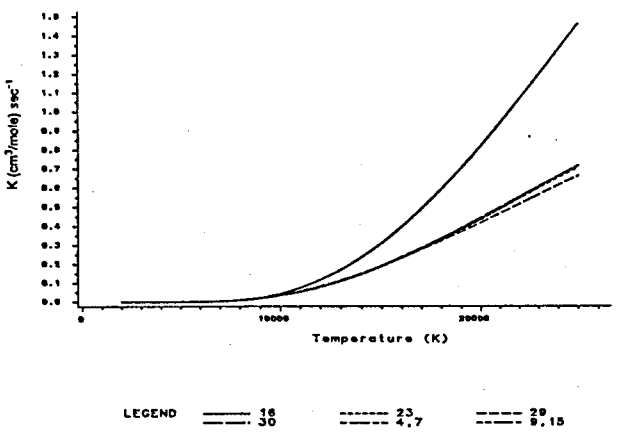

Fig. 2(a)–3 Equilibrium Constants K $O_2 + O_2 \rightleftharpoons O_2 + 2O$

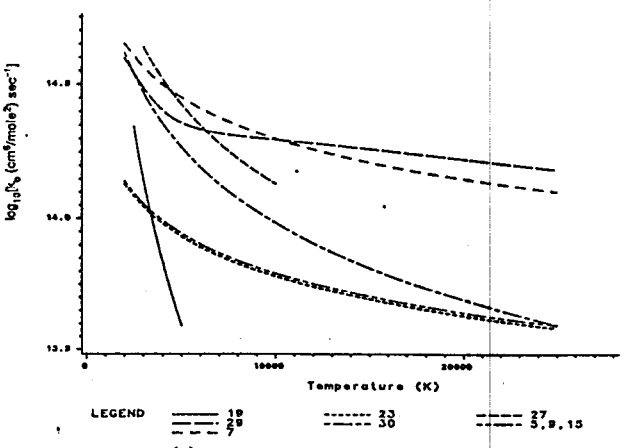

Fig. 2(c)–2 Backward Reaction Rate Kb $O_2 + N_2 \rightleftharpoons N_2 + 2O$

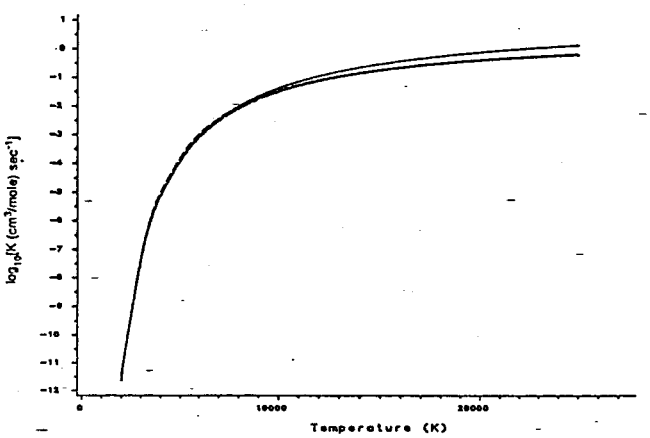

Fig. 2(a)–4 Equilibrium Constants K $O_2 + O_2 \rightleftharpoons O_2 + 2O$

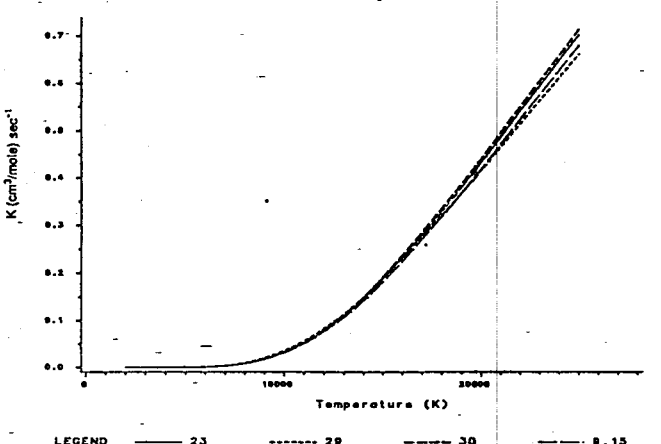

Fig. 2(c)–3 Equilibrium Constants K $O_2 + N_2 \rightleftharpoons N_2 + 2O$

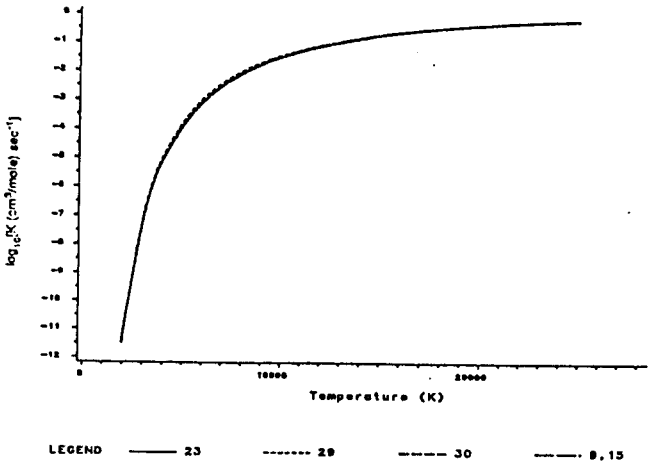

Fig. 2(c)–4 Equilibrium Constants K $O_2 + N_2 \rightleftharpoons N_2 + 2O$

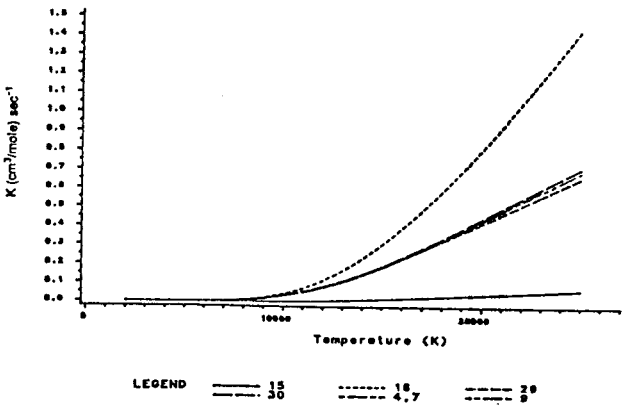

Fig. 2(b)–3 Equilibrium Constants K $O_2 + O \rightleftharpoons O + 2O$

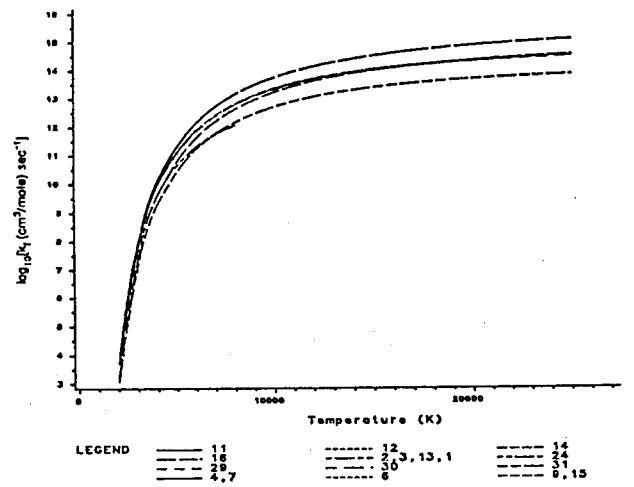

Fig. 2(b)–1 Forward Reaction Rate Kf $O_2 + O \rightleftharpoons O + 2O$

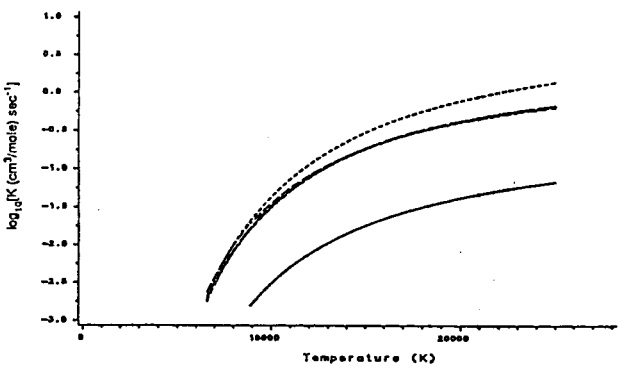

Fig. 2(b)–4 Equilibrium Constants K $O_2 + O \rightleftharpoons O + 2O$

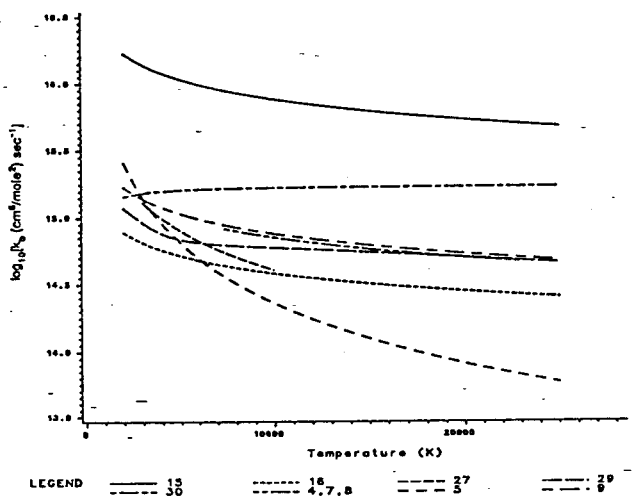

Fig. 2(b)–2 Backward Reaction Rate Kb $O_2 + O \rightleftharpoons O + 2O$