

# Introduction to Chemical Kinetics

AOSC / CHEM 433 & AOSC / CHEM 633

Ross Salawitch

Class Web Sites:

<http://www2.atmos.umd.edu/~rjs/class/fall2020>

<https://myelms.umd.edu/courses/1291919>

## 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

22 October 2020

# Announcements: Outside of Class

1) Today, 22 Oct : AOSC Weekly Seminar (3:30 pm)

Dr. Earle Wilson, California Institute of Technology

The role of polar gyres in the Southern Ocean overturning circulation

The polar gyres of the Southern Ocean form an important dynamical bridge between the Antarctic Circumpolar Current (ACC) and the major sites of bottom water formation around Antarctica. Among their many functions, these gyres advect upwelled Circumpolar Deep Water (CDW) toward the coastline and create modified water masses that serve as key end-members in the formation of Antarctic Bottom Water (AABW). Despite their uniquely important role, these gyres are rarely acknowledged in conceptual models of the Southern Ocean, which tend to focus on the overturning that occurs across the ACC. Here, we challenge this paradigm by presenting idealized simulations of the Southern Ocean that isolate the effect of a polar gyre on the residual-mean overturning. We find that the formation of a polar gyre coincides with a northward shift in the surface outcrop positions of mid-depth isopycnals. This northward shift is due to the steepening of isopycnals over the zonal ridge that exists along the northern periphery of the gyre. The deeper isopycnals that do not outcrop above the zonal ridge continue across the gyre, with relatively shallow slopes, before eventually outcropping near the Antarctic continental shelf. Thus, by preferentially steering denser isopycnals to the Antarctic coastline, polar gyres restrict the abyssal overturning to the higher density classes of the circumpolar flow. More generally, these results suggest polar gyre dynamics play a critical role in the bifurcation of CDW into AABW and the less dense Antarctic Intermediate Water.

<https://aosc.umd.edu/seminars/department-seminar>

Email Joseph Knisely at [jknisely@umd.edu](mailto:jknisely@umd.edu) for Zoom connection info

- 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***

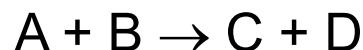
# Types of Reactions

Reading:

1. Unimolecular



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

- 1a. Photolysis : O<sub>3</sub> + photon → O + O<sub>2</sub>
- 1b. Heterogeneous: N<sub>2</sub>O<sub>5</sub> + H<sub>2</sub>O (aqueous) → 2 HONO<sub>2</sub>
- 1c. Thermal Decomposition: ClOOCl + heat → ClO + ClO

### 2. Bimolecular

- 2a. Gas Phase: OH + CH<sub>4</sub> → CH<sub>3</sub> + H<sub>2</sub>O
- 2b. Heterogenous: ClONO<sub>2</sub> + HCl (adsorbed) → Cl<sub>2</sub> + HONO<sub>2</sub>

### 3. Termolecular

3. OH + NO<sub>2</sub> + M → HONO<sub>2</sub> + M

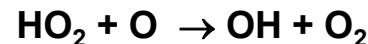
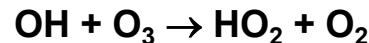
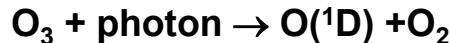
# Importance of Radicals

- 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

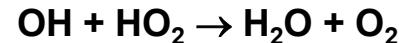
## Initiation



## Propagation



## Termination



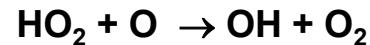
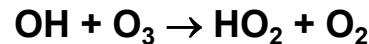
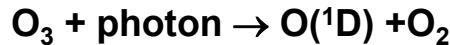
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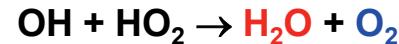
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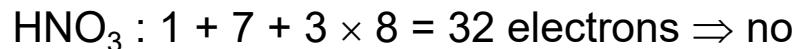
## Termination



# Radicals

- Radicals: unpaired electron in outer valence shell
- Is a species a radical?

Count the electrons:



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

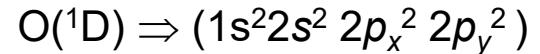
- Important exception:

Atomic oxygen :

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

What is O(<sup>1</sup>D) ?

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



O(<sup>1</sup>D) is even more reactive than O(<sup>3</sup>P) : it is hungry for more electrons !

# Admission Ticket Lecture 12

**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 quantify our understanding of atmospheric chemistry?**

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Enthalpy: measure of change in total energy (microscopic property)

Entropy: measured of change in order (macroscopic property)

Reactions tend to be favored if they release energy or if they create disorder ... i.e. reactions tend to occur in the direction of lower total energy or higher degrees of randomness

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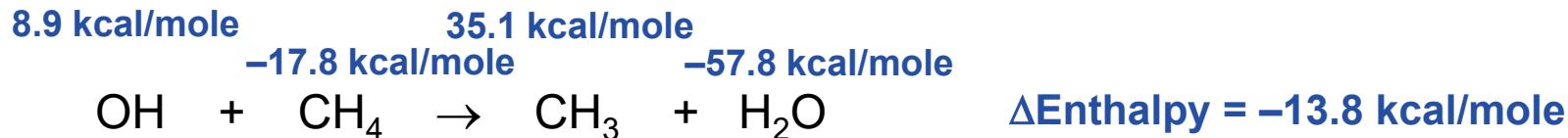
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**Briefly: why is kinetic information needed, in addition to thermodynamic information, to quantify our understanding of atmospheric chemistry?**

Kinetic information is needed because thermodynamic information "offers no clue to the time constant needed for equilibrium to be reached"

# Bimolecular Gas Phase Reactions



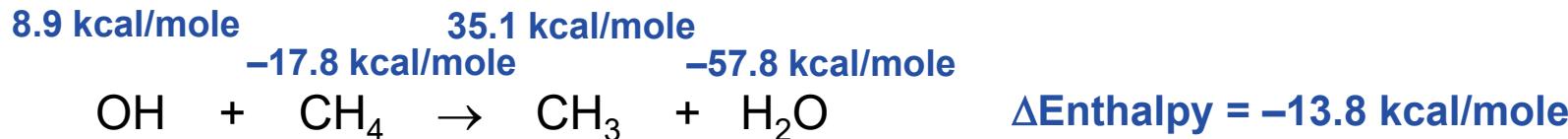
$$\text{Rate of Reaction} = \frac{d\text{CH}_4}{dt} = -k [\text{OH}][\text{CH}_4]$$

**Exothermic !**

Arrhenius Expression for rate constant:

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

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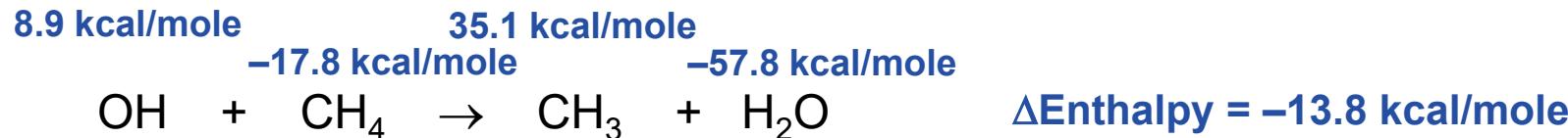
**E<sub>A</sub> / R**  $\Rightarrow$  Activation Energy / Gas Constant

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**A factor**

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**Energy Term**

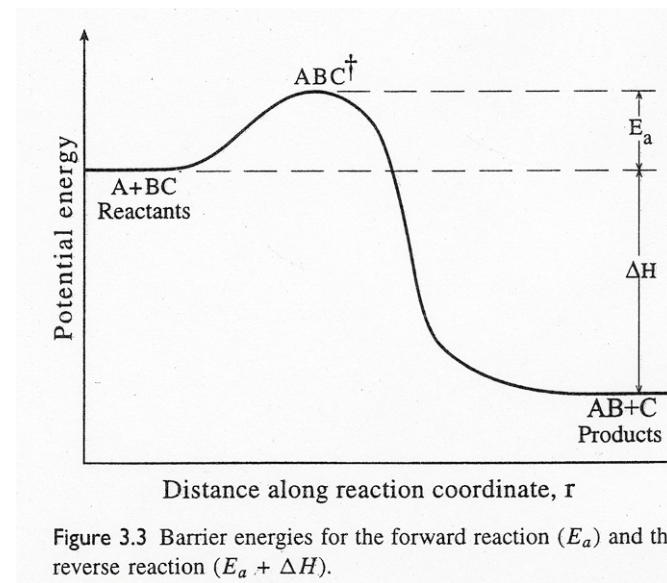
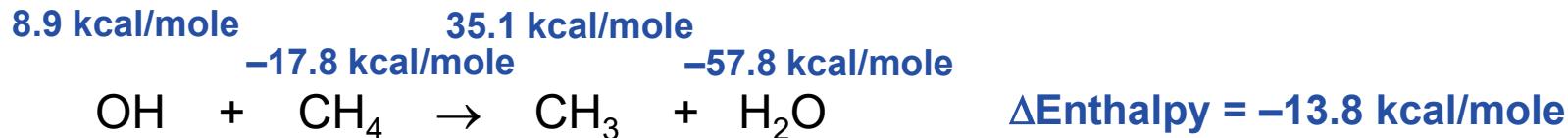


Figure 3.3 Barrier energies for the forward reaction ( $E_a$ ) and the reverse reaction ( $E_a + \Delta H$ ).

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

# Bimolecular Gas Phase Reactions



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A factor

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

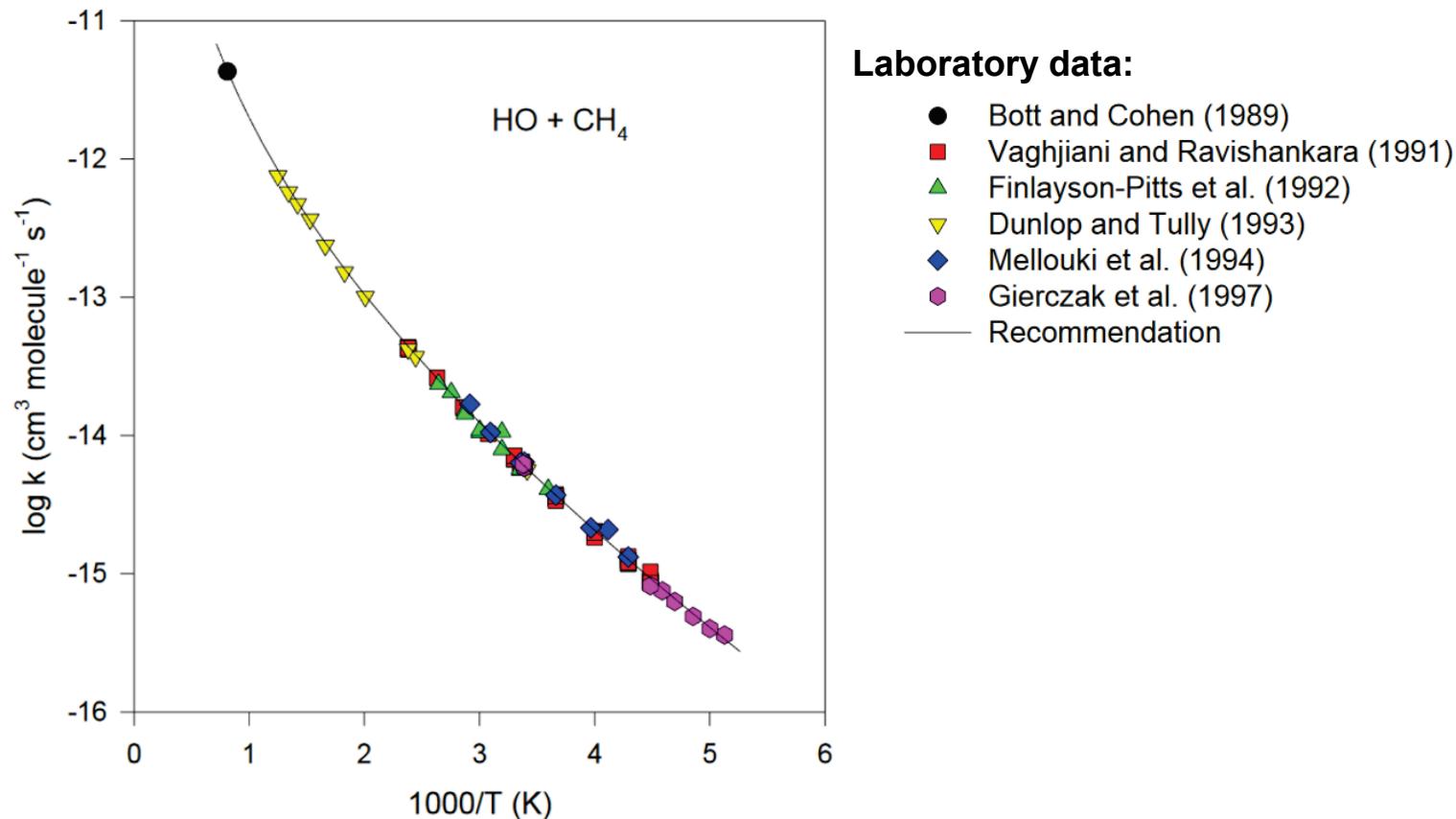
Entropy Term

# Bimolecular Gas Phase Reactions



Arrhenius:

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



IUPAC: International Union of Pure and Applied Chemistry website  
[http://iupac.pole-ether.fr/htdocs/datasheets/pdf/HOx\\_VOC1\\_HO\\_CH4.pdf](http://iupac.pole-ether.fr/htdocs/datasheets/pdf/HOx_VOC1_HO_CH4.pdf)

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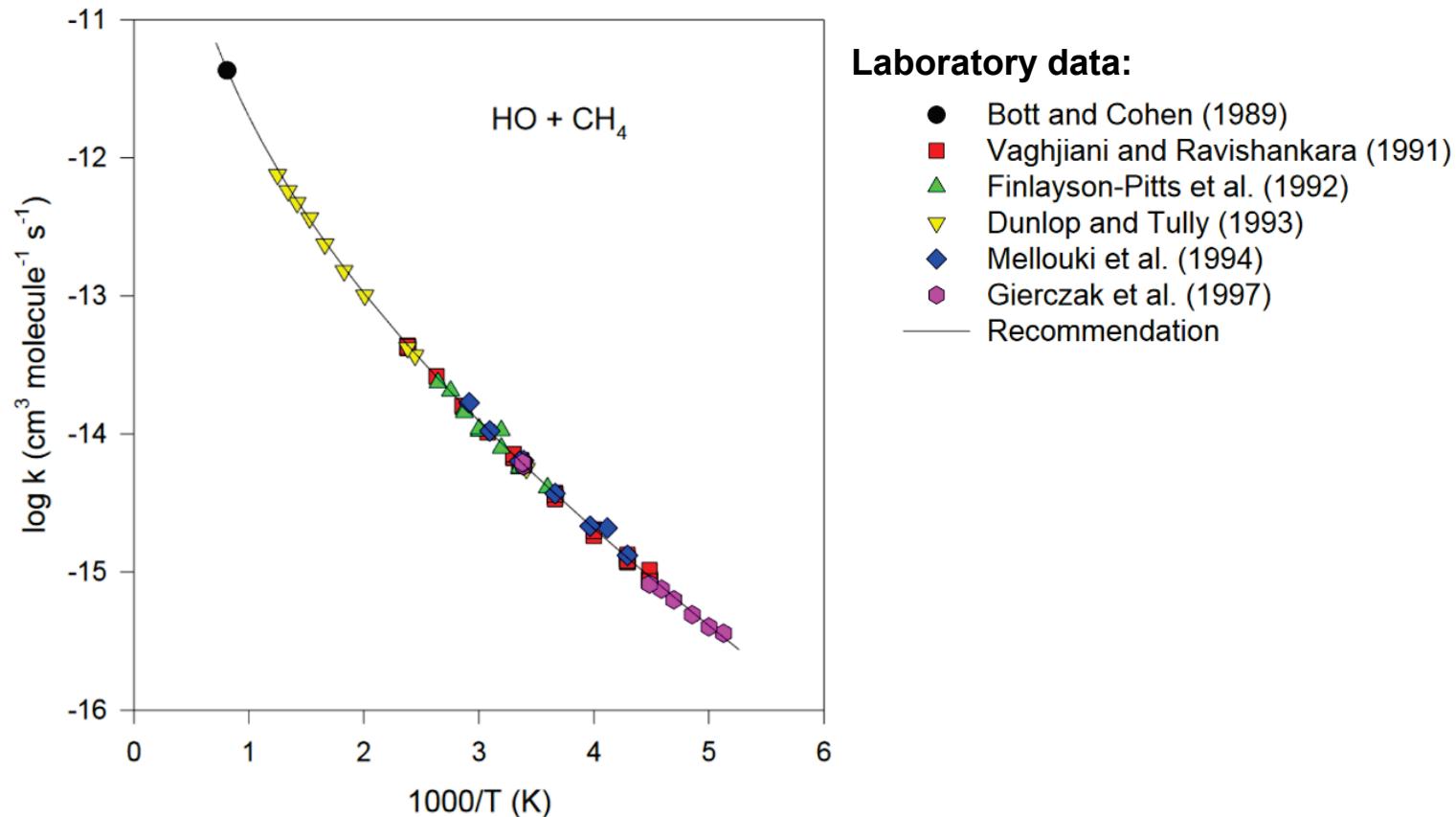


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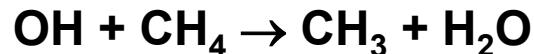
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IUPAC Report:

## Preferred Values

$$k = 6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 1.85 \times 10^{-12} \exp(-1690/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 200-300 \text{ K.}$$

## Reliability

$$\Delta \log k = \pm 0.06 \text{ at } 298 \text{ K}$$

$$\Delta(E/R) = \pm 100 \text{ K.}$$

IUPAC: International Union of Pure and Applied Chemistry website  
[http://iupac.pole-ether.fr/htdocs/datasheets/pdf/HOx\\_VOC1\\_HO\\_CH4.pdf](http://iupac.pole-ether.fr/htdocs/datasheets/pdf/HOx_VOC1_HO_CH4.pdf)

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## IUPAC Report:

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  $k = 1.85 \times 10^{-20} T^{2.82} \exp(-987/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  over the temperature range 195-420 K (Gierczak et al., 1997).

IUPAC: International Union of Pure and Applied Chemistry website  
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Arrhenius:

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

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Non-Arrhenius

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

$$k^{\text{NASA}} = 2.80 \times 10^{-14} \times T^{0.667} e^{-1575/T} \text{ cm}^3 \text{ sec}^{-1}$$

Reaction	Temperature Range of Exp. Data (K) <sup>a</sup>	A-Factor	E/R	$k(298 \text{ K})^b$	$f(298 \text{ K})^c$	$g$	Note
$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	178–2025	$2.45 \times 10^{-12}$	1775	$6.3 \times 10^{-15}$	1.1	100	<a href="#">D14</a>
$\text{OH} + {}^{13}\text{CH}_4 \rightarrow {}^{13}\text{CH}_3 + \text{H}_2\text{O}$		See Note					<a href="#">D15</a>
$\text{OH} + \text{CH}_3\text{D} \rightarrow \text{products}$	249–420	$3.5 \times 10^{-12}$	1950	$5.0 \times 10^{-15}$	1.15	200	<a href="#">D16</a>
$\text{OH} + \text{H}_2\text{CO} \rightarrow \text{H}_2\text{O} + \text{HCO}$	228–2500	$5.5 \times 10^{-12}$	-125	$8.5 \times 10^{-12}$	1.15	50	<a href="#">D17</a>
$\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{products}$	210–1350	$2.9 \times 10^{-12}$	345	$9.1 \times 10^{-13}$	1.10	60	<a href="#">D18</a>

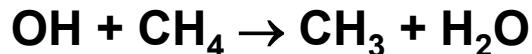
The rate constant tabulation for second-order reactions (Table 1) is given in Arrhenius form:

This is a minus sign

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

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

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- D14. **OH + CH<sub>4</sub>.** This reaction has been extensively studied. The most recent data are from Vaghjiani and Ravishankara,<sup>8</sup> Saunders et al.,<sup>6</sup> Finlayson-Pitts et al.,<sup>3</sup> Dunlop and Tully,<sup>2</sup> Mellouki et al.,<sup>5</sup> and Gierczak et al.,<sup>4</sup> who measured the absolute rate coefficients for this reaction using discharge flow and pulsed photolysis techniques. Sharkey and Smith<sup>7</sup> have reported a high value ( $7.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ) 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:  $k(T) = 2.80 \times 10^{-14} T^{0.667} \exp(-1575/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . This three-parameter fit may be preferred for lower stratosphere and upper troposphere calculations. A report on this rate coefficient by Bonard et al.<sup>1</sup> 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



Arrhenius:

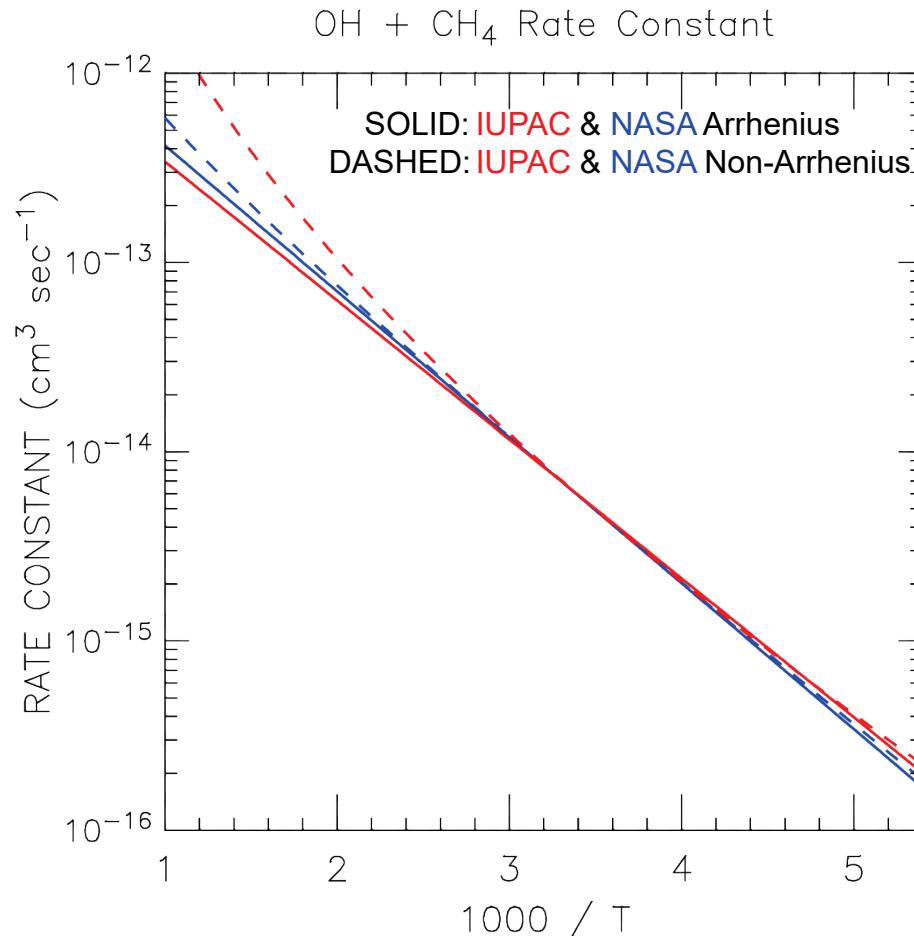
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# Bimolecular Gas Phase Reactions



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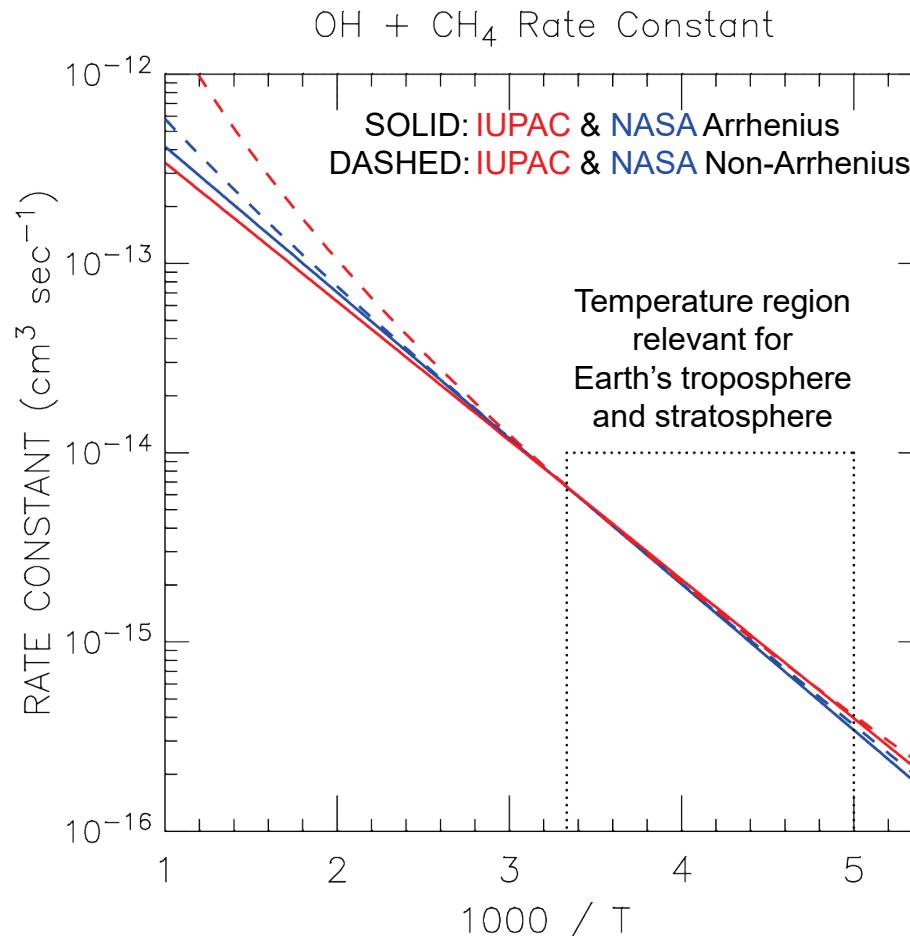
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# Photolytic Production of OH

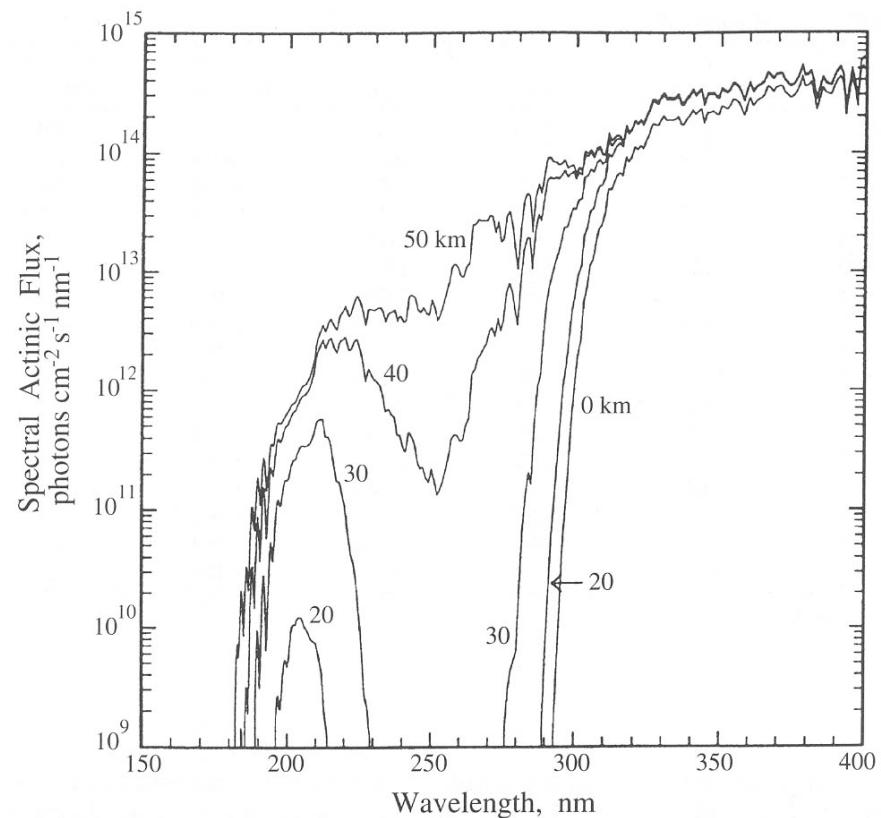


Figure 4.11, Seinfeld and Pandis, 2006  
(from DeMore et al., 1994)

# Photolytic Production of OH



Photons with  $\lambda < 242 \text{ nm}$  do not reach the surface;  
tropospheric OH not produced by photolysis of  $\text{H}_2\text{O}$

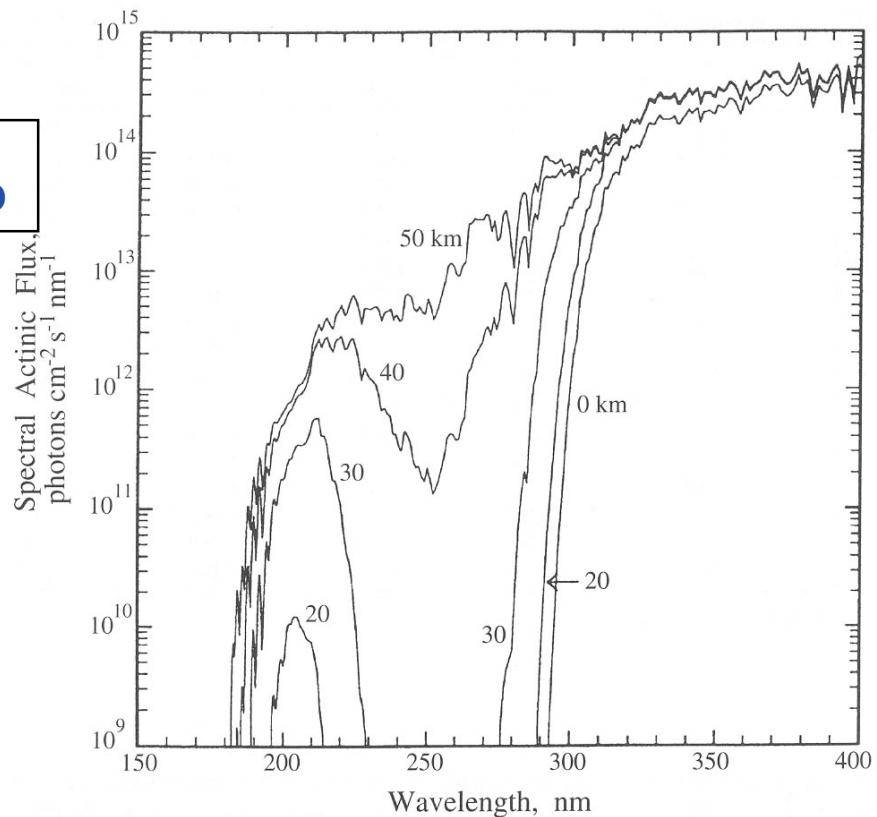
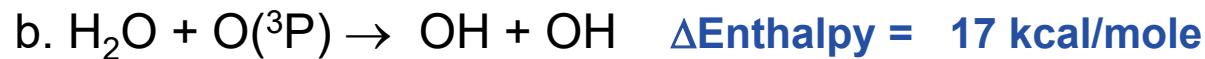


Figure 4.11, Seinfeld and Pandis, 2006  
(from DeMore et al., 1994)

# Bimolecular Production of OH



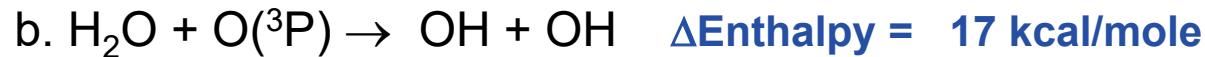
$$k_a = 1.63 \times 10^{-10} e^{(60/T)} \text{ cm}^3 \text{ s}^{-1}$$

$$k_b = 0.0$$

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

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

# Bimolecular Production of OH



$$k_a = 1.63 \times 10^{-10} e^{(60/T)} \text{ cm}^3 \text{ s}^{-1} = 2.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} @ 272 \text{ K}$$

$$k_b = 0.0$$

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

$$k_d = 1.6 \times 10^{-11} e^{(-4570/T)} \text{ cm}^3 \text{ s}^{-1} = 8.1 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1} @ 272 \text{ K}$$

# Bimolecular Production of OH



**272 K**

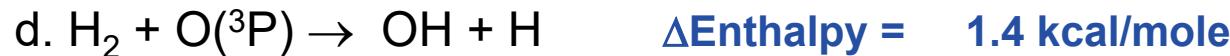
$$k_a = 2.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

~~$k_b = 0.0$~~

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

$$k_d = 8.1 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1}$$

# Bimolecular Production of OH



272 K

$$k_a = 2.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad \textit{prod(OH)} = 2 k_a [\text{H}_2\text{O}] [\text{O}({}^1\text{D})]$$

~~$k_b = 0.0$~~

$$k_c = 1.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad \textit{prod(OH)} = k_c [\text{H}_2] [\text{O}({}^1\text{D})]$$

$$k_d = 8.1 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1} \quad \textit{prod(OH)} = k_d [\text{H}_2] [\text{O}({}^3\text{P})]$$

# Bimolecular Production of OH



272 K

$$k_a = 2.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad \textit{prod(OH)} = 2 k_a [\text{H}_2\text{O}] [\text{O}({}^1\text{D})]$$

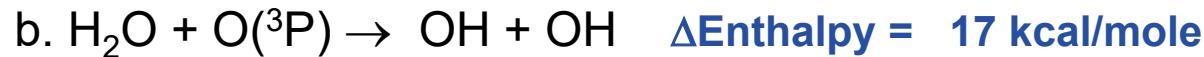
~~$k_b = 0.0$~~

$$k_c = 1.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad \textit{prod(OH)} = k_c [\text{H}_2] [\text{O}({}^1\text{D})]$$

$$k_d = 8.1 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1} \quad \textit{prod(OH)} = k_d [\text{H}_2] [\text{O}({}^3\text{P})]$$

What is relative abundance of  $[\text{O}({}^1\text{D})]$  and  $[\text{O}({}^3\text{P})]$  ?

# Bimolecular Production of OH



272 K

$$k_a = 2.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad \textit{prod(OH)} = 2 k_a [\text{H}_2\text{O}] [\text{O}({}^1\text{D})]$$

~~$k_b = 0.0$~~

$$k_c = 1.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad \textit{prod(OH)} = k_c [\text{H}_2] [\text{O}({}^1\text{D})]$$

$$k_d = 8.1 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1} \quad \textit{prod(OH)} = k_d [\text{H}_2] [\text{O}({}^3\text{P})]$$

What is relative abundance of  $[\text{O}({}^1\text{D})]$  and  $[\text{O}({}^3\text{P})]$  ?

What figures from last lecture are relevant ?!?

# Bimolecular Production of OH

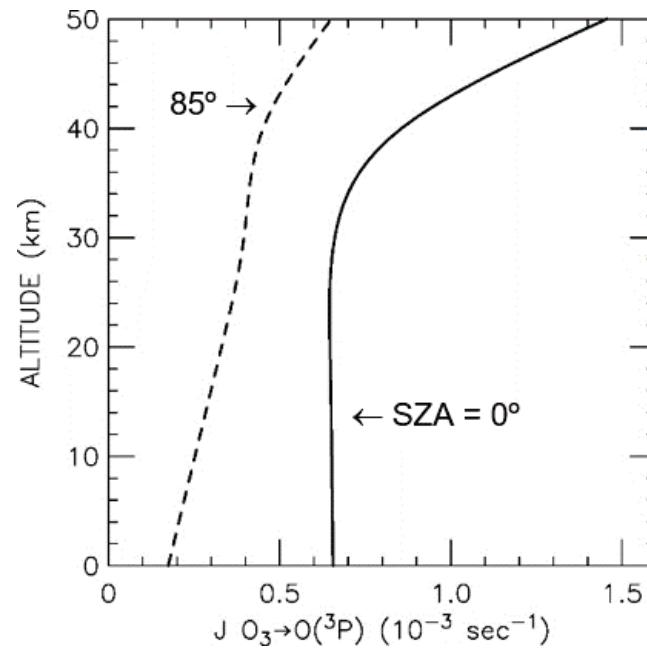
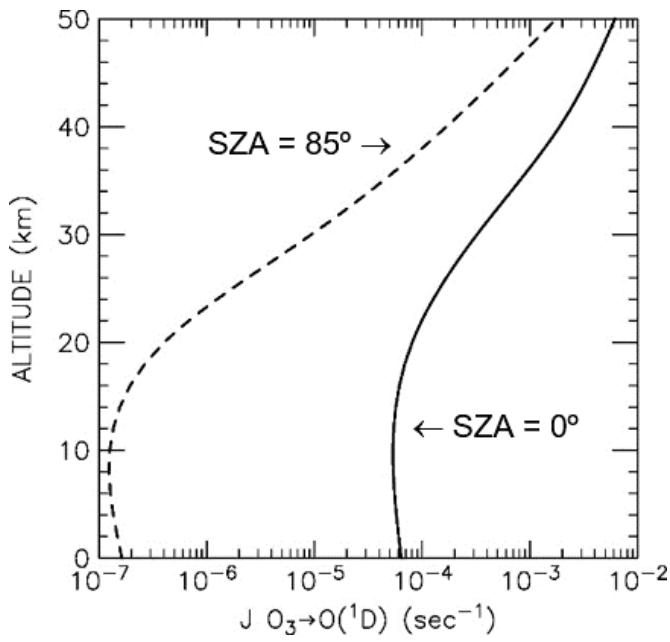


Figure indicates production rate of  $O(^1D)$  > production rate of  $O(^3P)$  at high altit  
& production rate of  $O(^1D)$  < production rate of  $O(^3P)$  at low altit

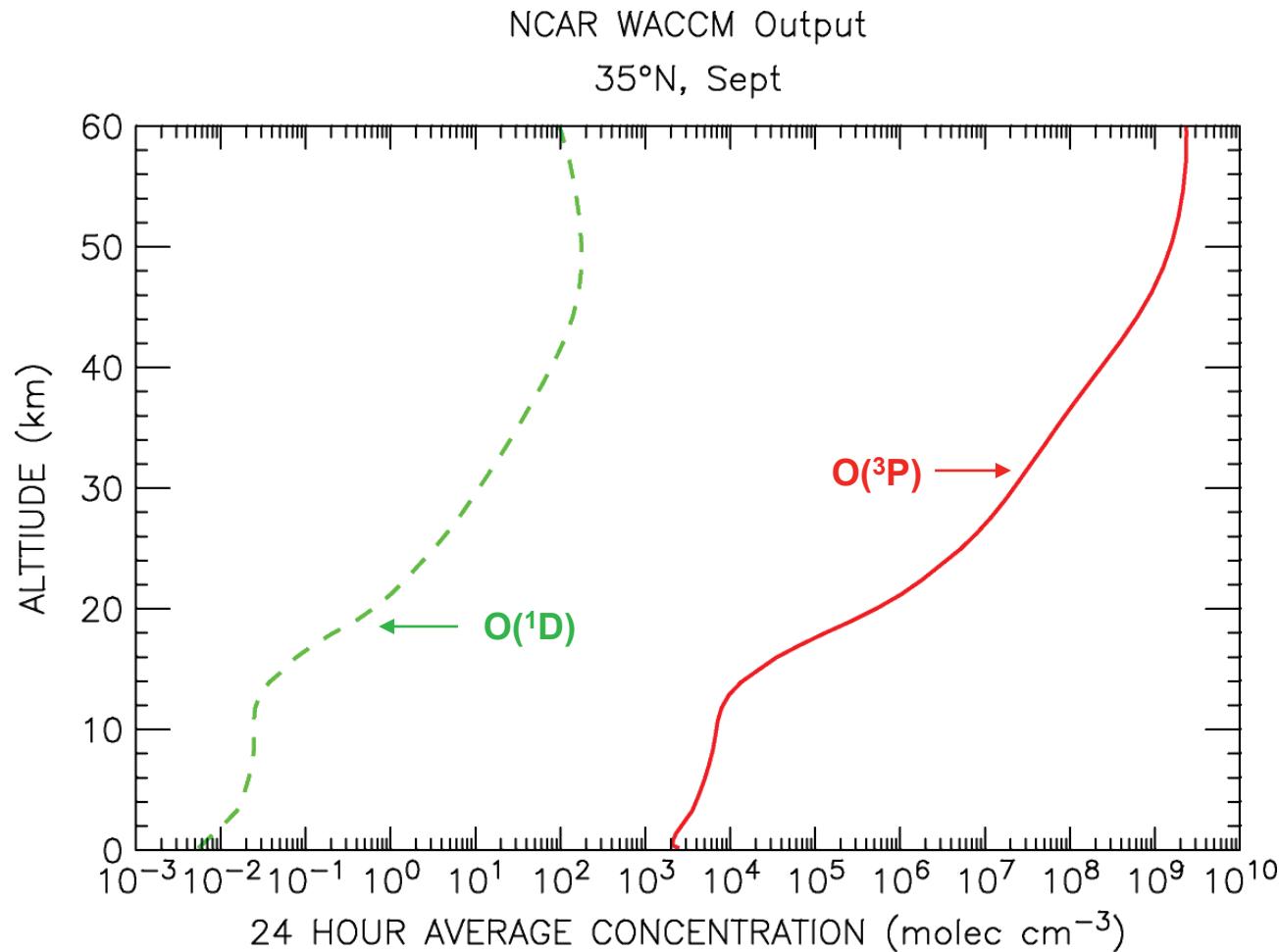
However,  $O(^1D)$  is converted to  $O(^3P)$  via collisions with  $N_2$ :



and  $O(^3P)$  is lost by reaction with  $O_2$  relatively slowly:



# Bimolecular Production of OH



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

# Bimolecular Production of OH



272 K

$$k_a = 2.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad \textit{prod(OH)} = 2 k_a [\text{H}_2\text{O}] [\text{O}({}^1\text{D})]$$

~~$k_b = 0.0$~~

$$k_c = 1.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad \textit{prod(OH)} = k_c [\text{H}_2] [\text{O}({}^1\text{D})] \approx k_c [\text{H}_2] 10^{-5} [\text{O}({}^3\text{P})]$$

$$k_d = 8.1 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1} \quad \textit{prod(OH)} = k_d [\text{H}_2] [\text{O}({}^3\text{P})]$$

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

# Bimolecular Production of OH



272 K

$$k_a = 2.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad \text{prod(OH)} = 2 k_a [\text{H}_2\text{O}] [\text{O}({}^1\text{D})]$$

~~$k_b = 0.0$~~

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~~$k_d = 8.1 \times 10^{-19} \text{ cm}^3 \text{ s}^{-1} \quad \text{prod(OH)} = k_d [\text{H}_2] [\text{O}({}^3\text{P})]$~~

**Reaction c will proceed much faster than reaction d near the surface, despite the unfavorable  $[\text{O}({}^1\text{D})]$  to  $[\text{O}({}^3\text{P})]$  ratio, because of the much faster rate constant**

# Bimolecular Production of OH



272 K

$$k_a = 2.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad \textit{prod(OH)} = 2 k_a [\text{H}_2\text{O}] [\text{O}({}^1\text{D})]$$

$$k_c = 1.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad \textit{prod(OH)} = k_c [\text{H}_2] [\text{O}({}^1\text{D})]$$

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

# Bimolecular Production of OH



272 K

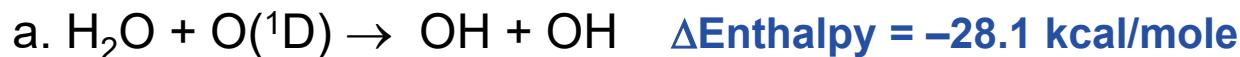
$$k_a = 2.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad \textit{prod(OH)} = 2 k_a [\text{H}_2\text{O}] [\text{O}({}^1\text{D})]$$

$$k_c = 1.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad \textit{prod(OH)} = k_c [\text{H}_2] [\text{O}({}^1\text{D})]$$

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

Relative abundance of  $[\text{H}_2\text{O}]$  and  $[\text{H}_2]$  ?!?

# Bimolecular Production of OH



272 K

$$k_a = 2.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad \textit{prod(OH)} = 2 k_a [\text{H}_2\text{O}] [\text{O}({}^1\text{D})]$$

$$k_c = 1.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad \textit{prod(OH)} = k_c [\text{H}_2] [\text{O}({}^1\text{D})]$$

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

Relative abundance of  $[\text{H}_2\text{O}]$  and  $[\text{H}_2]$  ?!?

[ $\text{H}_2$ ] is present at ~530 ppb in the troposphere

<http://www.atmos-chem-phys.net/11/3375/2011/acp-11-3375-2011.html>

[ $\text{H}_2\text{O}$ ] is present at 0.4 to 4 % in the troposphere

# Bimolecular Production of OH



272 K

$$k_a = 2.0 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1} \quad \text{prod(OH)} = 2 k_a [\text{H}_2\text{O}] [\text{O}({}^1\text{D})]$$

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[ $\text{H}_2\text{O}$ ] is present at 0.4 to 4 % in the troposphere

# Heterogeneous Reactions “Pseudo Uni-Molecular”

13.3 kcal/mole –57.8 kcal/mole  $2 \times -32$  kcal/mole



$\Delta\text{Enthalpy} = -19.5$  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

# 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)

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

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

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)*

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

For this type of reaction:

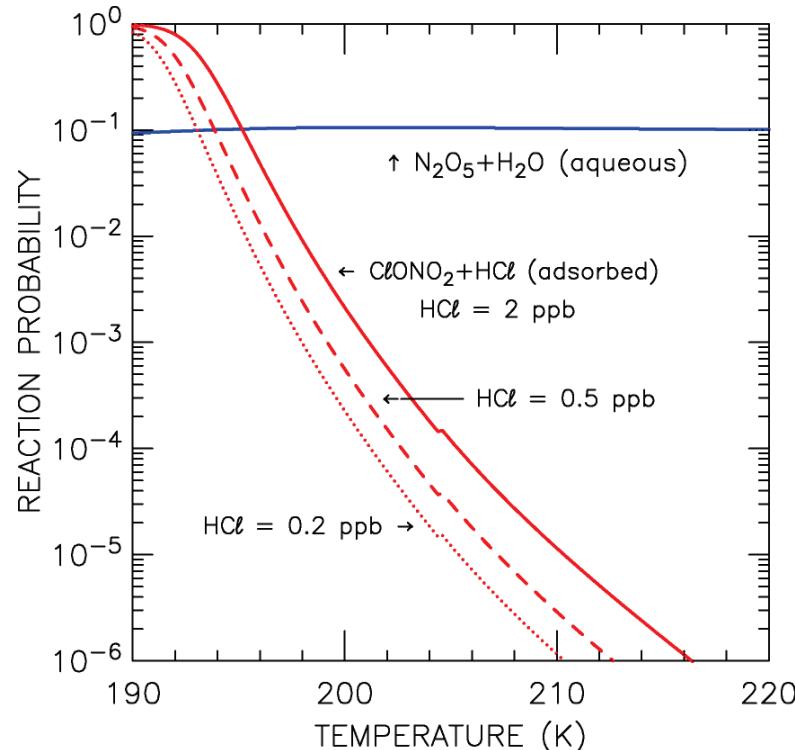
$\gamma$  will depend on temperature and aerosol type

$\gamma$  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

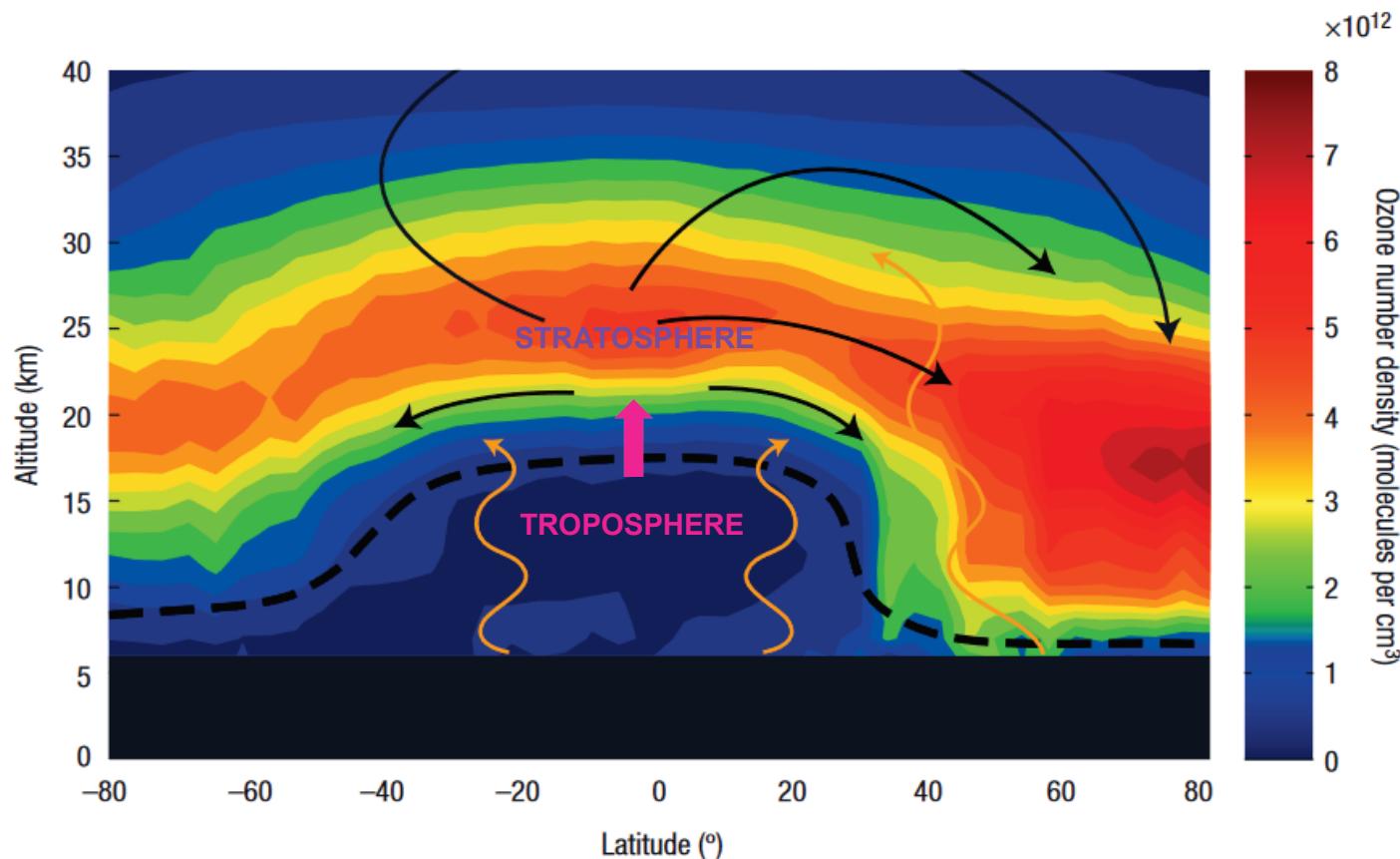
In all cases,  $\gamma$  must be measured in the laboratory



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.

# Tropopause versus Latitude



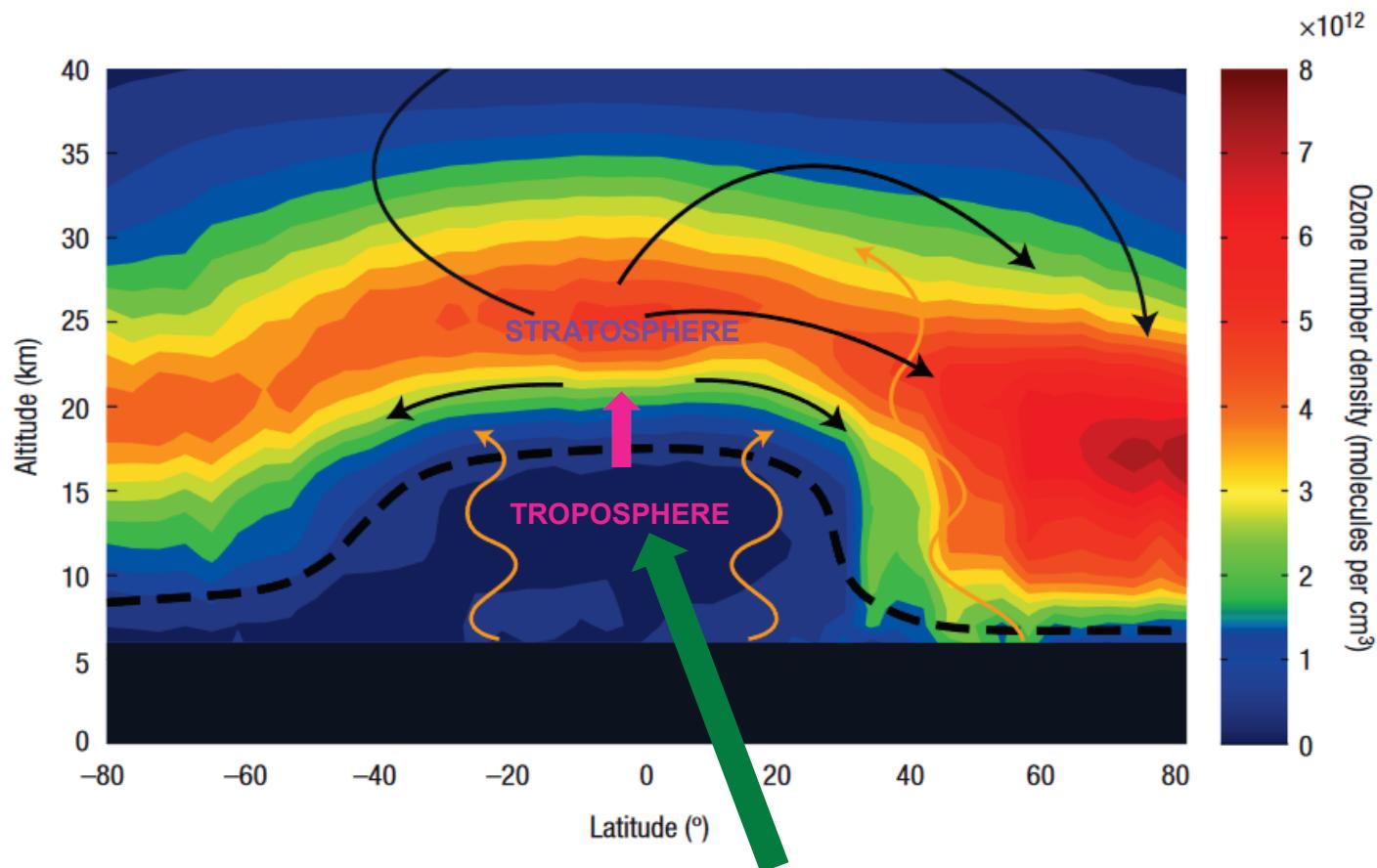
Brewer–Dobson circulation (arrows), ozone (colors), and tropopause (black dashed line).

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 in) 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.

Slide 43, Lecture 3

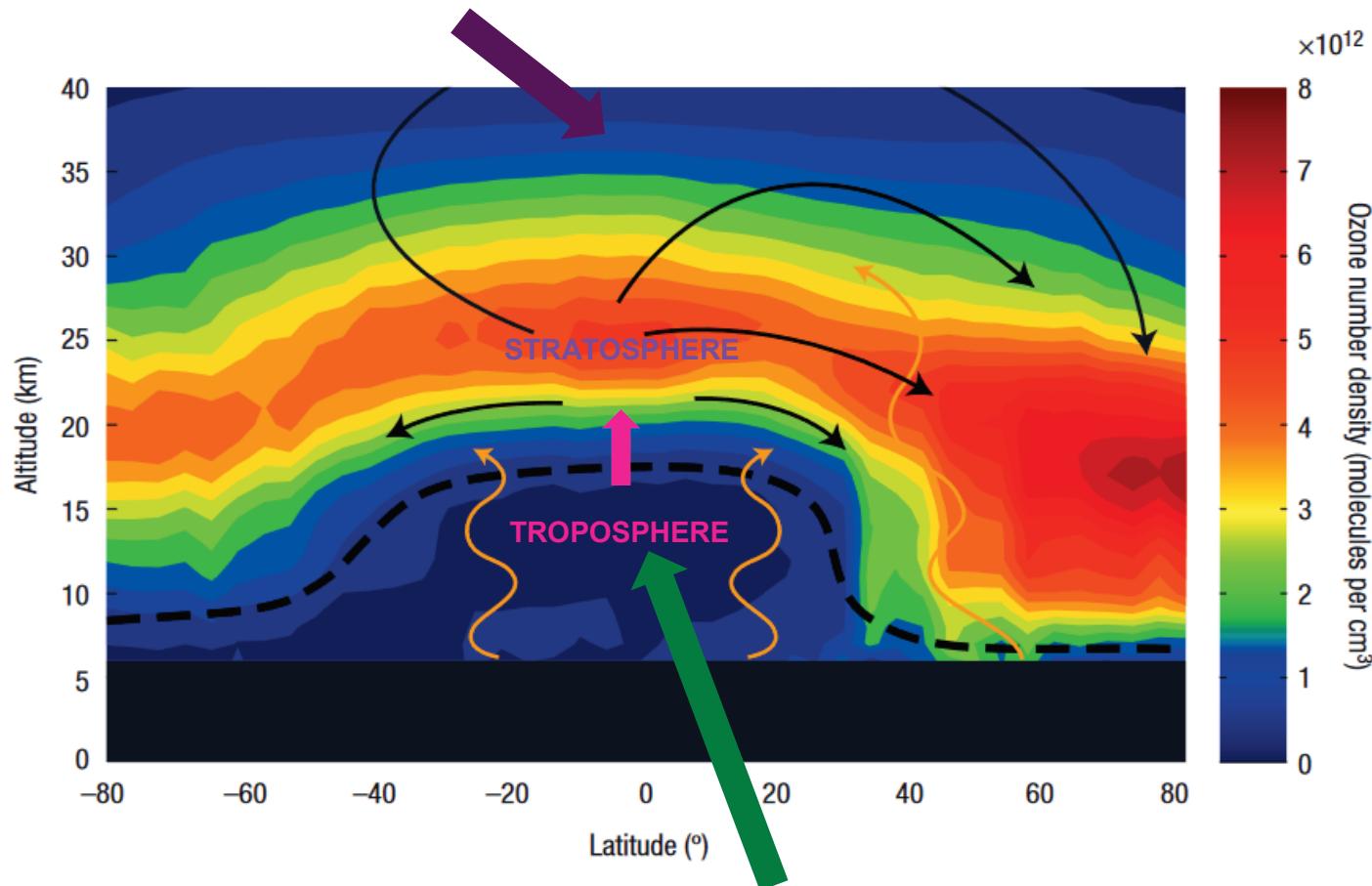
# Tropopause versus Latitude



Shaw and Shepherd, Nature Geoscience, 2008.

# Tropopause versus Latitude

Intense UV light in Earth's upper stratosphere cleaves molecules such as  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCI}_3$

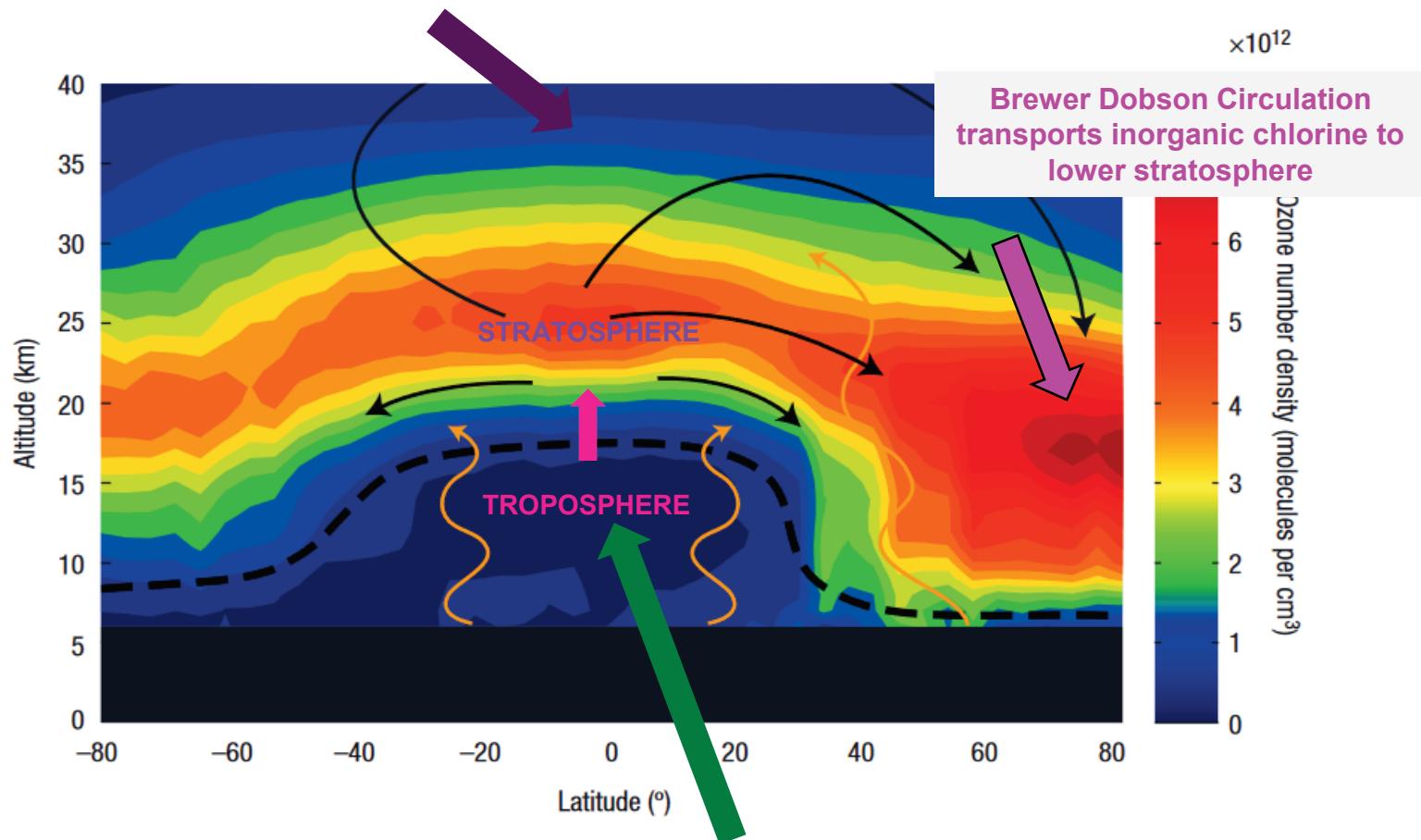


Chlorine present in organic form (i.e.,  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCI}_3$ , etc) in Earth's troposphere

Shaw and Shepherd, Nature Geoscience, 2008.

# Tropopause versus Latitude

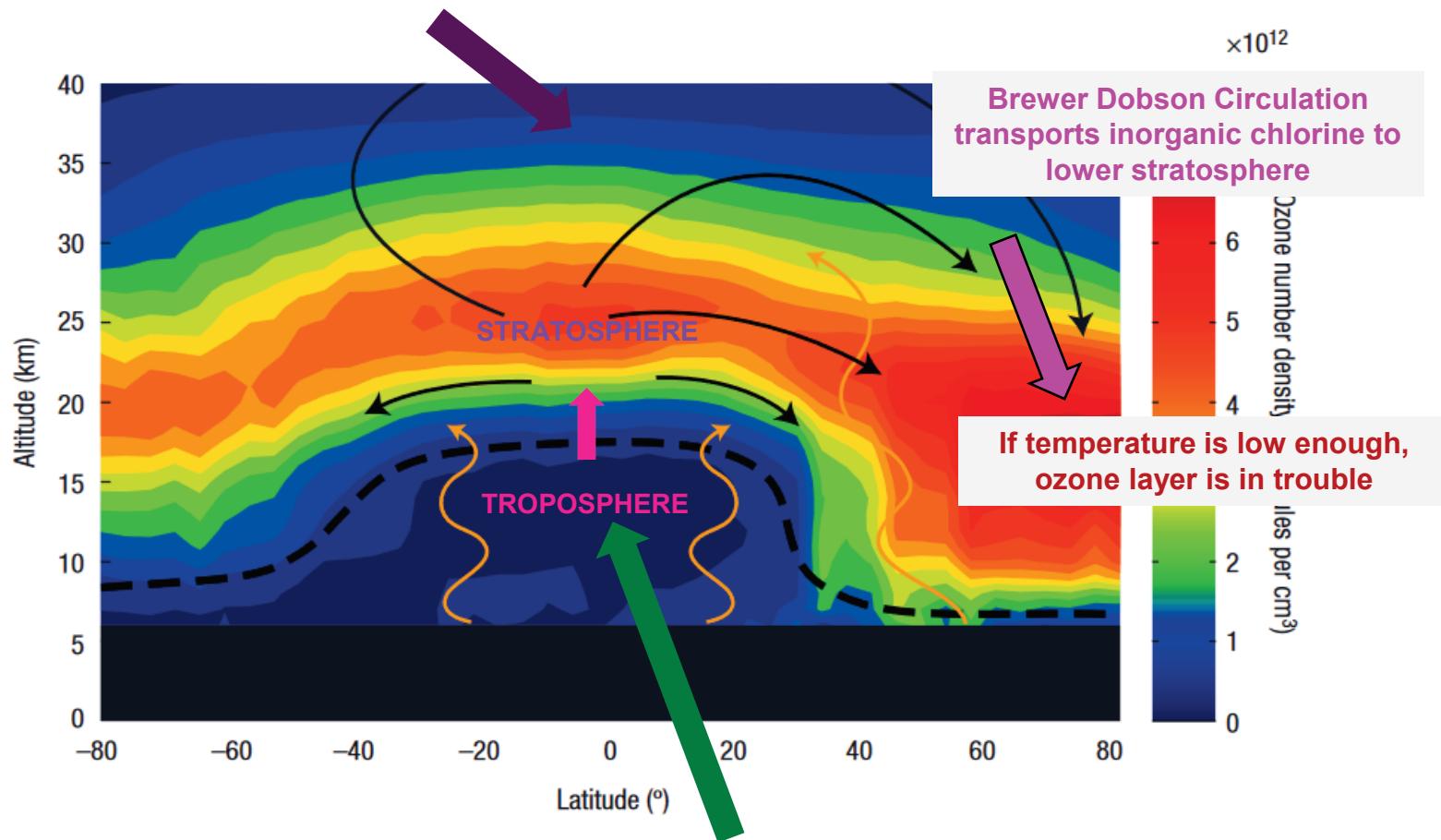
Intense UV light in Earth's upper stratosphere cleaves molecules such as  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCI}_3$



Shaw and Shepherd, Nature Geoscience, 2008.

# Tropopause versus Latitude

Intense UV light in Earth's upper stratosphere cleaves molecules such as  $\text{CF}_2\text{Cl}_2$ ,  $\text{CFCI}_3$



Shaw and Shepherd, Nature Geoscience, 2008.

# Thermal Decomposition

30.5 kcal/mole      **2 × 24.3 kcal/mole**



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

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

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

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       $2 \times 24.3$  kcal/mole



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

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:

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

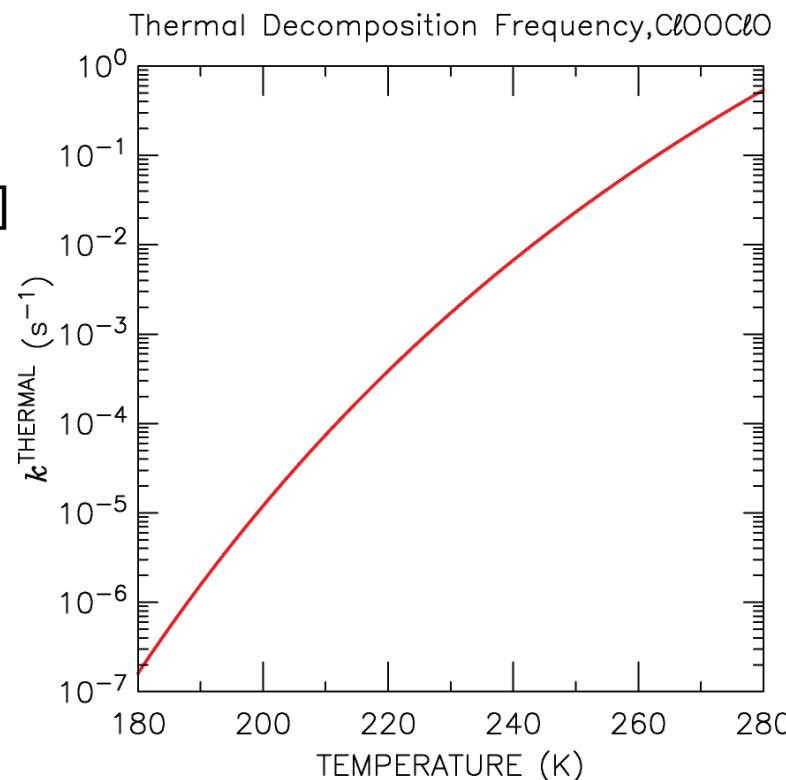
$$\text{where } k^{\text{THERMAL}} = k^{\text{FORMATION}} \times K^{\text{EQ}}$$

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

at low T, ClOOCl stable: energy wins !

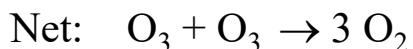
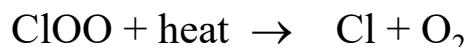
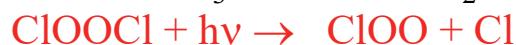
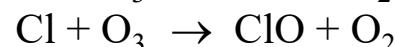
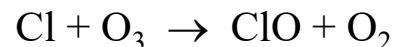
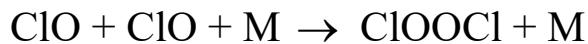
at high T, ClOOCl unstable: entropy rules !

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

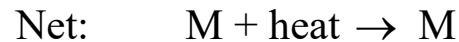
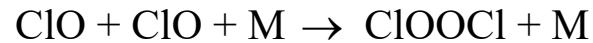


# Polar Ozone Loss Cycles

Route 1: ClOOCl photolysis:



Route 2: ClOOCl thermal decomposition:



USA

## Obama Awards Presidential Medals of Freedom, Pays Tribute to JFK

By Dan Robinson  
November 20, 2013 03:51 PM



President Barack Obama awards chemist, and Nobel Prize winner Mario Molina with the Presidential Medal of Freedom during a ceremony in the East Room of the White House in Washington, Nov. 20, 2013.

<https://www.voanews.com/usa/obama-awards-presidential-medals-freedom-pays-tribute-jfk>

[https://www.washingtonpost.com/local/obituaries/mario-molina-nobel-laureate-who-revealed-threat-to-ozone-layer-dies-at-77/2020/10/08/621f03f8-095f-11eb-9be6-cf25fb429f1a\\_story.html](https://www.washingtonpost.com/local/obituaries/mario-molina-nobel-laureate-who-revealed-threat-to-ozone-layer-dies-at-77/2020/10/08/621f03f8-095f-11eb-9be6-cf25fb429f1a_story.html)

# Extra Slides

# 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:  $k_1 [\text{OH}] [\text{NO}_2] = k_2 [\text{HONO}_2^\dagger] + k_3 [\text{HONO}_2^\dagger] [\text{M}]$

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

$$= \frac{k_1 k_3 [\text{OH}][\text{NO}_2][\text{M}]}{k_2 + k_3 [\text{M}]} = \frac{\frac{k_1 k_3}{k_2} [\text{OH}][\text{NO}_2][\text{M}]}{1 + \frac{k_3}{k_2} [\text{M}]}$$

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

# 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.

## 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:

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

- 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)