

SECTION 3. EQUILIBRIUM CONSTANTS

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3.1 Format

Some of the three-body reactions in Table 2-1 form products that are thermally unstable at atmospheric temperatures. In such cases the thermal decomposition reaction may compete with other loss processes, such as photodissociation or radical attack. Table 3-1 lists the equilibrium constants, $K(T)$, for several reactions which may fall into this category. The table has three column entries, the first two being the parameters A and B which can be used to express $K(T)$:

$$K(T)/\text{cm}^3 \text{ molecule}^{-1} = A \exp(B/T) \quad (200 < T < 300 \text{ K})$$

The third column entry in Table 3-1 is the calculated value of K at 298 K.

The data sources for $K(T)$ are described in the individual notes to Table 3-1.

3.2 Definitions

When values of the heats of formation and entropies of all species are known at the temperature T, we note that:

$$\log_{10} [K(T) / \text{cm}^3 \text{ molecule}^{-1}] = \frac{\Delta S_T^\circ}{2.303R} - \frac{\Delta H_T^\circ}{2.303RT} + \log_{10}(T) - 21.87$$

Where the superscript "o" refers to a standard state of one atmosphere. In some cases K values were calculated from this equation, using thermochemical data. In other cases the K values were calculated directly from kinetic data for the forward and reverse reactions. When available, JANAF values were used for the equilibrium constants. The following equations were then used to calculate the parameters A and B:

$$B/^\circ\text{K} = 2.303 \left[\frac{(300 \cdot 200)}{(300 - 200)} \right] \log_{10} \left(\frac{K_{200}}{K_{300}} \right) = 1382 \log_{10} \left(\frac{K_{200}}{K_{300}} \right)$$

$$\log_{10}(A) = \log_{10}(K(T)) - \frac{B}{2.303 T}$$

The relationships between the parameters A and B and the quantities $\Delta S^\circ(298 \text{ K})$ and $\Delta H^\circ(298 \text{ K})$ are as follows:

$$A = \frac{eR'T}{N_{\text{av}}} \exp\left(\frac{\Delta S^\circ}{R}\right) = 3.7 \times 10^{-22} T \exp\left(\frac{\Delta S^\circ}{R}\right)$$

where $R' = 82.1 \text{ cm}^3 \text{ atm mole}^{-1} \text{ K}^{-1}$, and $N_{\text{av}} = 6.02 \times 10^{23} \text{ molecule mole}^{-1}$ and

$$B/^\circ\text{K} = -\frac{\Delta H^\circ}{R}$$

Table 3-1. Equilibrium Constants

Reaction	A/cm ³ molecule ⁻¹	B/°K	K _{eq} (298 K)	f(298 K) ^a	g	Note
HO ₂ + NO ₂ → HO ₂ NO ₂	2.1×10 ⁻²⁷	10900	1.6×10 ⁻¹¹	5	1000	1
NO + NO ₂ → N ₂ O ₃	3.3×10 ⁻²⁷	4667	2.1×10 ⁻²⁰	2	100	2
NO ₂ + NO ₂ → N ₂ O ₄	5.9×10 ⁻²⁹	6643	2.8×10 ⁻¹⁹	1.2	250	3
NO ₂ + NO ₃ → N ₂ O ₅	3.0×10 ⁻²⁷	10990	3.1×10 ⁻¹¹	1.2	500	4
CH ₃ O ₂ + NO ₂ → CH ₃ O ₂ NO ₂	1.3×10 ⁻²⁸	11200	2.7×10 ⁻¹²	2	1000	5
CH ₃ C(O)O ₂ + NO ₂ → CH ₃ C(O)O ₂ NO ₂	9.0×10 ⁻²⁹	14000	2.3×10 ⁻⁸	2	200	6
CH ₃ CH ₂ C(O)O ₂ + NO ₂ → CH ₃ CH ₂ C(O)O ₂ NO ₂	9.0×10 ⁻²⁹	14000	2.3×10 ⁻⁸	10	800	7
CH ₃ C(O)CH ₂ + O ₂ → CH ₃ C(O)CH ₂ O ₂	7×10 ⁻²⁷	13000	6×10 ⁻⁸	10	800	8
F + O ₂ → FOO	3.2×10 ⁻²⁵	6100	2.5×10 ⁻¹⁶	10	1200	9
Cl + O ₂ → ClOO	5.7×10 ⁻²⁵	2500	2.5×10 ⁻²¹	2	750	10
Cl + CO → ClCO	1.6×10 ⁻²⁵	4000	1.1×10 ⁻¹⁹	5	500	11
ClO + O ₂ → ClO·O ₂	2.9×10 ⁻²⁶	<3700	<7.2×10 ⁻²¹			12
ClO + ClO → Cl ₂ O ₂	1.27×10 ⁻²⁷	8744	7.0×10 ⁻¹⁵	1.3	500	13
ClO + OClO → Cl ₂ O ₃	1.1×10 ⁻²⁴	5455	9.8×10 ⁻¹⁷	3	300	14
OCIO + NO ₃ → O ₂ ClONO ₂	1×10 ⁻²⁸	9300	3.6×10 ⁻¹⁵	5	1000	15
OH + CS ₂ → CS ₂ OH	4.5×10 ⁻²⁵	5140	1.4×10 ⁻¹⁷	1.4	500	16
CH ₃ S + O ₂ → CH ₃ SO ₂	1.8×10 ⁻²⁷	5545	2.2×10 ⁻¹⁹	1.4	300	17

K/cm³ molecule⁻¹ = A exp (B/T) [200 < T/K < 300]

a f(298 K) is the uncertainty factor at 298 K, and g is a measure of the uncertainty in the quantity B. To calculate the uncertainty at temperatures other than 298 K, use the expression:

$$f(T) = f(298 \text{ K}) \exp \left[g \left(\frac{1}{T} - \frac{1}{298} \right) \right]$$

Shaded areas indicate changes or additions since JPL 97-4 and/or JPL 00-3

3.3 Notes to Table 3

1. $\text{HO}_2 + \text{NO}_2$. The value was obtained by combining the data from Table 1-1 for the rate constant of the reaction as written and that of Graham et al. [27] and Zabel [56] for the reverse reaction. Values for the entropy and heat of formation of pernitric acid may be extracted. These values are: $S(298 \text{ K}) = 71.7 \text{ cal mole}^{-1} \text{ K}^{-1}$ and $\Delta H_f(298 \text{ K}) = -12.9 \text{ kcal mole}^{-1}$. If the entropy is calculated from the frequencies and moments of inertia given by Chen and Hamilton [19], the value becomes 71.0 and the heat is -13.1 . The values in the Appendix to this report reflect these results.
2. $\text{NO} + \text{NO}_2$. The data are from JANAF [33] and Chao et al. [17]. This process is included because a measurement of the rate constant by Smith and Yarwood [50] and Markwalder et al. [36] shows that it is too slow to be an important process in most atmospheric and laboratory systems.
3. $\text{NO}_2 + \text{NO}_2$. The data are from JANAF [33] and Vosper [54], Chao et al. [18] and Amoroso et al. [1]. Rate data for this process are reported by Brunning et al. [11], Borrell et al. [8] Gozel et al. [25] and Markwalder et al. [35]. A direct study by Harwood and Jones [28] at low temperatures is in agreement with the recommendation. Re-evaluation of the data suggests lower error limits than recommended in JPL 97-4. A typographical error in JPL 97-4 has been corrected.
4. $\text{NO}_2 + \text{NO}_3$. The recommendation is from Cantrell et al. [15]. They report rate constants for the decomposition reaction, which they combine with the rate constants of Orlando et al. [42] to obtain the equilibrium constant. Agreement is quite good with the data of Burrows et al. [13] and Cantrell et al. [14], and the room temperature data of Tuazon et al. [51], Perner et al. [44] and Hjorth et al. [30]. An evaluation by Pritchard [47] is also in excellent agreement with the recommendation. Pritchard [47] examined the data of Cantrell et al. [14], Burrows et al. [13], Graham and Johnston [26], Wangberg et al [55], Schott and Davidson [48], and the room temperature data of Tuazon et al. [51], Perner et al. [44] and Hjorth et al. [30]. He also included the values given by Smith et al. [49], and Kircher et al. [34], who combined data on the forward reaction, tabulated in Table 2-1, with decomposition data of by Connell and Johnston [20] and Viggiano et al. [53]. The latter was used as the basis for the value in JPL 00-3, but some uncertainties in the entropies of NO_3 and N_2O_5 justify the reversion to the JPL 97-4 basis. Wangberg et al. [55] measured the equilibrium constant between 280 and 294 K and report results in agreement with this recommendation.
5. $\text{CH}_3\text{O}_2 + \text{NO}_2$. Thermochemical values at 300 K for $\text{CH}_3\text{O}_2\text{NO}_2$ and CH_3O_2 are from Baldwin [6]. In the absence of data, ΔH° and ΔS° were assumed to be independent of temperature. Bahta et al. [5] have measured $k(\text{dissociation})$ at 263 K. Using the values of $k(\text{recombination})$ suggested in this evaluation, they compute $K(263 \text{ K}) = (2.68 \pm 0.26) \times 10^{-10} \text{ cm}^3$. Our values predict $3.94 \times 10^{-10} \text{ cm}^3$, in good agreement. Zabel et al. [57] have measured $k(\text{dissociation})$ as a function of pressure and temperature. ($\text{CH}_3\text{O}_2 + \text{NO}_2$, Table 2-1). Their values are in good agreement with Bahta et al. [5] and, taken together with $k(\text{recombination})$, would lead to $A = 5.2 \times 10^{-28}$ and $B = 10,766$. This is sufficiently close to the value in Table 3-1 to forego any change in parameters, but the uncertainty has been reduced. Bridier et al. [10] measure an equilibrium constant in good agreement with this recommendation.
6. $\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2$: From measurements of the rate constants in both directions by Bridier et al. [9].
7. $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{O}_2 + \text{NO}_2$. Assumed to be the same as for PAN (Note 6). Both sides of the of the reaction differ from PAN by the group $\text{C}-(\text{C})(\text{CO})(\text{H})_2$. Error limits are estimated and expanded from those for PAN.
8. $\text{CH}_3\text{COCH}_2 + \text{O}_2$. Estimated values of the entropy and enthalpy changes for the reaction are: $\Delta S = -33 \text{ e.u.}$ and $\Delta H = -26 \text{ kcal/mole}$. The entropy is from group additivity and the enthalpy from group additivity for the hydroperoxide followed by assuming that the O-H bond dissociation energy is 88 kcal/mole. Error limits are estimated from the uncertainties in this procedure.
9. $\text{F} + \text{O}_2$. Calculated from JANAF thermochemical values except for $\Delta H_{f,298}(\text{FO}_2) = 6.24 \pm 0.5 \text{ kcal mol}^{-1}$. The latter was taken from Pagsberg et al. [43]. This direct measurement, which falls between the earlier disputed values, would seem to settle that controversy, but the calculated value of k_0 is not in good agreement with the experiment (see $\text{F} + \text{O}_2$ of Table 2-1).
10. $\text{Cl} + \text{O}_2$. Baer et al. [4] determined K in the temperature range 180 to 300 K. Their value at 185.4 K ($5.23 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$) compares well with the Nicovich et al. [40] measurement $K = 4.77 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$, and within error with the Mauldin et al. [37] value of $2.55 \times 10^{-19} \text{ cm}^3 \text{ molecule}^{-1}$. A different expression for K by Avallone et al. [3] gives $S^\circ_{298}(\text{ClOO}) = 61.8 \text{ cal K}^{-1} \text{ molecu}l^{-1}$ and $\Delta H^\circ_{f,298}(\text{ClOO}) = 23.3 \text{ kcal mol}^{-1}$. Using known thermochemistry

for Cl and O₂ and computed entropy values for ClOO, $\Delta H_{f,298}(\text{ClOO}) = 23.3 \pm 0.6 \text{ kcal mole}^{-1}$ is obtained from the Nicovich et al. [40] data. The value of $S^\circ_{298}(\text{ClOO}) = 64.3 \text{ cal mole}^{-1} \text{ K}^{-1}$ used is computed from a structure with a 105° bond angle and Cl–O and O–O bond lengths of 0.173 and 0.130 nm respectively. Frequencies of 1441, 407, and 373 cm^{-1} are from Arkell and Schwager [2]. Symmetry number is 1 and degeneracy is 2.

11. Cl + CO. From Nicovich et al. [41] who measured both k and K between 185 and 260 K in N₂. They report $\Delta H_{f,298}(\text{ClCO}) = -5.2 \pm 0.7 \text{ kcal mole}^{-1}$.
12. ClO + O₂. DeMore [22] reports $K < 4 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1}$ at 197 K. His temperature dependence of the equilibrium constant is estimated using $S^\circ_{298}(\text{ClO}\cdot\text{O}_2) = 73 \text{ cal mol}^{-1} \text{ K}^{-1}$ and $\Delta H^\circ_{298} < 7.7 \text{ kcal mol}^{-1}$. A higher value of K has been proposed by Prasad [45], but it requires $S^\circ(\text{ClO}\cdot\text{O}_2)$ to be about 83 $\text{cal mol}^{-1} \text{ K}^{-1}$, which seems unreasonably high. Carter and Andrews [16] found no experimental evidence for ClO·O₂ in matrix experiments. Prasad and Lee [46] discuss these issues and question the validity of the upper limit reported by DeMore.
13. ClO + ClO. The value is from a third-law calculation based on the data from Cox and Hayman [21] (except for the two lowest temperature points) and Nickolaisen et al. [39]. The entropy of ClOOC1, the value of which is 72.2 $\text{cal mol}^{-1} \text{ K}^{-1}$ at 300 K, is calculated from structural and spectroscopic data given by Birk et al. [7]. The heat of formation at 300 K is $\Delta H^\circ_{f,300} = 30.8 \text{ kcal mol}^{-1}$. A study of branching ratios of ClO + ClO channels in Cl₂/O₂/O₃ mixtures by Horowitz et al.[31] also finds the equilibrium constant in O₂ at 285 K to be in agreement with the recommendation.
14. ClO + OC1O. The value in Table 3-1 is that of Burkholder et al. [12] who report a second law value combining their own data and those of Hayman and Cox [29] except for the lowest temperature point from the latter study. They deduce $\Delta H_f(\text{Cl}_2\text{O}_3) \approx 37 \text{ kcal mol}^{-1}$ and $S^\circ(\text{Cl}_2\text{O}_3) \approx 95 \text{ cal mol}^{-1} \text{ K}^{-1}$. The value from Hayman and Cox [29] is in agreement with entropy calculations based on molecular properties (3rd law). All calculations assume the chlorine chlorate structure (ClOCl(O)₂). The deviation that Burkholder et al. [12] observe from third law behavior may indicate that the reaction is more complex than written. Other structures might be stable at the lowest temperatures (i.e., ClOOC1O, OC1OC1O, OC1Cl(O)₂).
15. OC1O + NO₃. Deduced by Friedl et al. [24].
16. OH + CS₂. Average of the concordant recent measurements of Murrells et al. [38] and Diau and Lee [23] between 249 and 298 K. The measurements of Hynes et al. [32] indicate a less stable adduct, but agree within combined experimental error.
17. CH₃S + O₂. Turnipseed et al. [52] report the equilibrium constant for $216 \leq T/\text{K} \leq 258$. From a third law analysis using $\Delta S^\circ_{237} = -36.8 \pm 2.6 \text{ eu}$, they obtain $\Delta H^\circ_{237} = -11.5 \pm 0.9 \text{ kcal/mole}$.

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