

# Introduction to Chemical Kinetics AOSC 433/633 & CHEM 433/633

Ross Salawitch

Class Web Site: <http://www.atmos.umd.edu/~rjs/class/spr2013>

## 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 7 March 2013

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### • 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**

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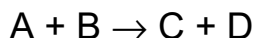
# Types of Reactions

Reading:

1. Unimolecular



2. Bimolecular



3. Termolecular



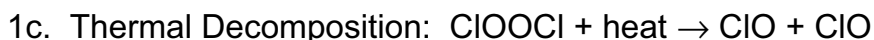
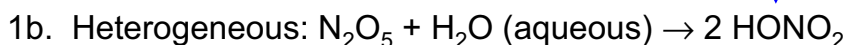
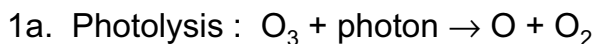
Of course, reactions must balance in a “stoichiometric” manner  
photochemical reactions break and reform chemical bonds;  
they do not rearrange protons

# Types of Reactions

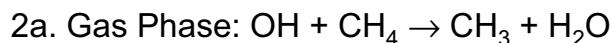
## Atmospheric Chemistry:

HONO<sub>2</sub> same as HNO<sub>3</sub> (nitric acid)  
We'll use both notations interchangeably

1. Unimolecular



2. Bimolecular



3. Termolecular



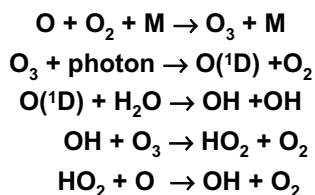
# Importance of Radicals

- 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

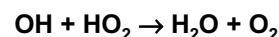
## Initiation



## Propagation



## Termination



# Radicals

- Radicals: unpaired electron in outer valence shell

- Is a species a radical?

Count the electrons:

$\text{HNO}_3$  :  $1 + 7 + 3 \times 8 = 32$  electrons  $\Rightarrow$  no

$\text{NO}$  :  $7 + 8 = 15$  electrons  $\Rightarrow$  yes

$\text{NO}_2$  : 23 electrons  $\Rightarrow$  yes

Other radicals: OH, HO<sub>2</sub>, Cl, Br, ClO, BrO

- Important exception:

Atomic oxygen :

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

What is  $\text{O}({}^1\text{D})$  ?

higher energy “singlet” state with all electrons paired:  $\text{O}({}^1\text{D}) \Rightarrow (1s^2 2s^2 2p_x^2 2p_y^2)$

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

# Admission Ticket Lecture 11

**Gibbs Free energy involves both enthalpy and entropy. Briefly described the relative roles of the change in enthalpy and entropy in affecting the rate of a chemical reaction.**

**Under what conditions will each term tend to dominate the rate of a chemical reaction.**

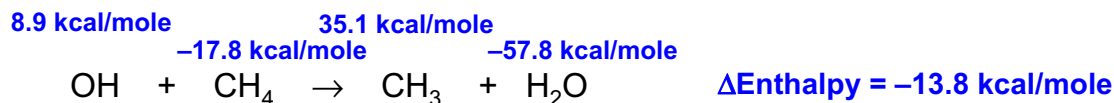
**Briefly: why is kinetic information needed, in addition to thermodynamic information, to quantify our understanding of atmospheric chemistry?**

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## Bimolecular Gas Phase Reactions



**Exothermic !**

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

Arrhenius Expression for rate constant:

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

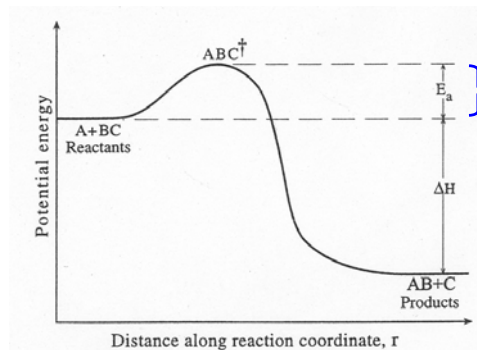


Figure 3.3 Barrier energies for the forward reaction ( $E_a$ ) and the reverse reaction ( $E_a + \Delta H$ ).

$$\begin{array}{l}
 R = 8.3143 \times 10^7 \text{ erg / (K mole)} \\
 = 2.87 \times 10^6 \text{ erg / (K gm) for air}
 \end{array}$$

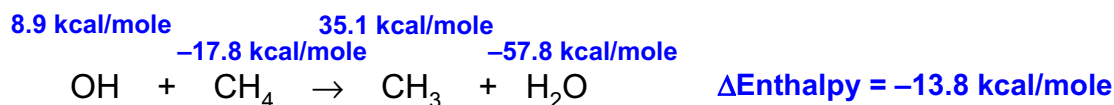
Yung and DeMore, *Photochemistry of Planetary Atmospheres*, Oxford, 1999.

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## Bimolecular Gas Phase Reactions



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

**Exothermic !**

Arrhenius Expression for rate constant:

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

OH + CH <sub>4</sub> → CH <sub>3</sub> + H <sub>2</sub> O	2.45×10 <sup>-12</sup>	1775	6.3×10 <sup>-15</sup>	1.1	100	<u>D12</u>
OH + <sup>13</sup> CH <sub>4</sub> → <sup>13</sup> CH <sub>3</sub> + H <sub>2</sub> O	(See Note)					<u>D13</u>
OH + CH <sub>3</sub> D → products	3.5×10 <sup>-12</sup>	1950	5.0×10 <sup>-15</sup>	1.15	200	<u>D14</u>
OH + H <sub>2</sub> CO → H <sub>2</sub> O + HCO	5.5×10 <sup>-12</sup>	-125	8.5×10 <sup>-12</sup>	1.15	50	<u>D15</u>
OH + CH <sub>3</sub> OH → products	2.9×10 <sup>-12</sup>	345	9.1×10 <sup>-13</sup>	1.10	60	<u>D16</u>
OH + CH <sub>3</sub> OOH → products	3.8×10 <sup>-12</sup>	-200	7.4×10 <sup>-12</sup>	1.4	150	<u>D17</u>

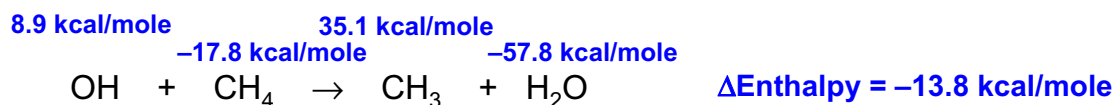
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<http://jpldataeval.jpl.nasa.gov> (2010 Evaluation)

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## Bimolecular Gas Phase Reactions



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

**Exothermic !**

Arrhenius Expression for rate constant:

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

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

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

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.

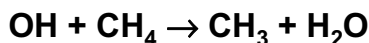
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## Bimolecular Gas Phase Reactions



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

D12. OH + CH<sub>4</sub>. This reaction has been extensively studied. The most recent data are from Vaghjiani and Ravishankara [1506], Saunders et al. [1264], Finlayson-Pitts et al. [507], Dunlop and Tully [468], Mellouki et al. [1007], and Gierczak et al. [549], who measured the absolute rate coefficients for this reaction using discharge flow and pulsed photolysis techniques. Sharkey and Smith [1297] have reported a high value ( $7.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) for  $k(298 \text{ K})$ , and this value has not been considered here. The current recommendation for  $k(298 \text{ K})$  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:  $k = 2.80 \times 10^{-14} T^{0.667} \exp(-1575/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This three-parameter fit may be preferred for lower stratosphere and upper troposphere calculations. A report on this rate coefficient by Bonard et al. [175] agrees very well with the value recommended here. (Table: 97-4, Note: 06-2) [Back to Table](#)

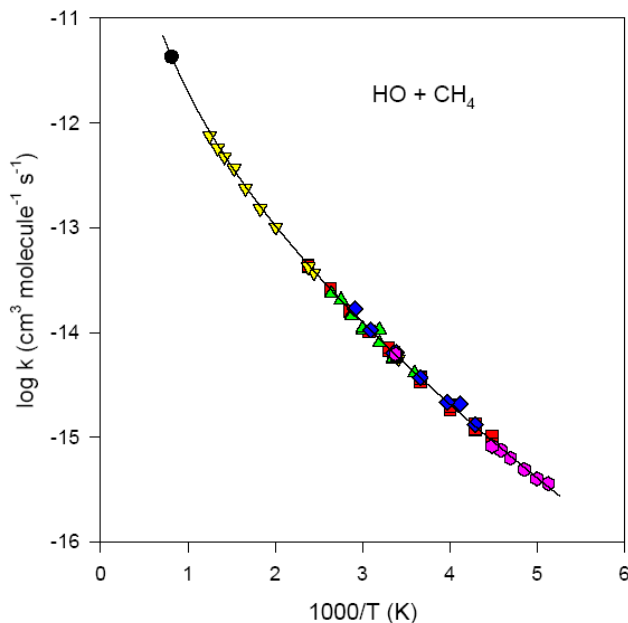
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## Bimolecular Gas Phase Reactions



- Bott and Cohen (1989)
- Vaghjiani and Ravishankara (1991)
- ▲ Finlayson-Pitts et al. (1992)
- ▼ Dunlop and Tully (1993)
- ◆ Mellouki et al. (1994)
- ◆ Gierczak et al. (1997)
- Recommendation

IUPAC recommendation:

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

[http://www.iupac-kinetic.ch.cam.ac.uk/datasheets/pdf/HOx\\_VOC1\\_HO\\_CH4.pdf](http://www.iupac-kinetic.ch.cam.ac.uk/datasheets/pdf/HOx_VOC1_HO_CH4.pdf)

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## Photolytic Production of OH

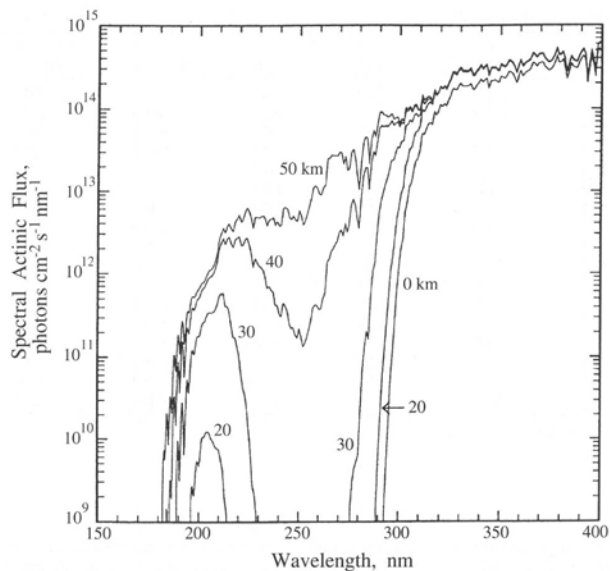


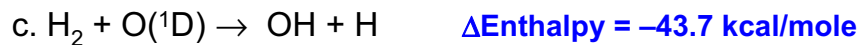
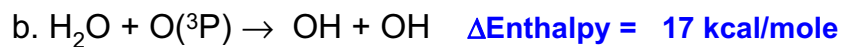
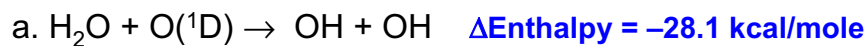
Figure 4.11, Seinfeld and Pandis, 2006  
(from DeMore et al., 1994)

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## Bimolecular Production of OH



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

$$k_b = 0.0$$

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

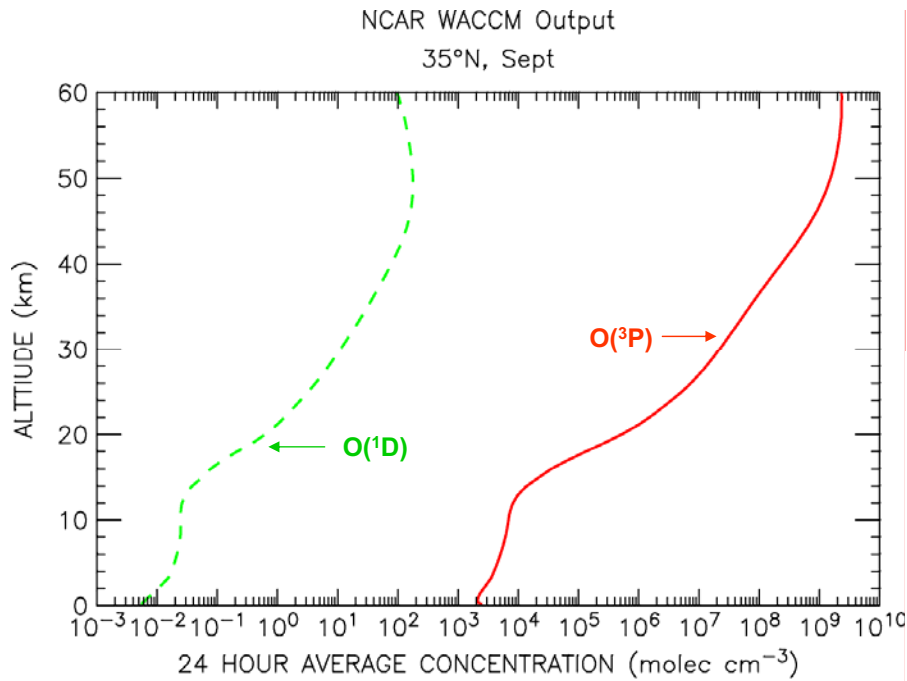
$$k_d = 1.6 \times 10^{-11} e^{(-4570/T)} \text{ cm}^3 \text{ s}^{-1}$$

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# Bimolecular Production of OH



At surface, [O<sup>1</sup>D] ≈ 10<sup>-5</sup> [O(<sup>3</sup>P)]

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## Heterogeneous Reactions “Pseudo Uni-Molecular”

13.3 kcal/mole    -57.8 kcal/mole    2 × -32 kcal/mole



ΔEnthalpy = -19.5 kcal/mole

HONO<sub>2</sub> same as HNO<sub>3</sub> (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<sub>2</sub>O provides access to a *reaction mechanism* that is not accessible in the gas phase

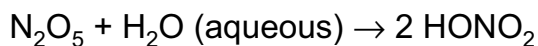
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## Heterogeneous Reactions “Pseudo Uni-Molecular”



Rate of Reaction =  $k [\text{N}_2\text{O}_5]$  ; Units of  $k$  are  $\text{s}^{-1}$

$$k = \frac{1}{4} \gamma (\text{Velocity}_{\text{N}_2\text{O}_5}) (\text{Aerosol Surface Area per Unit Volume})$$

$\gamma$  = sticking coefficient or reaction probability (dimensionless)

$$\text{Velocity}_{\text{N}_2\text{O}_5} = (8 k T / \pi m)^{1/2} = 1.45 \times 10^4 (T / 108)^{1/2} \text{ cm/sec}$$

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

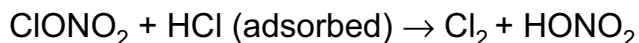
where 108 = Molecular Weight of  $\text{N}_2\text{O}_5$   
 $r_a$  = radius of aerosol  
 $N_a$  = number density of aerosol

For this type of reaction:

$\gamma$  will depend on temperature and aerosol type

$\gamma$  **does not depend on gas phase abundance of  $\text{H}_2\text{O}$**   
because, **reacting surface is primarily composed of  $\text{H}_2\text{O}$**

## Heterogeneous Reactions “Pseudo Bi-molecular”



$$k = \frac{1}{4} \gamma (\text{Velocity}_{\text{ClONO}_2}) (\text{Aerosol Surface Area per Unit Volume})$$

$\gamma$  = sticking coefficient or reaction probability (dimensionless)

$$\text{Velocity}_{\text{ClONO}_2} = 1.45 \times 10^4 (T / 97.5)^{1/2} \text{ cm/sec}$$

For this type of reaction:

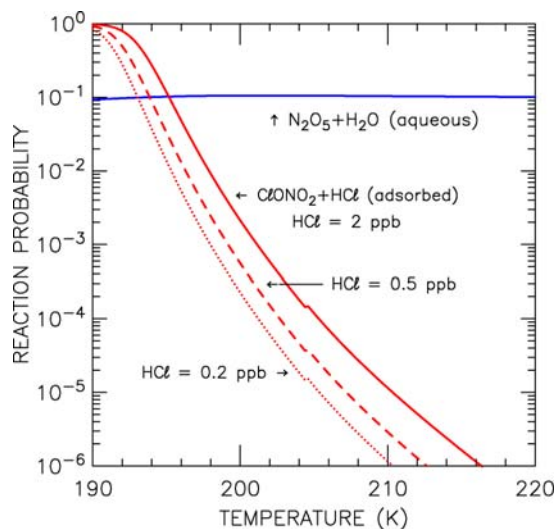
$\gamma$  will depend on temperature and aerosol type

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

Gas phase  $\text{H}_2\text{O} \gg$  gas phase  $\text{N}_2\text{O}_5$   
 $\text{N}_2\text{O}_5 + \text{H}_2\text{O (aqueous)}$  can never deplete gas phase  $\text{H}_2\text{O}$

# Heterogeneous Reactions

In all cases,  $\gamma$  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.

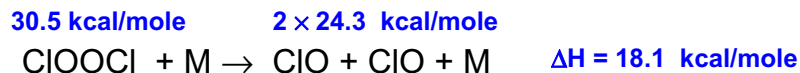
*Atmospheric Chemistry and Physics* by Seinfeld and Pandis provides extensive treatment of aqueous phase chemistry, properties of atmospheric aerosol, organic aerosols, etc.

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## Thermal Decomposition



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

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

$$G - \text{Gibbs Free Energy} = H - T S$$

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

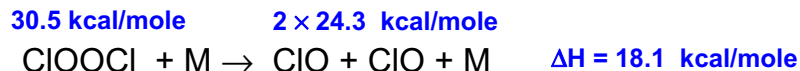
See section 3.2, Chapter 3, Yung and DeMore, for an excellent "intuitive" discussion of enthalpy, entropy, and Gibbs free energy

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# Thermal Decomposition



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

JPL Data Evaluation gives values of  $K^{\text{EQUILIBRIUM}}$  and  $k_{\text{FORMATION}}$

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

In equilibrium:

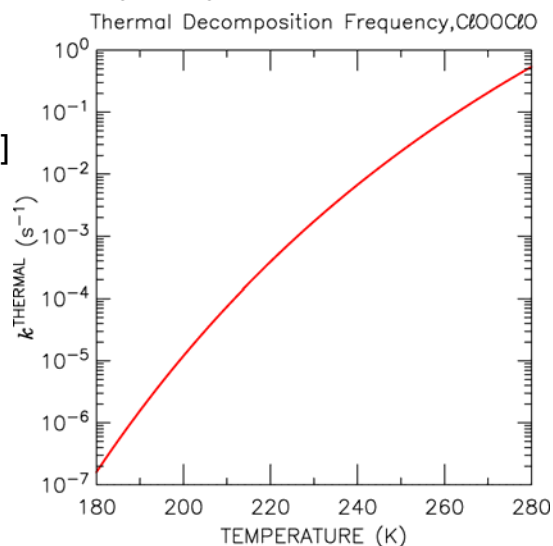
$$k^{\text{THERMAL}} [\text{ClOOCI}] = k^{\text{FORMATION}} [\text{ClO}] [\text{ClO}]$$

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

- Energetically, system favors ClOOCI
- Entropically, system favors ClO & ClO

at low T, ClOOCI stable: energy wins !  
 at high T, ClOOCI unstable: entropy rules !

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

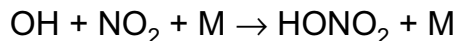


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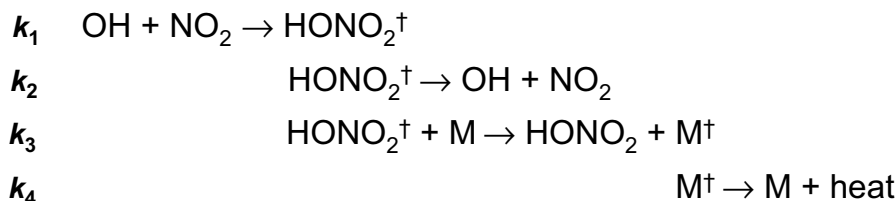
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## Extra Slide #1: Termolecular Reactions



HONO<sub>2</sub> same as HNO<sub>3</sub> (nitric acid)  
 We'll use both notations interchangeably

What is M? Why is M needed?



Rate of first reaction:  $k_1 [\text{OH}] [\text{NO}_2] = k_2 [\text{HONO}_2^\ddagger] + k_3 [\text{HONO}_2^\ddagger] [\text{M}]$

Production of HONO<sub>2</sub>:  $\frac{d \text{HONO}_2}{dt} = k_3 [\text{HONO}_2^\ddagger] [\text{M}]$

$$\begin{aligned} &= \frac{k_1 k_3 [\text{OH}] [\text{NO}_2] [\text{M}]}{k_2 + k_3 [\text{M}]} = \frac{\frac{k_1 k_3}{k_2} [\text{OH}] [\text{NO}_2] [\text{M}]}{1 + \frac{k_3}{k_2} [\text{M}]} \\ &= \frac{k_0 [\text{OH}] [\text{NO}_2] [\text{M}]}{1 + \frac{k_0}{k_\infty} [\text{M}]} \end{aligned}$$

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## Extra Slide #2: Termolecular Reactions

$$\text{Production of HONO}_2 = \frac{k_0 [\text{OH}][\text{NO}_2][\text{M}]}{1 + \frac{k_0}{k_\infty} [\text{M}]}$$

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

$$\text{Production of HONO}_2 = k_0 [\text{OH}][\text{NO}_2][\text{M}]$$

High pressure limit,  $[\text{M}] \rightarrow \infty$

$$\text{Production of HONO}_2 = k_\infty [\text{OH}][\text{NO}_2]$$

**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:

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

- 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)