Introduction to Chemical Kinetics

AOSC / CHEM 433 & AOSC 633

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Class Web Site: http://www.atmos.umd.edu/~rjs/class/spr2019

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 11

14 March 2019

- 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 !

Admission Ticket Lecture 11

Gibbs Free energy involves both enthalpy and entropy. Briefly describe the relative roles of the change in enthalpy and entropy in affecting the equilibrium state of a chemical system.

Under what conditions will enthalpy dominate the equilibrium state?

Under what conditions will entropy dominate the equilibrium state?

Briefly: why is kinetic information needed, in addition to thermodynamic information, to quantity our understanding of atmospheric chemistry?

Bimolecular Gas Phase Reactions

$$\overset{\textbf{8.9 kcal/mole}}{\text{OH}} \quad + \quad \overset{\textbf{–17.8 kcal/mole}}{\text{CH}_4} \quad \rightarrow \quad \overset{\textbf{35.1 kcal/mole}}{\text{CH}_3} \quad + \quad \overset{\textbf{–57.8 kcal/mole}}{\text{H}_2\text{O}}$$

ΔEnthalpy = –13.8 kcal/mole

Exothermic !

$$\text{Rate of Reaction} = \frac{d\text{CH}_4}{dt} = -k\,[\text{OH}][\text{CH}_4]$$

Arrhenius Expression for rate constant:

$$k = 2.45 \times 10^{-12} \times e^{-1775/T} \ \text{cm}^3 \ \text{sec}^{-1}$$

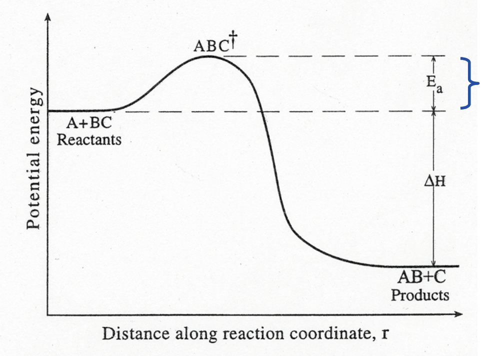

Figure 3.3 Barrier energies for the forward reaction (E_a) and the reverse reaction ($E_a + \Delta H$).

R = 8.3143 ×10⁷ erg / (K mole)
= 2.87 ×10⁶ erg / (K gm) for air

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

Bimolecular Gas Phase Reactions

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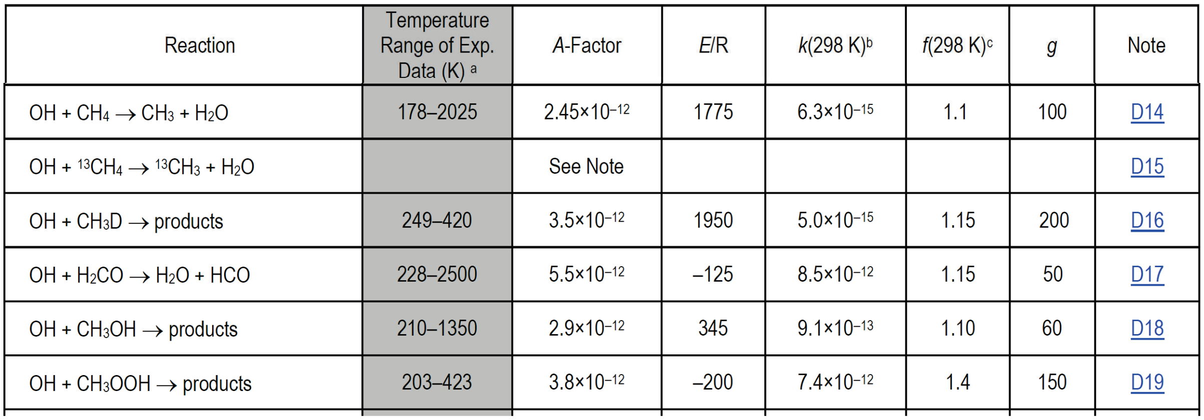

Reaction	Temperature Range of Exp. Data (K) [a]	*A*-Factor	*E*/R	*k*(298 K)[b]	*f*(298 K)[c]	*g*	Note
$\mathrm{OH + CH_4 \rightarrow CH_3 + H_2O}$	178–2025	2.45×10^{-12}	1775	6.3×10^{-15}	1.1	100	D14
$\mathrm{OH + {}^{13}CH_4 \rightarrow {}^{13}CH_3 + H_2O}$		See Note					D15
$\mathrm{OH + CH_3D \rightarrow}$ products	249–420	3.5×10^{-12}	1950	5.0×10^{-15}	1.15	200	D16
$\mathrm{OH + H_2CO \rightarrow H_2O + HCO}$	228–2500	5.5×10^{-12}	–125	8.5×10^{-12}	1.15	50	D17
$\mathrm{OH + CH_3OH \rightarrow}$ products	210–1350	2.9×10^{-12}	345	9.1×10^{-13}	1.10	60	D18
$\mathrm{OH + CH_3OOH \rightarrow}$ products	203–423	3.8×10^{-12}	–200	7.4×10^{-12}	1.4	150	D19

http://jpldataeval.jpl.nasa.gov (2015 Evaluation)

Bimolecular Gas Phase Reactions

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$$\mathrm{OH} + \mathrm{CH_4} \rightarrow \mathrm{CH_3} + \mathrm{H_2O}$$

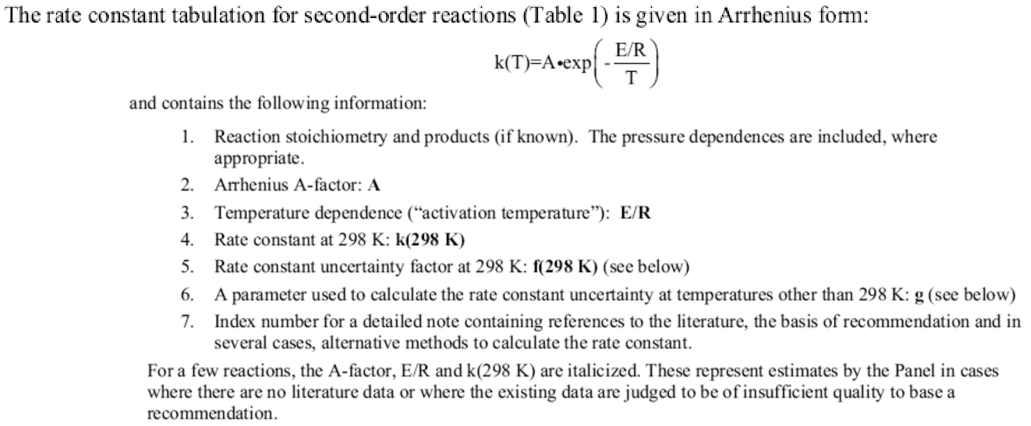
ΔEnthalpy = –13.8 kcal/mole

Exothermic !

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

Arrhenius Expression for rate constant:

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



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

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

and contains the following information:

1. Reaction stoichiometry and products (if known). The pressure dependences are included, where appropriate.
2. Arrhenius A-factor: **A**
3. Temperature dependence ("activation temperature"): **E/R**
4. Rate constant at 298 K: **k(298 K)**
5. Rate constant uncertainty factor at 298 K: **f(298 K)** (see below)
6. A parameter used to calculate the rate constant uncertainty at temperatures other than 298 K: **g** (see below)
7. Index number for a detailed note containing references to the literature, the basis of recommendation and in several cases, alternative methods to calculate the rate constant.

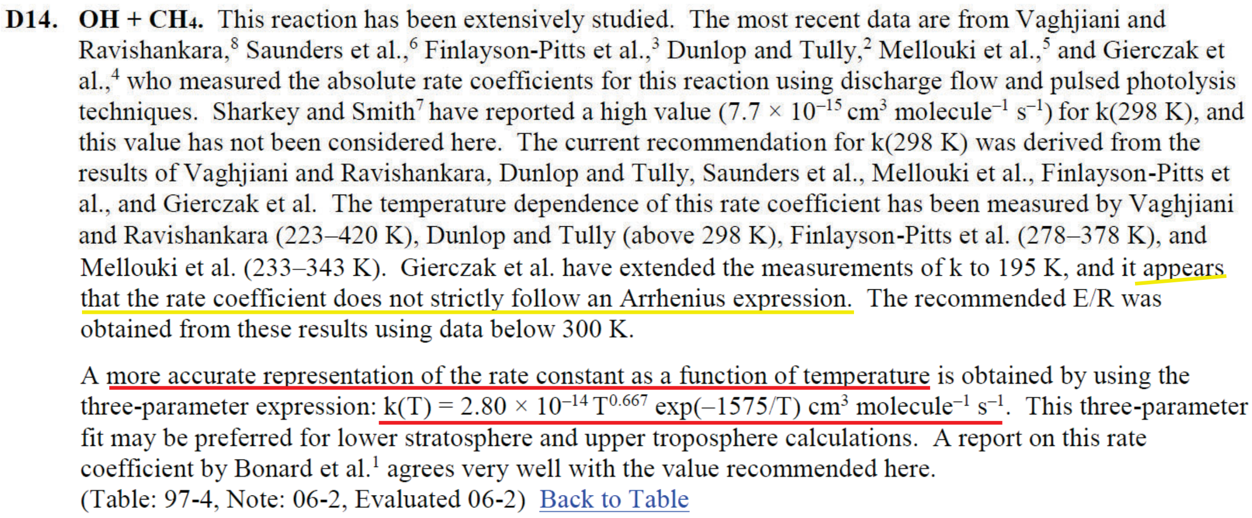
For a few reactions, the A-factor, E/R and k(298 K) are italicized. These represent estimates by the Panel in cases where there are no literature data or where the existing data are judged to be of insufficient quality to base a recommendation.

http://jpldataeval.jpl.nasa.gov (2015 Evaluation)

Bimolecular Gas Phase Reactions

$OH + CH_4 \rightarrow CH_3 + H_2O$

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

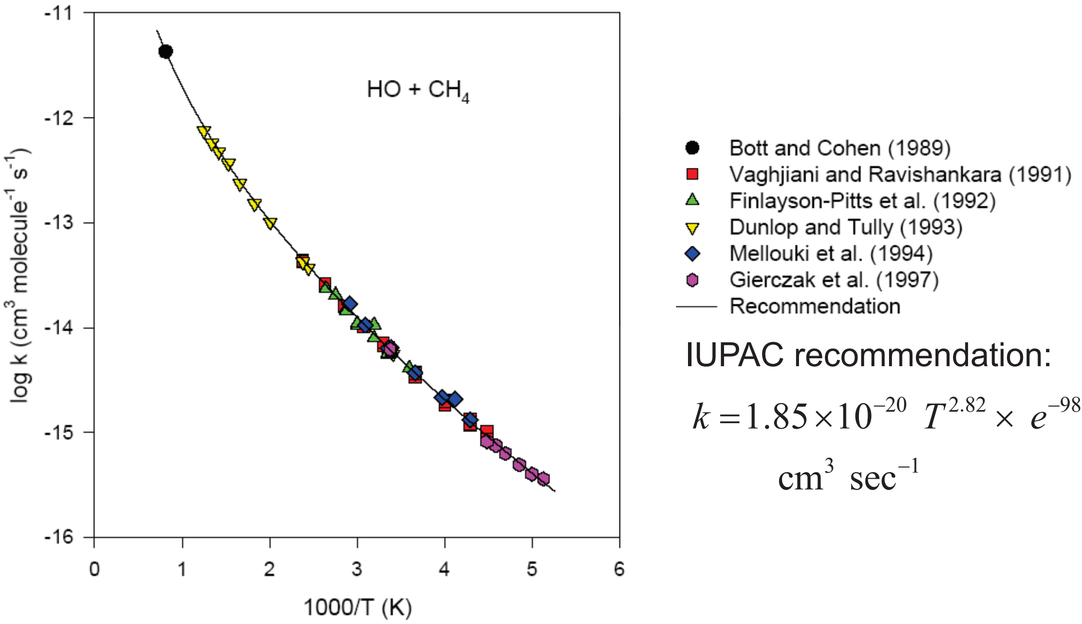


D14. **$OH + CH_4$.** This reaction has been extensively studied. The most recent data are from Vaghjiani and Ravishankara,[8] Saunders et al.,[6] Finlayson-Pitts et al.,[3] Dunlop and Tully,[2] Mellouki et al.,[5] and Gierczak et al.,[4] who measured the absolute rate coefficients for this reaction using discharge flow and pulsed photolysis techniques. Sharkey and Smith[7] have reported a high value (7.7×10^{-15} cm^3 $molecule^{-1}$ 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: $k(T) = 2.80 \times 10^{-14}\, T^{0.667} \exp(-1575/T)$ cm^3 $molecule^{-1}$ 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 (2015 Evaluation)

Bimolecular Gas Phase Reactions



IUPAC recommendation:

$$k = 1.85\times10^{-20}\ T^{2.82}\times e^{-987/T}$$

$$\text{cm}^3\ \text{sec}^{-1}$$

http://www.iupac-kinetic.ch.cam.ac.uk/datasheets/pdf/HOx_VOC1_HO_CH4.pdf

Photolytic Production of OH

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

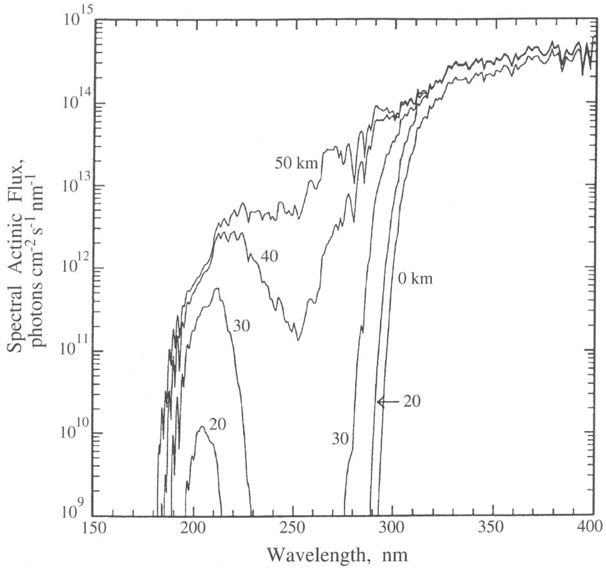


Figure 4.11, Seinfeld and Pandis, 2006
(from DeMore et al., 1994)

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**

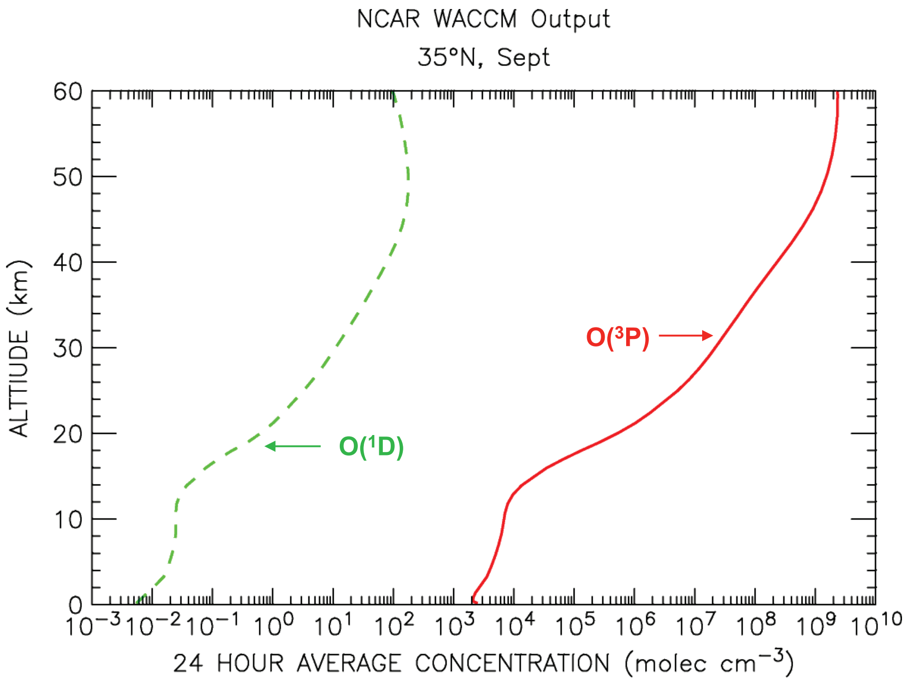
$k_a = 1.63\ 10^{-10}\ e^{(60/T)}\ cm^3\ s^{-1}$

$k_b = 0.0$

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

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

Bimolecular Production of OH



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

Heterogeneous Reactions “Pseudo Uni-Molecular”

13.3 kcal/mole **–57.8 kcal/mole** **2 × –32 kcal/mole**

N_2O_5 + H_2O (aqueous) → 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 (aqueous) → 2 $HONO_2$

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

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

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 + $HONO_2$

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

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

Velocity $ClONO_2 = 1.45\times10^4\ (T / 97.5)^{1/2}$ cm/sec

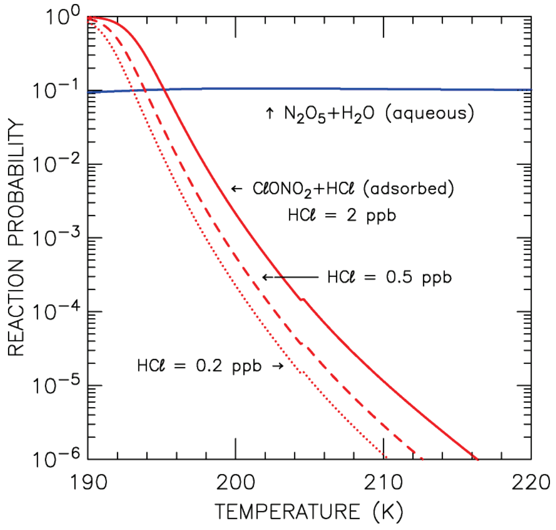
For this type of reaction:

- 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.

Thermal Decomposition

30.5 kcal/mole **2 × 24.3 kcal/mole**

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

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

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

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

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

JPL Data Evaluation gives values of $\mathrm{K}^{\mathrm{EQUILBRIUM}}$ 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.