$NO_2 + NO_2 \longrightarrow NO + NO + O_2$

THERMODYNAMIC DATA

T (K)	ΔH^o (kJ mol^{-1})	ΔS^o (J K^{-1} mol^{-1})	log K_p (K_p in atm)	log K_c (K_c in mol cm^{-3})
298	114.28	146.35	-12.40	-16.79
300	114.31	146.45	-12.26	-16.66
500	116.29	151.70	- 4.23	- 8.84
1000	116.76	152.64	1.88	- 3.04
1500	115.73	151.81	3.90	- 1.19
2000	114.68	151.20	4.91	- 0.31
2500	113.99	150.89	5.51	0.19
3000	113.79	150.82	5.90	0.51
3500	114.08	150.90	6.19	0.73
4000	114.81	151.09	6.40	0.88
4500	115.92	151.35	6.57	1.00
5000	117.34	151.65	6.70	1.09

SI Units: $\log(K_p/N\ m^{-2}) = \log(K_p/atm) + 5.006$

$\log(K_c/mol\ m^{-3}) = \log(K_c/mol\ cm^{-3}) + 6$

● RECOMMENDED RATE CONSTANT

$k = 2.0 \times 10^{12} \exp(-13\ 500/T)\ cm^3\ mol^{-1}\ s^{-1}$

$= 3.3 \times 10^{-12} \exp(-13\ 500/T)\ cm^3\ molecule^{-1}\ s^{-1}$

(k is defined by $-\frac{1}{2}d[NO_2]/dt = k[NO_2]^2$.)

Temperature Range: 600 - 2000 K

Suggested Error Limits for Calculated Rate Constant: ±30% in temperature range 600 - 1000 K, but slightly greater at higher temperatures.
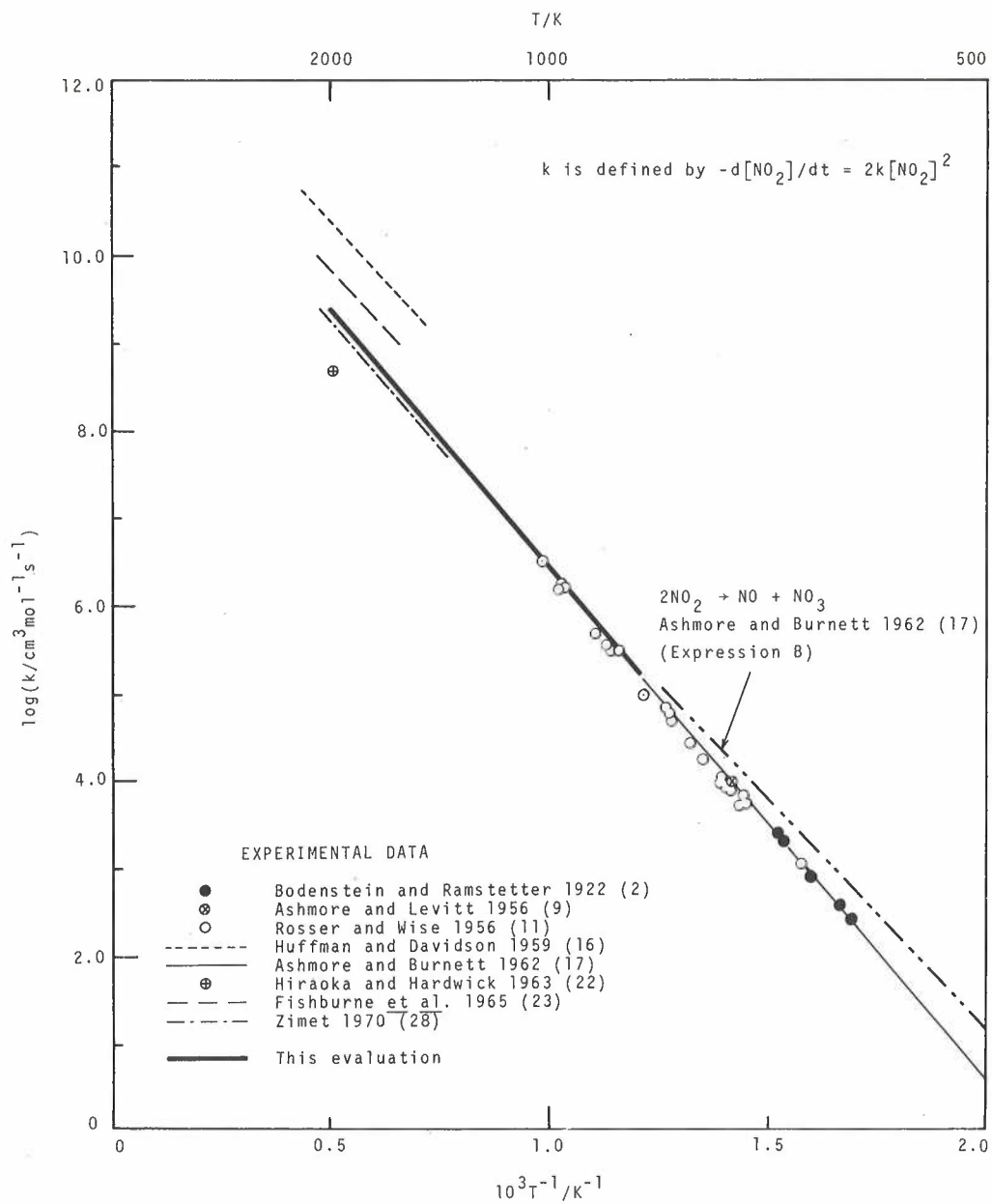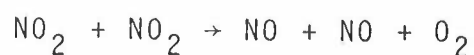
Note: Expression is that of ROSSER and WISE (11).

Rate Parameters: $\log(A/cm^3\ mol^{-1}\ s^{-1})$ = 12 30 ± 0.07

$\log(A/cm^3\ molecule^{-1}\ s^{-1})$ = -11.48 ± 0.07

E/J mol^{-1} = 112 550 ± 600

E/cal mol^{-1} = 26 900 ± 200

$NO_2 + NO_2 \longrightarrow NO + NO + O_2$

T/K

k is defined by $-d[NO_2]/dt = 2k[NO_2]^2$

$\log(k/cm^3mol^{-1}s^{-1})$

$2NO_2 \rightarrow NO + NO_3$
Ashmore and Burnett 1962 (17)
(Expression B)

EXPERIMENTAL DATA

●	Bodenstein and Ramstetter 1922 (2)
⊗	Ashmore and Levitt 1956 (9)
○	Rosser and Wise 1956 (11)
-----	Huffman and Davidson 1959 (16)
———	Ashmore and Burnett 1962 (17)
⊕	Hiraoka and Hardwick 1963 (22)
— —	Fishburne et al. 1965 (23)
—·—·—	Zimet 1970 (28)
▬▬	This evaluation

$10^3T^{-1}/K^{-1}$

$$NO_2 + NO_2 \rightarrow NO + NO + O_2$$

Rate Constant k $(cm^3 \, mol^{-1} \, s^{-1})$	Temperature (K)	Method and Reference	Comments
2.6×10^2	592	Static system. NO_2 at	Data discussed by NORRISH (4)
3.8×10^2	603	~ 200 mm Hg (27 kN m^{-2}).	although incorrect temperature
8.5×10^2	627	Reaction followed mano-	coefficient taken (see (6)).
2.0×10^3	651	metrically.	Value of k_1 at 656 K used by (7).
2.5×10^3	656	BODENSTEIN and	$NO_2 + NO_2 \rightarrow NO + NO + O_2$ 1
		RAMSTETTER 1922 (2)	Data shown by LEVITT to give
			$k_1 = 4.9 \times 10^{12} \exp(-13\,640/T)$
			$cm^3 mol^{-1} s^{-1}$ (quoted in (17)).
9.5×10^3	707	Static system. NO_2 at	Initial rapid rate of NO_2
		pressures ~ 20 mm Hg	removal attributed to a second
		(2.7 kN m^{-2}). Reaction	bimolecular reaction, 2
		followed by monitoring NO_2	$NO_2 + NO_2 \rightarrow NO + NO_3$ 2
		photometrically.	(see Discussion).
		ASHMORE and LEVITT 1956 (9)	
1.17×10^3	636	Static system. NO_2 at	Disappearance second-order in
5.60×10^3	693	pressures < 10 mm Hg	NO_2. No surface or pressure
6.45×10^3	695	(1.3 kN m^{-2}). NO_2 dis-	effects observed. Points
5.90×10^3	698	appearance monitored by	measured from Fig. 2 of (11).
7.60×10^3	708	photometry at 440 nm.	Authors deduce $k_1 = 2 \times 10^{12}$
8.55×10^3	712	ROSSER and WISE 1956 (11)	$\exp(-13\,500/T)$ $cm^3 mol^{-1} s^{-1}$.
1.06×10^4	718		Used in (15,19,24 and 26).
9.20×10^3	721		Recommended by (27).
1.74×10^4	740		
2.65×10^4	756		
4.88×10^4	782		
5.60×10^4	786		
6.45×10^4	790		
9.60×10^4	823		
2.97×10^5	868		
3.11×10^5	876		
3.58×10^5	887		
5.00×10^5	906		
1.61×10^6	966		
1.65×10^6	973		
1.50×10^6	978		
3.16×10^6	1018		

$$NO_2 + NO_2 \longrightarrow NO + NO + O_2$$

k is defined by $-d[NO_2]/dt = 2k[NO_2]^2$

REVIEW ARTICLES

- .... Kassel 1932 (6)
- — — Bortner 1963 (20)
- ——— Schofield 1967 (25)
- —— This evaluation

$$NO_2 + NO_2 \rightarrow NO + NO + O_2$$

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$1.3 \times 10^{13} \exp(-(12\ 500 \pm 2500)/T)$	1400-2300	Shock tube study, NO_2 (0.3-15%) in Ar. NO_2 disappearance monitored by spectrophotometry. HUFFMAN and DAVIDSON 1959 (16)	Large scatter apparent on the raw data. Disappearance of NO_2 due to two concurrent mechanisms, one initiated by the unimolecular dissociation of NO_2 (see Discussion), the other being the bimolecular reaction 1 $NO_2 + NO_2 \rightarrow NO + NO + O_2$ 1 Authors suggest that results of STEINBERG and LYON (15) on the thermal decomposition of NO_2 can be interpreted in the same way.
$2 \times 10^{12} \exp(-(13\ 500 \pm 50)/T)$	473-823	Static system. Reaction followed manometrically (for large $[NO_2]$) and photometrically (for small $[NO_2]$). ASHMORE and BURNETT 1962 (17)	Initial rapid rate of NO_2 removal attributed to a second bimolecular reaction, 2 (see also (9)). $NO_2 + NO_2 \rightarrow NO + NO_3$ 2 Rate parameters for k_2 determined as $\log A = 11.59 \pm 0.25$ (in $cm^3 mol^{-1} s^{-1}$ units) and $E = 100 \pm 3\ kJ\ mol^{-1}$ ($23.9 \pm 0.6\ kcal\ mol^{-1}$). See Discussion. Used in (21).
$\sim 5 \times 10^8$	2000	Shock tube study, 1% NO_2 in Ar. NO_2 disappearance monitored by u.v. emission measurements. HIRAOKA and HARDWICK 1963 (22)	Approximate value only. Authors found that the NO_2 decay was first order in $[NO_2]$ which they expressed as $-\frac{1}{2}d[NO_2]/dt = k_1[NO_2]^2 + k_4[NO_2][Ar]$ $NO_2 + NO_2 \rightarrow NO + NO + O_2$ 1 $NO_2 + M \rightarrow NO + O + M$ 4 (where M = Ar). Assuming that $k_1 \simeq k_4$ at 2000 K, this was approximated to $k'[NO_2][M]$ (where $[M] = [Ar] + [NO_2]$). From this, they calculated that $k_1 \simeq 5 \times 10^8\ cm^3 mol^{-1} s^{-1}$ at 2000 K.

$$NO_2 + NO_2 \rightarrow NO + NO + O_2$$

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$4.5 \times 10^{12}\ exp(-12\ 900/T)$	1500-2100	Shock tube study, 0.5-3% NO_2 in Ar. NO_2 disappearance monitored by emission and absorption measurements. FISHBURNE, BERGBAUER and EDSE 1965 (23)	Rate constant refers to NO_2 removal by reactions 1 and 2 $NO_2 + NO_2 \rightarrow NO + NO + O_2$ 1 $NO_2 + NO_2 \rightarrow NO + NO_3$ 2 and may be high. Rate expression gives best fit to experimental results, and is based on an activation energy derived from results of ROSSER and WISE (11) and ASHMORE and BURNETT (17).
$1.5 \times 10^{12}\ exp(-13\ 500/T)$	1300-2100	Shock tube study, NO_2 (<10%) in Ar. NO_2 disappearance monitored by absorption measurements at 435 nm. ZIMET 1970 (28)	Best fit to the experimental results. Few details given. Activation energy apparently taken from (11).

REVIEW ARTICLES

Rate Constant k ($cm^3\ mol^{-1}\ s^{-1}$)	Temperature (K)	Method and Reference	Comments
$2 \times 10^{10}\ T^{\frac{1}{2}}\ exp(-13\ 370/T)$	470-660	Evaluation. KASSEL 1932 (6)	Based on the results of BODENSTEIN and RAMSTETTER (2) and data on the reverse reaction combined with the equilibrium constant of BODENSTEIN and LINDNER (1). Quoted in (10).
$5 \times 10^{12}\ T^{\frac{1}{2}}\ exp(-15\ 200/T)$	Unspecified	Recommended expression. BORTNER 1963 (20)	Based on figures quoted by HARTECK and DONDES (14). This expression lies far above the existing data.
$1.1 \times 10^{13}\ exp(-14\ 270/T)$	375-2300	Evaluation. SCHOFIELD 1967 (25)	Least squares fit to data of (11,16,17 and 23). E_1 too high (25).
$2 \times 10^{12}\ exp(-13\ 500/T)$	600-2000	Evaluation. BAULCH, DRYSDALE and HORNE 1970 (27)	Based on (2,9,11,16,17,22 and 23).

$$NO_2 + NO_2 \rightarrow NO + NO + O_2$$
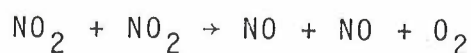
DISCUSSION

The bimolecular decomposition of NO_2 is the reverse of the NO oxidation reaction. The mechanism, which may be complex, is discussed in detail above (this Volume, p.294).

$$NO_2 + NO_2 \rightarrow NO + NO + O_2 \qquad\qquad 1$$
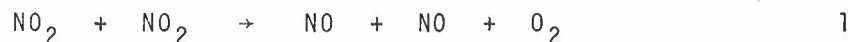
In this evaluation, the rate constant (k_1) is defined by the expression

$$-\tfrac{1}{2} d[NO_2]/dt = k_1 [NO_2]^2$$

All of the rate data quoted in the table have been divided by two to conform with this definition.

The thermal equilibrium between NO_2 and NO was examined in detail by Bodenstein and Lindner (1) as part of a comprehensive study of the NO_2 and NO/O_2 systems: their equilibrium data have been modified only slightly by subsequent work. Norrish has examined the photochemical equilibrium by subjecting NO_2 to ultraviolet radiation (350-400 nm) and observing the pressure change (3,5). The results are compatible with the photosensitive equilibrium

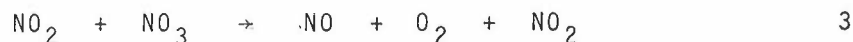$$NO_2 + NO_2 \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} NO + NO + O_2.$$
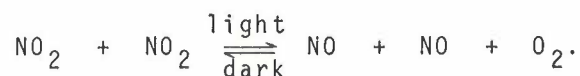
The photo-initiated reaction has also been observed by Blacet, Hall and Leighton (18).

Considerable evidence exists for an alternative reaction (9, 12, 13, 17)

$$NO_2 + NO_2 \rightarrow NO + NO_3 \qquad\qquad 2$$
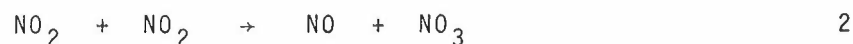
giving rise to the reactive species NO_3 which then reacts with NO_2.

$$NO_2 + NO_3 \rightarrow NO + O_2 + NO_2 \qquad\qquad 3$$

The species NO_3 is believed to be the symmetric nitrate radical (17) rather than the unsymmetric peroxynitrite radical (ONOO) which may be the intermediate in reaction 1 (see this Volume, p.294). In the thermal decomposition of NO_2 at temperatures below 1000 K, the rate commences at a high value but falls quite

$$NO_2 + NO_2 \rightarrow NO + NO + O_2$$
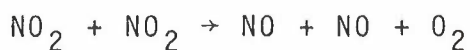
quickly to a value associated with reaction 1. Ashmore and his co-workers
(9,17) have shown that this is due to the participation of reactions 2 and 3,
but as the NO concentration builds up, NO_2 is regenerated efficiently by
reaction -2,

$$NO + NO_3 \rightarrow NO_2 + NO_2 \qquad\qquad -2$$
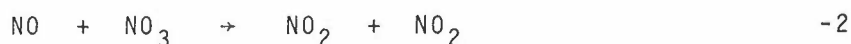
and only reaction 1 contributes to the overall removal of NO_2. If it is
assumed that the NO_3 concentration reaches a steady state, then from the above,

$$-\frac{1}{[NO_2]^2} \cdot \frac{d[NO_2]}{dt} = k_1 + \frac{k_2 k_3 [NO_2]}{\frac{1}{2}k_{-2}[NO] + k_3[NO_2]} \qquad\qquad A$$

A plot of $1/[NO_2]$ v. time will have an initial slope of $k_1 + k_2$. However, as
reaction proceeds and $[NO]$ increases, then provided $k_{-2} \gg k_3$ the second term on
the right hand side of equation A will become insignificant, and the slope
decreases to k_1. Addition of nitric oxide initially suppresses the curvature
of the plot completely (9). Ashmore and Burnett (17) deduced the following
expression for the rate constant of reaction 2:

$$\log(k_2/cm^3 mol^{-1}s^{-1}) = (11.59 \pm 0.25) - (12\ 030 \pm 300)/2.303T \qquad B$$

This is plotted on the Arrhenius diagram for comparison (see also p.357).

In the temperature range 600-1000 K, the results of Bodenstein and
Ramstetter (2), Rosser and Wise (11) and Ashmore and Burnett (17) are in
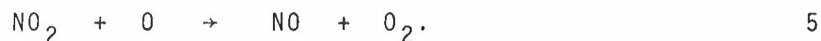excellent agreement with one another. They predict

$$k_1 = 2.0 \times 10^{12} \exp(-13\ 500/T)\ cm^3 mol^{-1}s^{-1} \qquad C$$

The high temperature data from shock tube studies are scattered (16,22,23,28)
although the expressions of Fishburne et al. (23) and Zimet (28) lie within a
factor of two of expression C in the temperature range 1500-2100 K. The
scatter probably reflects the difficulty of separating the effects of the
bimolecular reactions (1 and 2) from the dissociation

$$NO_2 + NO_2 \rightarrow NO + NO + O_2$$

$$NO_2 + M \rightarrow NO + O + M \qquad\qquad 4$$
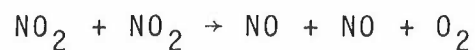
and the subsequent oxygen atom reaction

$$NO_2 + O \rightarrow NO + O_2. \qquad\qquad 5$$

Apparently, Zimet (28) did not consider reaction 5 in his determination of k_1.

The available data suggest that expression C, originally derived by Rosser and Wise (11) may be applied with considerable accuracy over the temperature range 470-2000 K: in the range 470-1000 K, expression C describes the data to better than 30%. However, it predicts the reverse reaction will have a small positive activation energy ($\sim$ 1.7 kJ mol^{-1} (0.4 kcal mol^{-1})) between 500 and 1000 K, whereas the data on the reverse reaction indicates a negative activation energy of about -4.2 kJ mol^{-1} (-1 kcal mol^{-1}) from 300-700 K. The discrepancy may lie in the occurrence of a complex mechanism as discussed elsewhere (this Volume, p.294). However, it is significant that the results from both forward and reverse reactions are compatible with the equilibrium constant in the temperature range 500-700 K (6).

The mechanism of reaction 1 is not known in detail; the various possibilities have been discussed in the evaluation of the reverse reaction (this Volume, p.294). Herschbach et al. (10) have calculated an A-factor for the reaction and have shown that it is more likely to proceed through a linear than a cyclic transition state.

$$NO_2 + NO_2 \rightarrow NO + NO + O_2$$

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