Introduction to Chemical Kinetics

AOSC / CHEM 433 & AOSC / CHEM 633

Ross Salawitch

Class Web Sites:
http://www2.atmos.umd.edu/~rjs/class/spr2022
https://myelms.umd.edu/courses/137772

Goals for today:

- **Overview of Chemical Kinetics in the context of Atmospheric Chemistry**
- **Physical meaning of rate expression numbers**
- **Description of different types of reactions**

Lecture 12

15 March 2022

- Reading
  - Chapter 3, “Chemical Kinetics”, from *Photochemistry of Planetary Atmospheres*, Yung and DeMore.

- Additional material for interested students:
  - Chapter 9, “Chemical Kinetics”, from *Introduction to Atmospheric Chemistry*, Jacob. ***Short, easy to read overview***
  - Chapter 2, “Chemical Concepts in the Atmosphere”, *Aeronomy of the Middle Atmosphere*, Brasseur and Solomon. ***Treatment of partition functions and quantum effects relevant to atmospheric chemistry***
  - Chapter 28, “Chemical Kinetics I: Rate Laws”, Physical Chemistry: A Molecular Approach, McQuarrie and Simon. ***Rigorous treatment of kinetics from a “pchem” point of view***

Types of Reactions

Reading:

1. Unimolecular

   $A \rightarrow B + C$

2. Bimolecular

   $A + B \rightarrow C + D$

3. Termolecular

   $A + B + M \rightarrow C + M$

Of course, reactions must balance in a “stoichiometric” manner

photochemical reactions break and reform chemical bonds;

they do not rearrange protons

Types of Reactions

Atmospheric Chemistry:

$HONO_2$ same as HNO_3 (nitric acid)
We'll use both notations interchangeably

1. Unimolecular
   - 1a. Photolysis : O_3 + photon $\rightarrow$ O + O_2
   - 1b. Heterogeneous: $N_2O_5 + H_2O$ (aqueous) $\rightarrow 2\ HONO_2$
   - 1c. Thermal Decomposition: $ClOOCl$ + heat $\rightarrow ClO + ClO$

2. Bimolecular
   - 2a. Gas Phase: $OH + CH_4 \rightarrow CH_3 + H_2O$
   - 2b. Heterogenous: $ClONO_2$ + HCl (adsorbed) $\rightarrow Cl_2 + HONO_2$

3. Termolecular
   - 3. $OH + NO_2 + M \rightarrow HONO_2 + M$

Importance of Radicals

- With a few exceptions, the only reactions between molecules that proceed at appreciable rates are those involving at least one radical

- Radicals require significant energy to form: a bond must be broken

- Radical formation is tied to absorption of photons that "photodissociate" a compound, leading to radical formation

Initiation

O_2 + photon → O + O

Propagation

$O + O_2 + M \rightarrow O_3 + M$

O_3 + photon → $O(^1D) + O_2$

$O(^1D) + H_2O \rightarrow OH + OH$

$OH + O_3 \rightarrow HO_2 + O_2$

$HO_2 + O \rightarrow OH + O_2$

Termination

$OH + HO_2 \rightarrow H_2O + O_2$

Radicals

- Radicals: unpaired electron in outer valence shell

- Is a species a radical?

  Count the electrons:

  HNO_3 : 1 + 7 + 3 × 8 = 32 electrons ⇒ no
  NO : 7 + 8 = 15 electrons ⇒ yes
  NO_2 : 23 electrons ⇒ yes
  Other radicals: OH, HO_2, Cl, Br, ClO, BrO

- Important exception:

  Atomic oxygen :

  two unpaired electrons in its “triplet” ground state $O(^3P) \Rightarrow (1s^2 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1)$
  therefore a *biradical* : we’ll call $O(^3P)$ a radical

  What is $O(^1D)$?

  higher energy “singlet” state with all electrons paired but last orbital empty:

  $O(^1D) \Rightarrow (1s^2 2s^2\ 2p_x^2\ 2p_y^2)$

  $O(^1D)$ is even more reactive than $O(^3P)$: it is hungry for more electrons !

Bimolecular Gas Phase Reactions

8.9 kcal/mole **–17.8 kcal/mole** **35.1 kcal/mole** **–57.8 kcal/mole**

$$OH + CH_4 \rightarrow CH_3 + H_2O$$

ΔEnthalpy = –13.8 kcal/mole

Exothermic !

$$\text{Rate of Reaction} = \frac{dCH_4}{dt} = -k\,[OH][CH_4]$$

E_A / R ⇒ Activation Energy / Gas Constant

Arrhenius Expression for rate constant:

$$k = 1.85 \times 10^{-12} \times e^{-1690/T} \text{ cm}^3 \text{ molecule}^{-1} \text{ sec}^{-1}$$

Energy Term

A factor

$$k_c \; e^{\Delta S / R}$$

Entropy Term

R = 8.3143 ×10^7 erg / (K mole)
= 2.87 ×10^6 erg / (K gm) for air

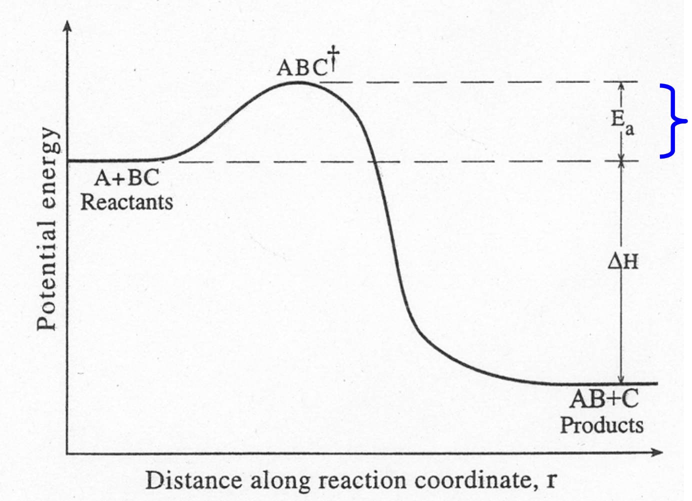


Figure 3.3 Barrier energies for the forward reaction (E_a) and the reverse reaction ($E_a + \Delta H$).

Yung and DeMore, *Photochemistry of Planetary Atmospheres*, Oxford, 1999.

Bimolecular Gas Phase Reactions

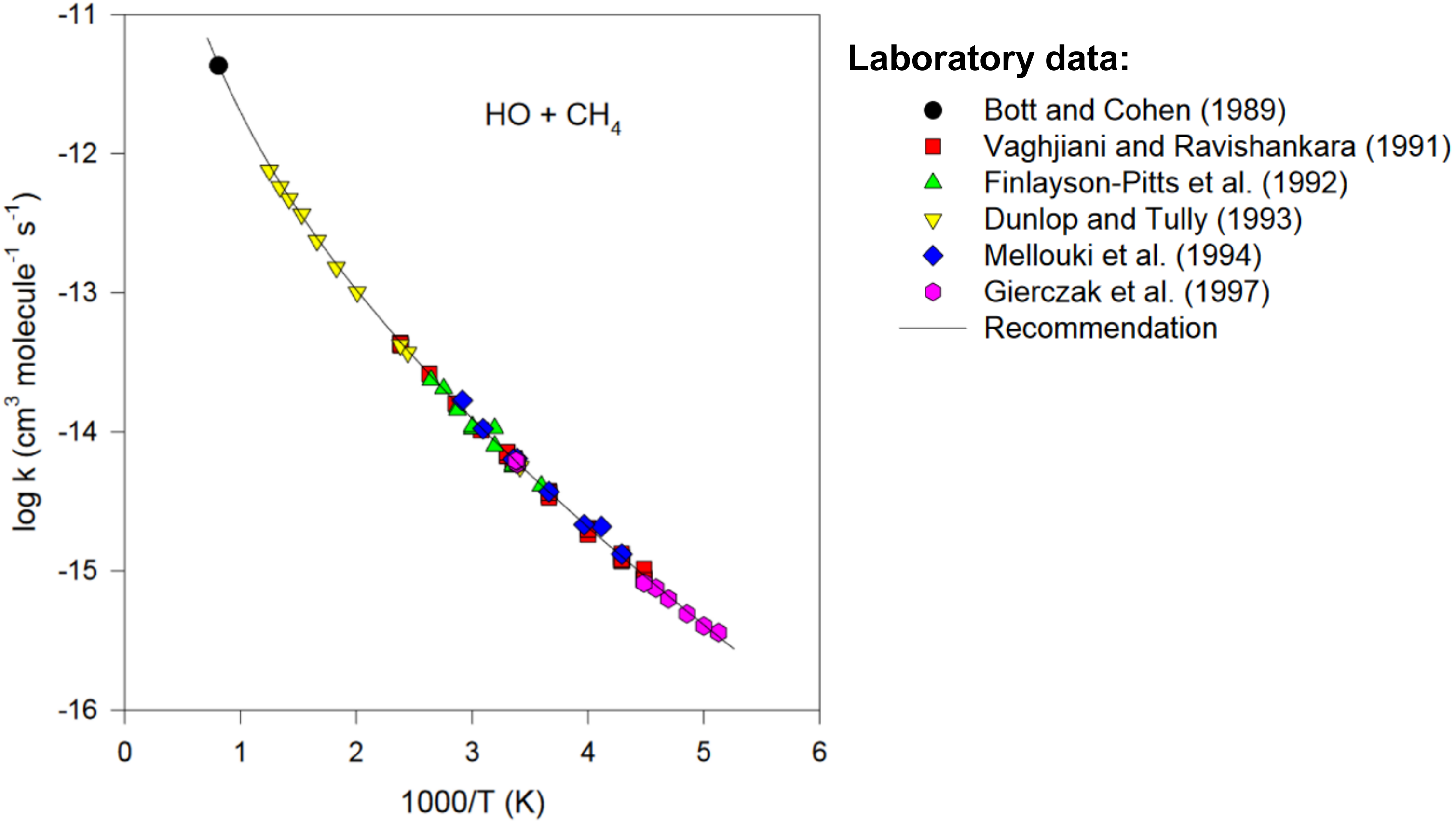
$OH + CH_4 \rightarrow CH_3 + H_2O$

Arrhenius:

$$k^{\mathrm{IUPAC}} = 1.85\times10^{-12} \times e^{-1690/T} \ \mathrm{cm}^3 \ \mathrm{sec}^{-1}$$

Non-Arrhenius

$$k^{\mathrm{IUPAC}} = 1.85\times10^{-20} \times \ \mathrm{T}^{2.82} e^{-987/T} \ \mathrm{cm}^3 \ \mathrm{sec}^{-1}$$



IUPAC: International Union of Pure and Applied Chemistry website
http://iupac.pole-ether.fr/htdocs/datasheets/pdf/HOx_VOC1_HO_CH4.pdf

Bimolecular Gas Phase Reactions

$OH + CH_4 \rightarrow CH_3 + H_2O$

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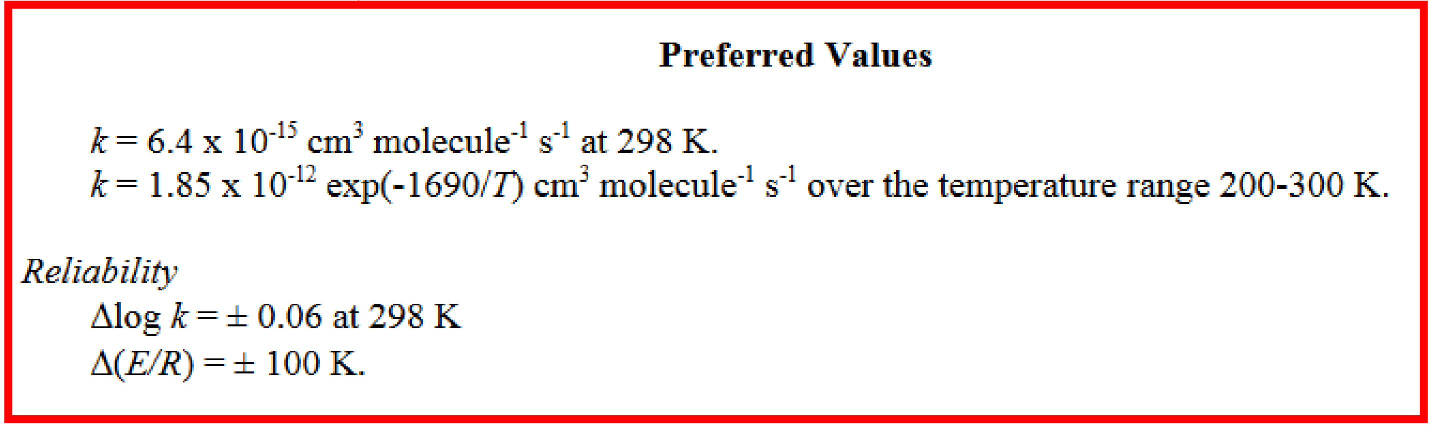
IUPAC Report:

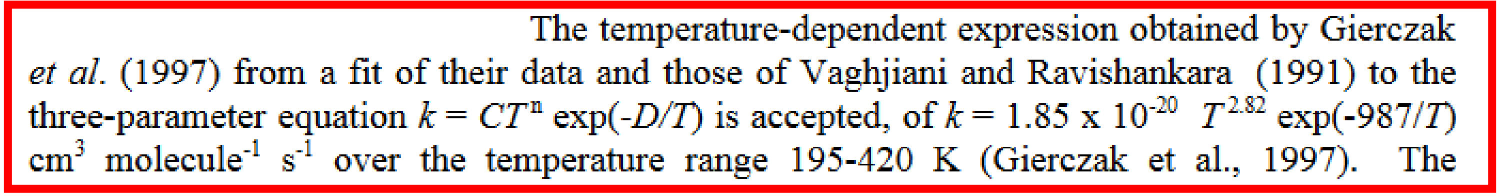


Preferred Values

k = 6.4 x 10^{-15} cm^3 molecule^{-1} s^{-1} at 298 K.
k = 1.85 x 10^{-12} exp(-1690/T) cm^3 molecule^{-1} s^{-1} over the temperature range 200-300 K.

Reliability

$\Delta\log k = \pm 0.06$ at 298 K
$\Delta(E/R) = \pm 100$ K.



The temperature-dependent expression obtained by Gierczak *et al.* (1997) from a fit of their data and those of Vaghjiani and Ravishankara (1991) to the three-parameter equation $k = CT^n \exp(-D/T)$ is accepted, of k = 1.85 x 10^{-20} $T^{2.82}$ exp(-987/T) cm^3 molecule^{-1} s^{-1} over the temperature range 195-420 K (Gierczak et al., 1997). The

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http://iupac.pole-ether.fr/htdocs/datasheets/pdf/HOx_VOC1_HO_CH4.pdf

Bimolecular Gas Phase Reactions

$OH + CH_4 \rightarrow CH_3 + H_2O$

Arrhenius:

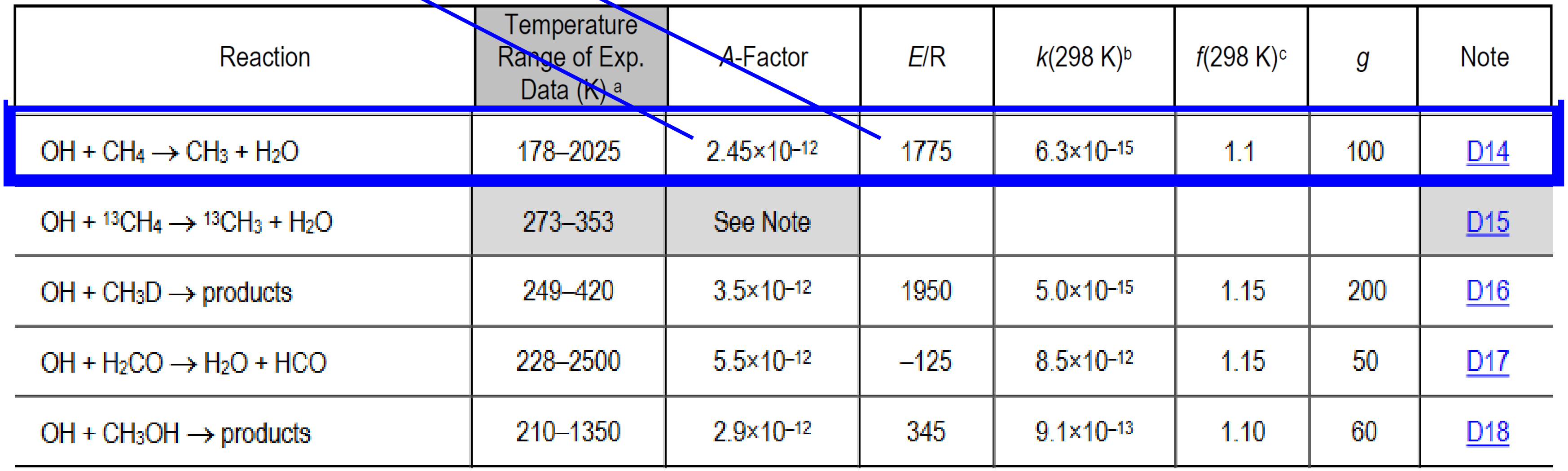
$$k^{\mathrm{IUPAC}} = 1.85\times10^{-12}\times e^{-1690/T}\ \mathrm{cm^3\ sec^{-1}}$$

$$k^{\mathrm{NASA}} = 2.45\times10^{-12}\times e^{-1775/T}\ \mathrm{cm^3\ sec^{-1}}$$

Non-Arrhenius

$$k^{\mathrm{IUPAC}} = 1.85\times10^{-20}\times\ \mathrm{T}^{2.82}e^{-987/T}\ \mathrm{cm^3\ sec^{-1}}$$

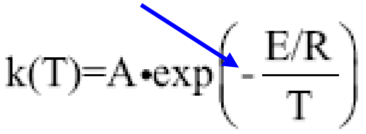
$$k^{\mathrm{NASA}} = 2.80\times10^{-14}\times\ \mathrm{T}^{0.667}e^{-1575/T}\ \mathrm{cm^3\ sec^{-1}}$$



Reaction	Temperature Range of Exp. Data (K) [a]	A-Factor	*E*/R	*k*(298 K)[b]	*f*(298 K)[c]	*g*	Note
$OH + CH_4 \rightarrow CH_3 + H_2O$	178–2025	2.45×10^{-12}	1775	6.3×10^{-15}	1.1	100	D14
$OH + {}^{13}CH_4 \rightarrow {}^{13}CH_3 + H_2O$	273–353	See Note					D15
$OH + CH_3D \rightarrow$ products	249–420	3.5×10^{-12}	1950	5.0×10^{-15}	1.15	200	D16
$OH + H_2CO \rightarrow H_2O + HCO$	228–2500	5.5×10^{-12}	–125	8.5×10^{-12}	1.15	50	D17
$OH + CH_3OH \rightarrow$ products	210–1350	2.9×10^{-12}	345	9.1×10^{-13}	1.10	60	D18

The rate constant tabulation for second-order reactions (Table 1) is given in Arrhenius form:

This is a minus sign



$$k(T)=A\bullet\exp\left(-\frac{E/R}{T}\right)$$

http://jpldataeval.jpl.nasa.gov (2019 Evaluation)

Bimolecular Gas Phase Reactions

$OH + CH_4 \rightarrow CH_3 + H_2O$

Arrhenius:

$$k^{\text{IUPAC}} = 1.85\times10^{-12}\times e^{-1690/T}\ \text{cm}^3\ \text{sec}^{-1}$$

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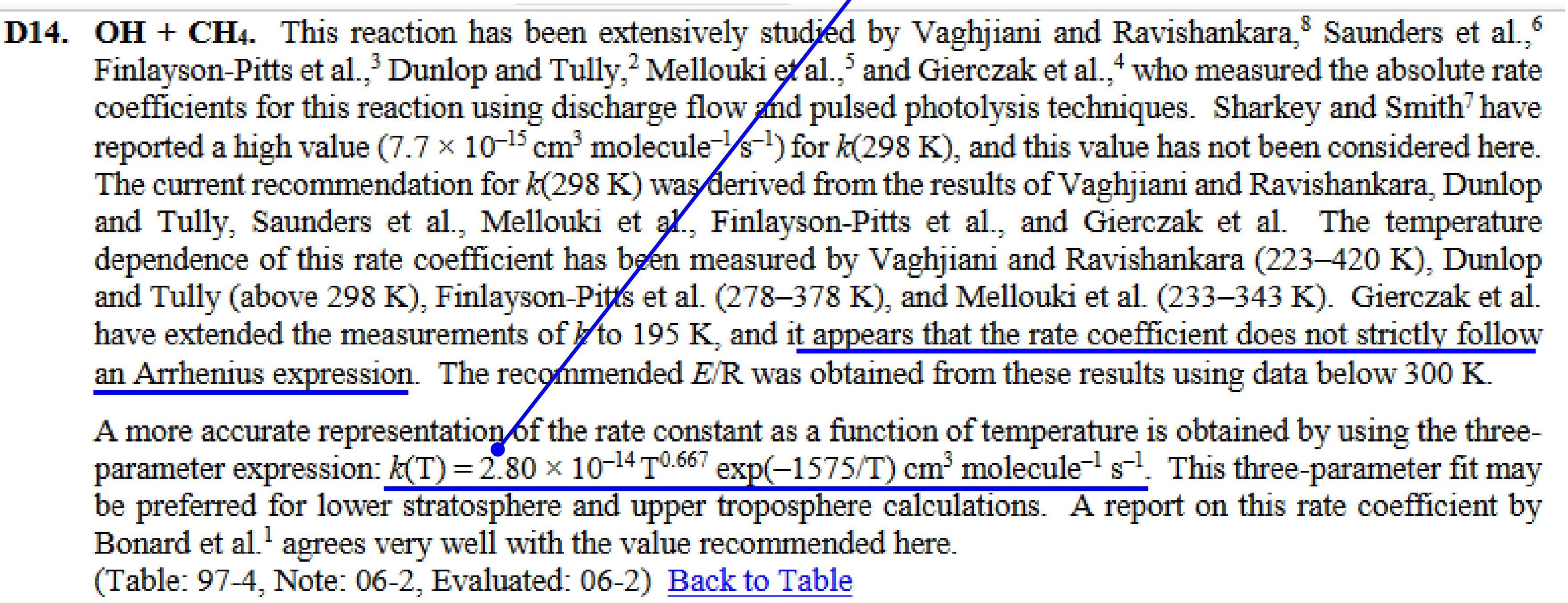

D14. OH + CH_4. This reaction has been extensively studied by Vaghjiani and Ravishankara,[8] Saunders et al.,[6] Finlayson-Pitts et al.,[3] Dunlop and Tully,[2] Mellouki et al.,[5] and Gierczak et al.,[4] who measured the absolute rate coefficients for this reaction using discharge flow and pulsed photolysis techniques. Sharkey and Smith[7] have reported a high value (7.7×10^{-15} cm³ molecule⁻¹ s⁻¹) for *k*(298 K), and this value has not been considered here. The current recommendation for *k*(298 K) was derived from the results of Vaghjiani and Ravishankara, Dunlop and Tully, Saunders et al., Mellouki et al., Finlayson-Pitts et al., and Gierczak et al. The temperature dependence of this rate coefficient has been measured by Vaghjiani and Ravishankara (223–420 K), Dunlop and Tully (above 298 K), Finlayson-Pitts et al. (278–378 K), and Mellouki et al. (233–343 K). Gierczak et al. have extended the measurements of *k* to 195 K, and it appears that the rate coefficient does not strictly follow an Arrhenius expression. The recommended *E*/R was obtained from these results using data below 300 K.

A more accurate representation of the rate constant as a function of temperature is obtained by using the three-parameter expression: $k(\text{T}) = 2.80 \times 10^{-14}\ \text{T}^{0.667} \exp(-1575/\text{T})$ cm³ molecule⁻¹ s⁻¹. This three-parameter fit may be preferred for lower stratosphere and upper troposphere calculations. A report on this rate coefficient by Bonard et al.[1] agrees very well with the value recommended here.
(Table: 97-4, Note: 06-2, Evaluated: 06-2) Back to Table

http://jpldataeval.jpl.nasa.gov (2019 Evaluation)

Bimolecular Gas Phase Reactions

$OH + CH_4 \rightarrow CH_3 + H_2O$

Arrhenius:

$k^{\mathrm{IUPAC}} = 1.85 \times 10^{-12} \times e^{-1690/T}\ \mathrm{cm}^3\ \mathrm{sec}^{-1}$

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Non-Arrhenius

$k^{\mathrm{IUPAC}} = 1.85 \times 10^{-20} \times \mathrm{T}^{2.82} e^{-987/T}\ \mathrm{cm}^3\ \mathrm{sec}^{-1}$

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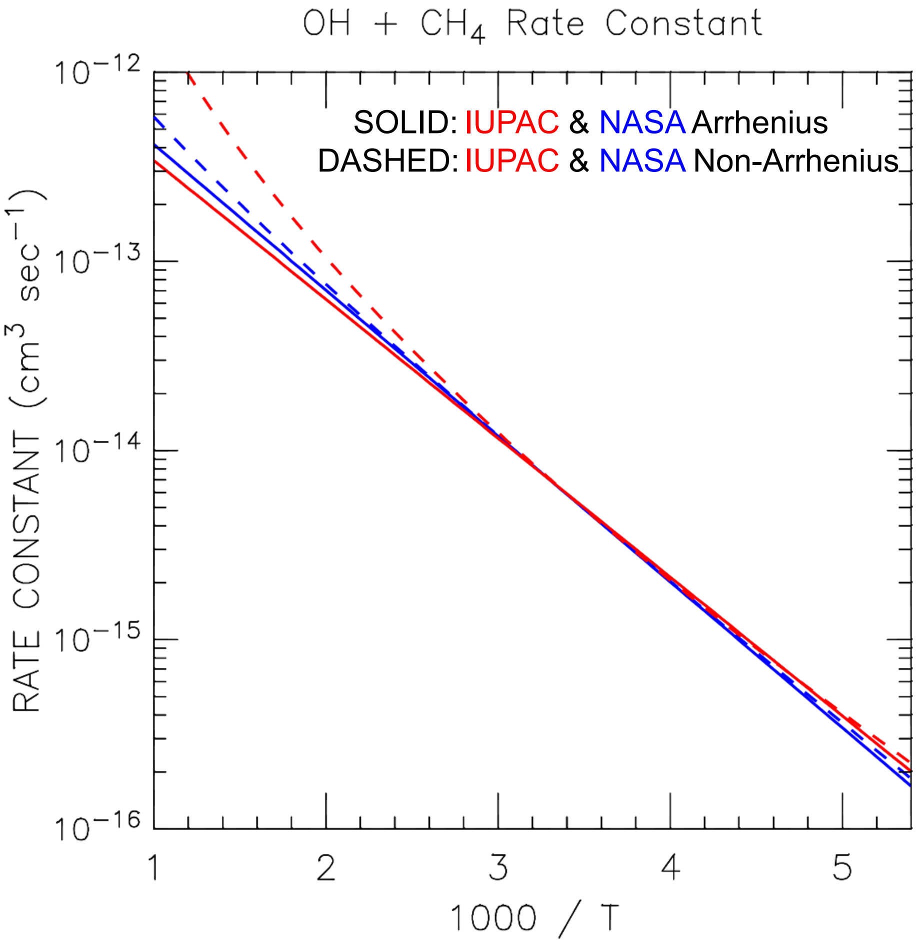


Photolytic Production of OH

$H_2O + h\nu \rightarrow H + OH$ **λ_{MAX} = 242 nm**

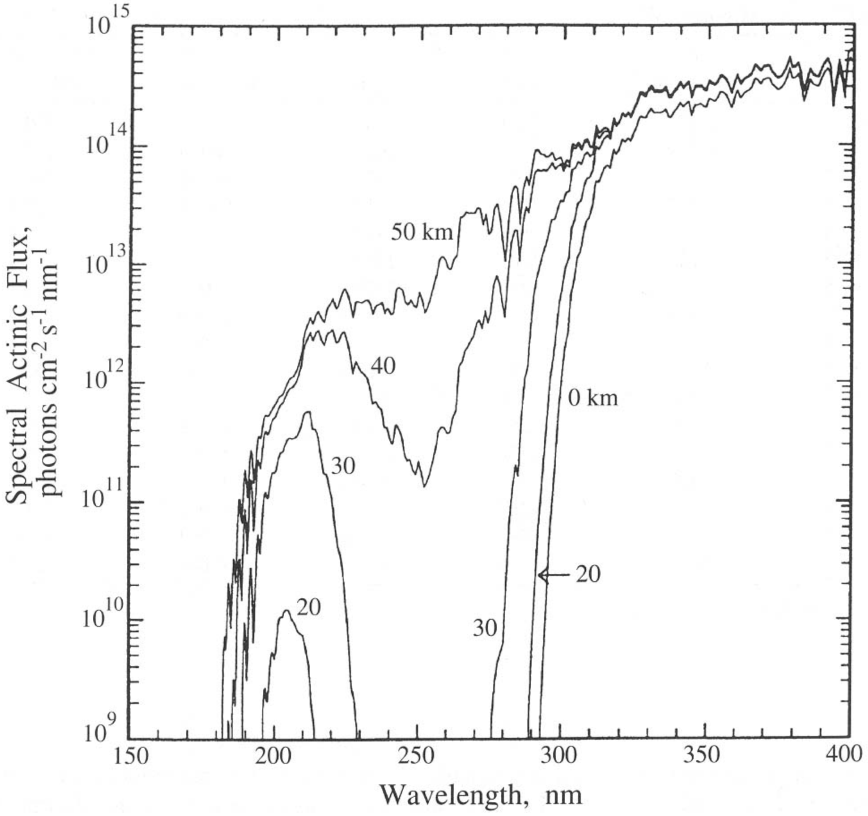


Figure 4.11, Seinfeld and Pandis, 2006
(from DeMore et al., 1994)

Bimolecular Production of OH

a. $H_2O + O(^1D) \rightarrow OH + OH$ **ΔEnthalpy = –28.1 kcal/mole**

b. $H_2O + O(^3P) \rightarrow OH + OH$ **ΔEnthalpy = 17 kcal/mole**

c. $H_2 + O(^1D) \rightarrow OH + H$ **ΔEnthalpy = –43.7 kcal/mole**

d. $H_2 + O(^3P) \rightarrow OH + H$ **ΔEnthalpy = 1.4 kcal/mole**

$$k_a = 1.63\ 10^{-10}\ e^{(60/T)}\ \text{cm}^3\ \text{s}^{-1}$$

$$k_b = 0.0$$

$$k_c = 1.1 \times 10^{-10}\ \text{cm}^3\ \text{s}^{-1}$$

$$k_d = 1.6 \times 10^{-11}\ e^{(-4570/T)}\ \text{cm}^3\ \text{s}^{-1}$$

Bimolecular Production of OH

a. $H_2O + O(^1D) \rightarrow OH + OH$ **ΔEnthalpy = –28.1 kcal/mole**

~~b. $H_2O + O(^3P) \rightarrow OH + OH$~~ **$\Delta$Enthalpy = 17 kcal/mole**

c. $H_2 + O(^1D) \rightarrow OH + H$ **ΔEnthalpy = –43.7 kcal/mole**

d. $H_2 + O(^3P) \rightarrow OH + H$ **ΔEnthalpy = 1.4 kcal/mole**

272 K

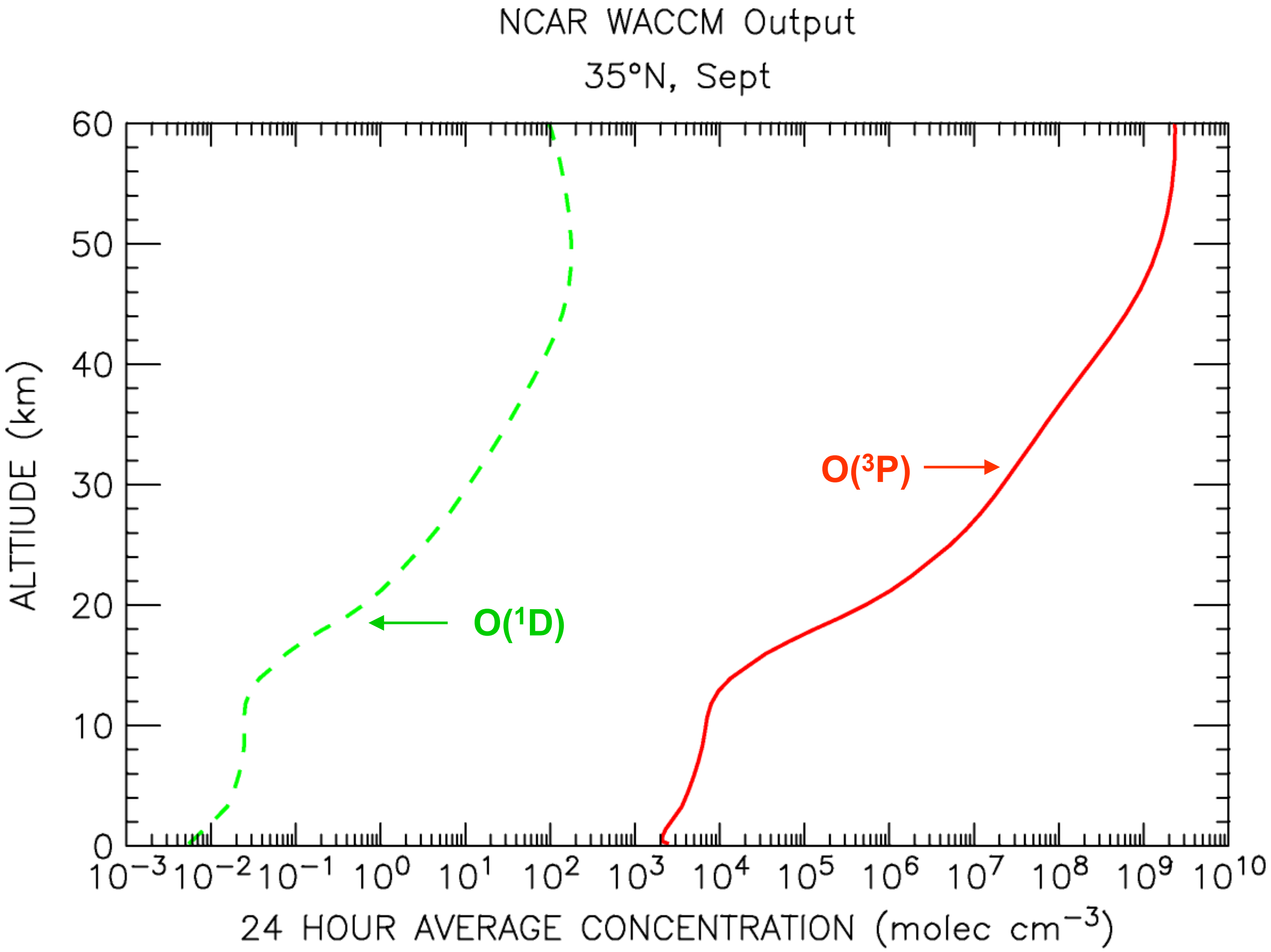
$k_a = 2.0 \times 10^{-10}$ cm^3 s^{-1} ***prod (OH)*** $= 2\, k_a [H_2O] [O(^1D)]$

~~$k_b = 0.0$~~

$k_c = 1.1 \times 10^{-10}$ cm^3 s^{-1} ***prod (OH)*** $= k_c [H_2] [O(^1D)]$

$k_d = 8.1 \times 10^{-19}$ cm^3 s^{-1} ***prod (OH)*** $= k_d [H_2] [O(^3P)]$

Bimolecular Production of OH



At surface, $[O^1D] \approx 10^{-5} [O(^3P)]$

Bimolecular Production of OH

a. $H_2O + O(^1D) \rightarrow OH + OH$ **ΔEnthalpy = –28.1 kcal/mole**

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272 K

$k_a = 2.0 \times 10^{-10}$ cm^3 s^{-1} ***prod (OH)*** $= 2\ k_a\,[H_2O]\ [O(^1D)]$

$k_c = 1.1 \times 10^{-10}$ cm^3 s^{-1} ***prod (OH)*** $= k_c\,[H_2]\ [O(^1D)]$

What is the next critical question to answer, in order to understand how OH is produced near the surface ?

Heterogeneous Reactions “Pseudo Uni-Molecular”

$$\overset{\textbf{13.3 kcal/mole}}{N_2O_5} + \overset{\textbf{–57.8 kcal/mole}}{H_2O\text{ (aqueous)}} \rightarrow \overset{\textbf{2 × –32 kcal/mole}}{2\ HONO_2}$$

ΔEnthalpy = –19.5 kcal/mole

$HONO_2$ same as HNO_3 (nitric acid)
We’ll use both notations interchangeably

- Reaction is exothermic
- Gas phase rate is exceedingly slow
- Proceeds on surfaces (e.g., sulfate aerosols) because the ionic state of H_2O provides access to a *reaction mechanism* that is not accessible in the gas phase

Heterogeneous Reactions "Pseudo Uni-Molecular"

$N_2O_5 + H_2O\ (\text{aqueous}) \rightarrow 2\ HONO_2$

$$\text{Rate of Reaction} = k\,[N_2O_5] \quad ;\ \text{Units of } k \text{ are } s^{-1}$$

$$k = \frac{1}{4}\,\gamma\,(\text{Velocity}_{N2O5})\,(\text{Aerosol Surface Area per Unit Volume})$$

γ = *sticking coefficient* or *reaction probability (dimensionless)*

Velocity $N_2O_5 = (8\ k\ T\ /\ \pi\ m)^{1/2} = 1.45\times10^4\ (\ T\ /\ 108\ )^{1/2}$ cm/sec

Aerosol Surface Area per Unit Volume = $4\ \pi\ r_a^2\ N_a$

where 108 = Molecular Weight of N_2O_5
r_a = radius of aerosol
N_a = number density of aerosol

For this type of reaction:

γ will depend on temperature and aerosol type

γ **does not depend on gas phase abundance of H_2O**
because, ***reacting surface is primarily composed of H_2O***

Heterogeneous Reactions "Pseudo Bi-molecular"

$ClONO_2$ + HCl (adsorbed) → Cl_2 + $HONO_2$

$$k = \frac{1}{4}\gamma\,(\text{Velocity}_{\text{ClONO2}})\,(\text{Aerosol Surface Area per Unit Volume})$$

γ = *sticking coefficient* or *reaction probability (dimensionless)*

Velocity $ClONO_2 = 1.45 \times 10^4 \, (T / 97.5)^{1/2}$ cm/sec

For this type of reaction:

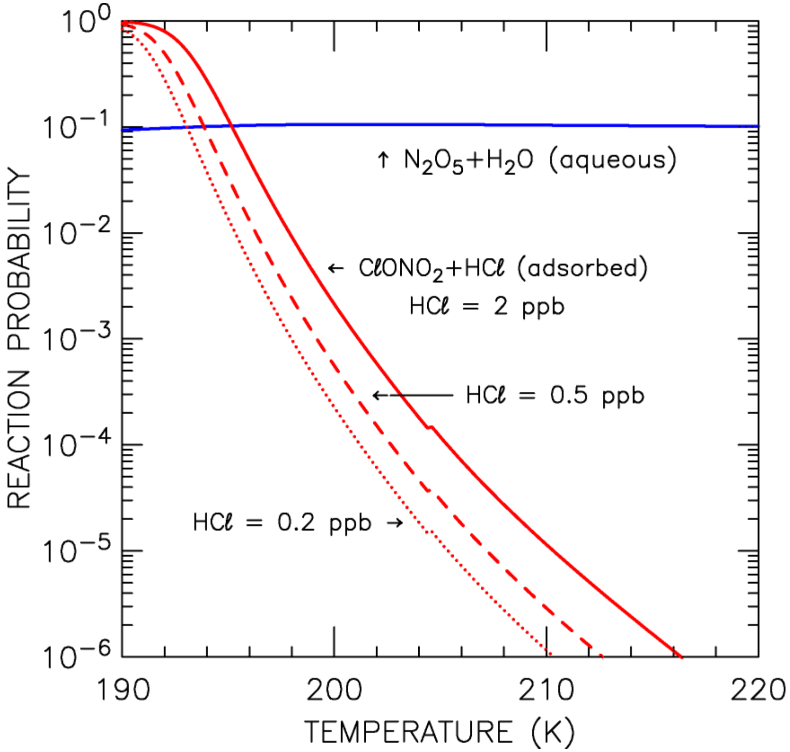
γ will depend on temperature and aerosol type

γ depends on partial pressure (e.g., gas phase abundance) of HCl
because, ***reacting surface is not primarily composed of HCl***

Gas phase H_2O >> gas phase N_2O_5
N_2O_5+H_2O(aqueous) can never deplete gas phase H_2O

Heterogeneous Reactions

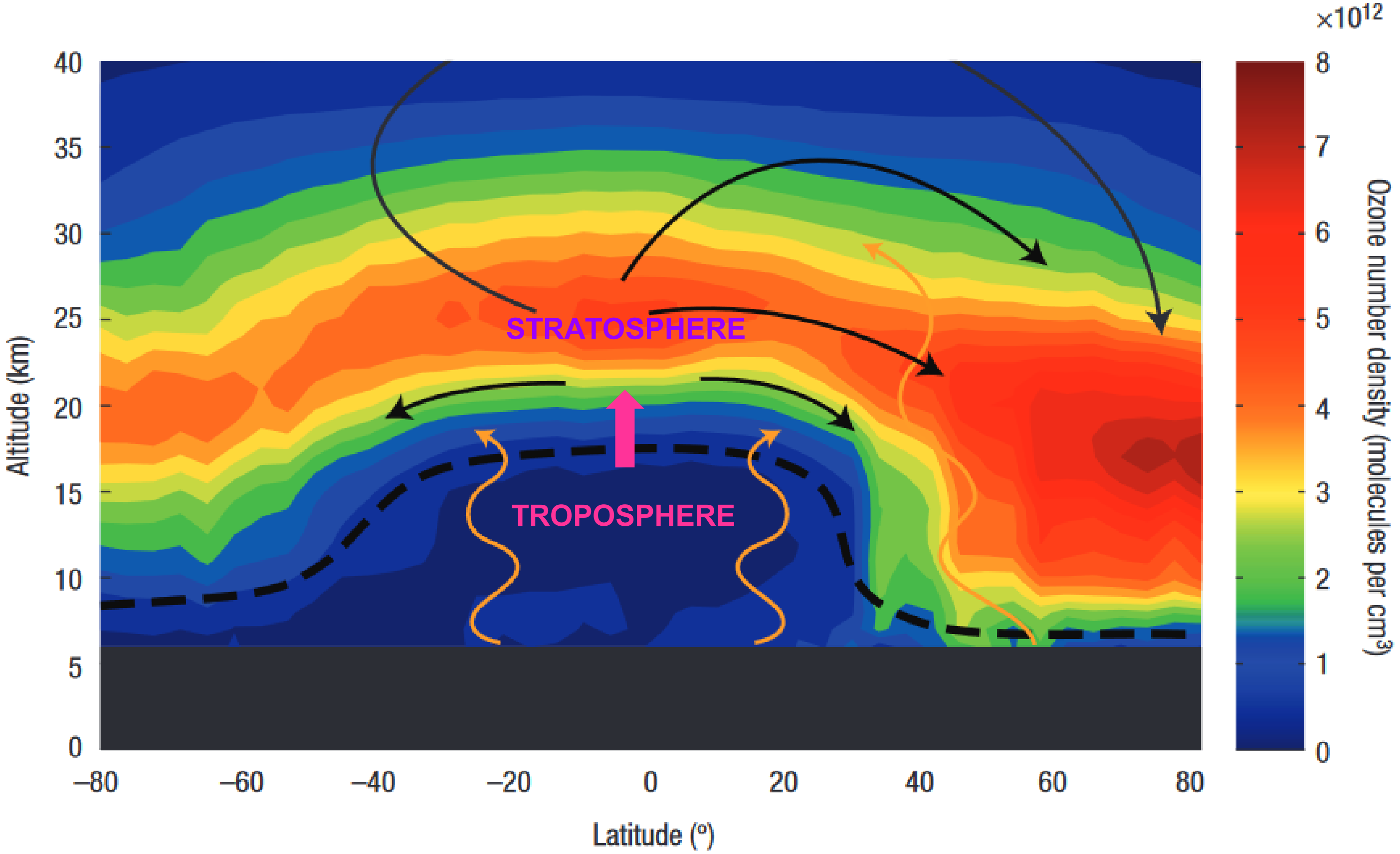
In all cases, γ must be measured in the laboratory



Reaction probabilities given for various surface types, with formulations of various degrees of complexity, in **Section 5** of the JPL Data Evaluation.

Atmospheric Chemistry and Physics by Seinfeld and Pandis provides extensive treatment of aqueous phase chemistry, properties of atmospheric aerosol, organic aerosols, etc.

Tropopause versus Latitude



Brewer–Dobson circulation (arrows), ozone (colors), and tropopause (black dashed line).

The ozone distribution as measured by the OSIRIS satellite instrument in March 2004. The circulation is forced by waves propagating up from the troposphere (orange arrows), especially in the winter hemisphere. Generally, air enters the stratosphere in tropics (slow leak it) and exits at high latitudes, in the winter hemisphere (slow leak out), as noted by the pink & purple block arrows, respectively.

Shaw and Shepherd, Nature Geoscience, 2008.

Lecture 3, Slide 38 (Class)

Thermal Decomposition

30.5 kcal/mole **2 × 24.3 kcal/mole**

$ClOOCl + M \leftrightarrow ClO + ClO + M$ **ΔH = 18.1 kcal/mole**

$$\frac{k_{\mathrm{THERMAL}}}{k_{\mathrm{FORMATION}}} = e^{(G_{\mathrm{REACTANTS}} - G_{\mathrm{PRODUCTS}})/\mathrm{RT}} = \mathrm{K}^{\mathrm{EQUILIBRIUM}}$$

$$\text{Rate of Reaction} = k_{\mathrm{THERMAL}}\,[\mathrm{ClOOCl}]\,; \quad \text{Units of } k_{\mathrm{THERMAL}} \text{ are } \mathrm{s}^{-1}$$

G – Gibbs Free Energy = *H* – *T S*

where *H* = enthalpy
T = temperature
S = entropy

See section 3.2, Chapter 3, Yung and DeMore, for an excellent “intuitive” discussion of enthalpy, entropy, and Gibbs free energy

Thermal Decomposition

30.5 kcal/mole **2 × 24.3 kcal/mole**

$ClOOCl + M \leftrightarrow ClO + ClO + M$ **ΔH = 18.1 kcal/mole**

$$\frac{k_{\mathrm{THERMAL}}}{k_{\mathrm{FORMATION}}} = e^{(G_{\mathrm{REACTANTS}} - G_{\mathrm{PRODUCTS}})/\mathrm{RT}} = \mathrm{K}^{\mathrm{EQUILIBRIUM}}$$

JPL Data Evaluation gives values of $K^{\mathrm{EQUILBRIUM}}$ and $k_{\mathrm{FORMATION}}$

$$K^{\mathrm{EQ}} = 1.27 \times 10^{-27}\, e^{(8744/T)}\, \mathrm{cm}^{-3}$$

In equilibrium:

$$k^{\mathrm{THERMAL}}\,[\mathrm{ClOOCl}] = k^{\mathrm{FORMATION}}\,[\mathrm{ClO}]\,[\mathrm{ClO}]$$

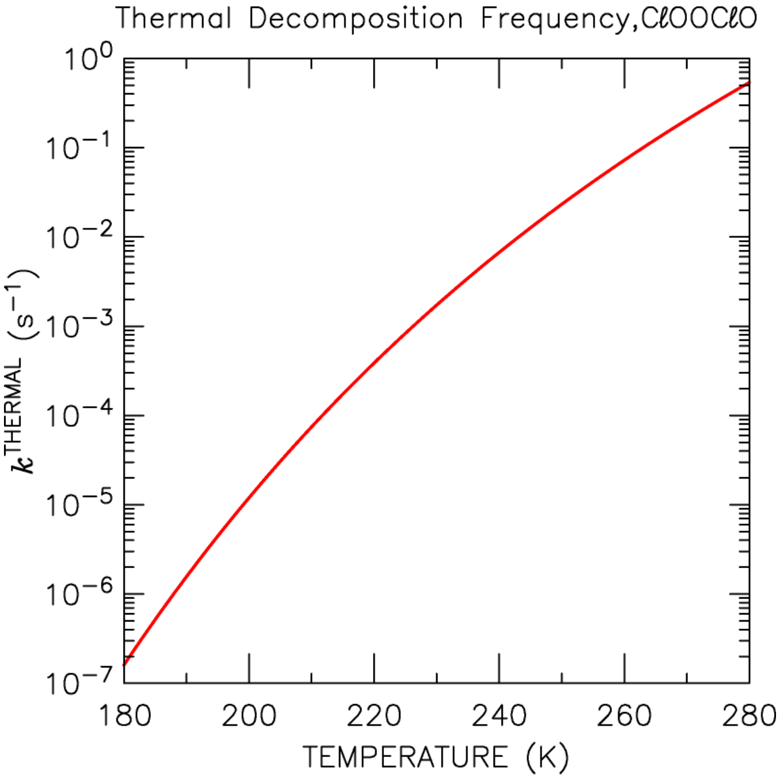
where $k^{\mathrm{THERMAL}} = k^{\mathrm{FORMATION}} \times K^{\mathrm{EQ}}$

- **Energetically, system favors ClOOCl**
- **Entropically, system favors ClO & ClO**

at low T, ClOOCl stable: energy wins !

at high T, ClOOCl unstable: entropy rules !

Equilibrium constants given in **Section 3** of the JPL Data Evaluation.



Polar Ozone Loss Cycles

Route 1: ClOOCl photolysis:

$$\mathrm{ClO + ClO + M \rightarrow ClOOCl + M}$$
$$\mathrm{Cl + O_3 \rightarrow ClO + O_2}$$
$$\mathrm{Cl + O_3 \rightarrow ClO + O_2}$$
$$\mathrm{ClOOCl} + h\nu \rightarrow \mathrm{ClOO + Cl}$$
$$\mathrm{ClOO + heat \rightarrow Cl + O_2}$$

Net: $\mathrm{O_3 + O_3 \rightarrow 3\ O_2}$

Route 2: ClOOCl thermal decomposition:

$$\mathrm{ClO + ClO + M \rightarrow ClOOCl + M}$$
$$\mathrm{ClOOCl + heat \rightarrow ClO + ClO}$$

Net: $\mathrm{M + heat \rightarrow M}$

Extra Slide 1: Termolecular Reactions

$OH + NO_2 + M \rightarrow HONO_2 + M$ ←

$HONO_2$ same as HNO_3 (nitric acid)
We'll use both notations interchangeably

What is M ?   Why is M needed?

$$k_1 \quad OH + NO_2 \rightarrow HONO_2^\dagger$$

$$k_2 \quad HONO_2^\dagger \rightarrow OH + NO_2$$

$$k_3 \quad HONO_2^\dagger + M \rightarrow HONO_2 + M^\dagger$$

$$k_4 \quad M^\dagger \rightarrow M + \text{heat}$$

Rate of first reaction: $k_1\,[OH]\,[NO_2] = k_2\,[HONO_2^\dagger] + k_3[HONO_2^\dagger]\,[M]$

Production of $HONO_2$: $$\frac{d\,\mathrm{HONO_2}}{dt} = k_3\,[\mathrm{HONO_2}^\dagger][\mathrm{M}]$$

$$= \frac{k_1\,k_3\,[\mathrm{OH}][\mathrm{NO_2}][\mathrm{M}]}{k_2 + k_3\,[\mathrm{M}]} = \frac{\dfrac{k_1\,k_3}{k_2}[\mathrm{OH}][\mathrm{NO_2}][\mathrm{M}]}{1 + \dfrac{k_3}{k_2}[\mathrm{M}]}$$

$$= \frac{k_0\,[\mathrm{OH}][\mathrm{NO_2}][\mathrm{M}]}{1 + \dfrac{k_0}{k_\infty}[\mathrm{M}]}$$

Extra Slide 2: Termolecular Reactions

$$\text{Production of HONO}_2 = \frac{k_0\,[\mathrm{OH}][\mathrm{NO_2}][\mathrm{M}]}{1 + \dfrac{k_0}{k_\infty}[\mathrm{M}]}$$

Low pressure limit, [M] $\rightarrow 0$:

$$\text{Production of HONO}_2 = k_0\,[\mathrm{OH}][\mathrm{NO_2}][\mathrm{M}]$$

High pressure limit, [M] $\rightarrow \infty$

$$\text{Production of HONO}_2 = k_\infty\,[\mathrm{OH}][\mathrm{NO_2}]$$

Lindemann-Hinshelwood mechanism: fails to give a good approximation to experimental data in "falloff region" (e.g., transition between two body and three body limits).

Termolecular rate constants given in **Section 2** of the JPL Data Evaluation.

Extra Slide 3: Soft Collisions

To account for the fact that not all collisions are fully deactivating, Jurgen Troe developed a modification to the Lindemann-Hinshelwood rate expression:

$$\mathrm{k_{Troe}} = \mathrm{k_{L-H}} F_c^{\left(1+\left(\log_{10}\left[\mathrm{k_0[M]/k_\infty}\right]\right)^2\right)^{-1}} = \frac{\mathrm{k_0[M]}}{1+\mathrm{k_0[M]/k_\infty}} F_c^{\left(1+\left(\log_{10}\left[\mathrm{k_0[M]/k_\infty}\right]\right)^2\right)^{-1}}$$

- Pressure-dependent reaction rate data can generally be fit well to this expression.
- JPL Committee: $F_c = 0.6$
- IUPAC Committee: F_c is an additional free parameter (often, but not always 0.6)