

Introduction to Chemical Kinetics AOSC 433/633 & CHEM 433

Ross Salawitch

Class Web Site: <http://www.atmos.umd.edu/~rjs/class/spr2017>

Goals for today:

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

Lecture 11
9 March 2017

Loose Ends

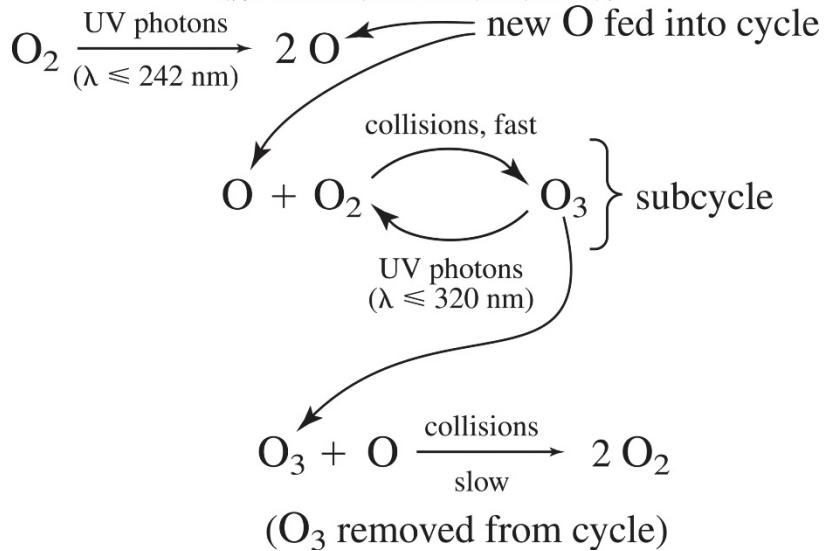
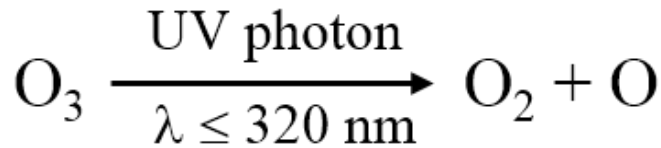


Figure 2.10, Chemistry in Context



Equation 2.5, Chemistry in Context

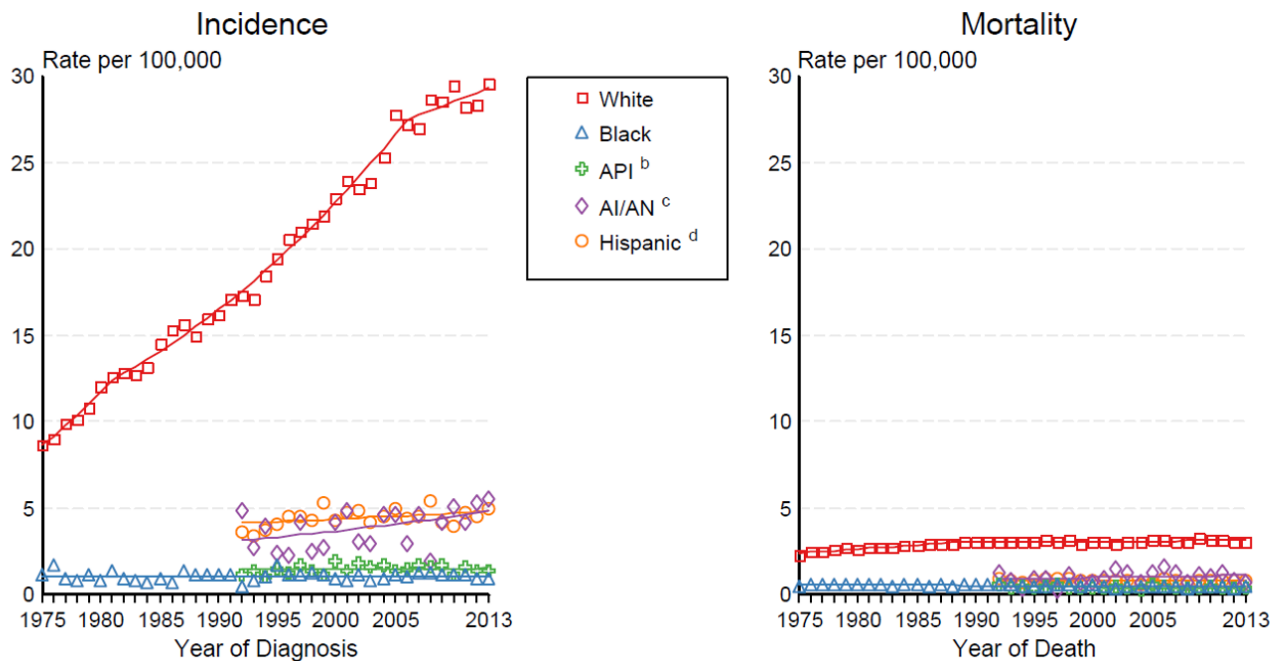


Loose Ends

According to calculations, a given percent decrease in stratospheric ozone is expected to increase the biological damage done by UV radiation by twice that percentage. For example, from a 6% decrease in stratospheric ozone we predict a 12% rise in skin cancer, especially the more easily treated forms such as basal cell and squamous cell carcinomas (non-melanoma)

Page 83, Chemistry in Context

Melanoma of the Skin, Both Sexes
Joinpoint Analyses for Whites and Blacks from 1975-2013
and for Asian/Pacific Islanders, American Indians/Alaska Natives and Hispanics from 1992-2013



https://seer.cancer.gov/csr/1975_2013/results_merged/topic_race_ethnicity.pdf

SEER: Surveillance, Epidemiology, and End Results Program of the National Cancer Institute

As far as we can tell, census data is used to determine ethnicity

Relationship Between UV and Column Ozone

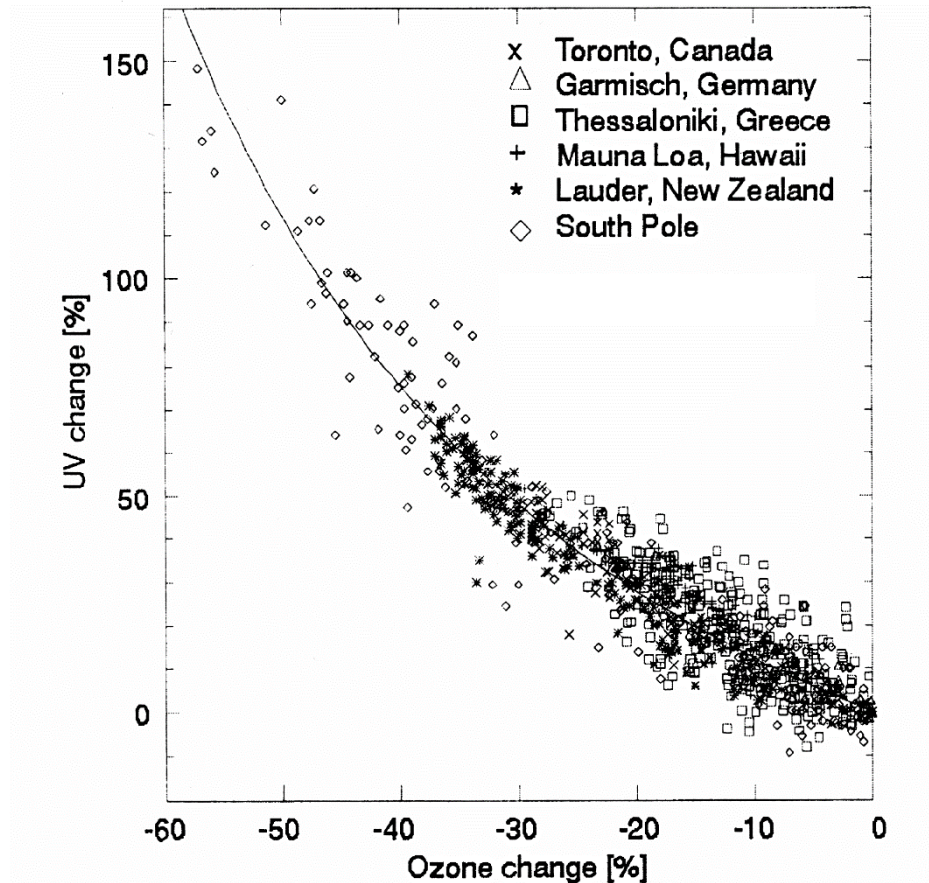
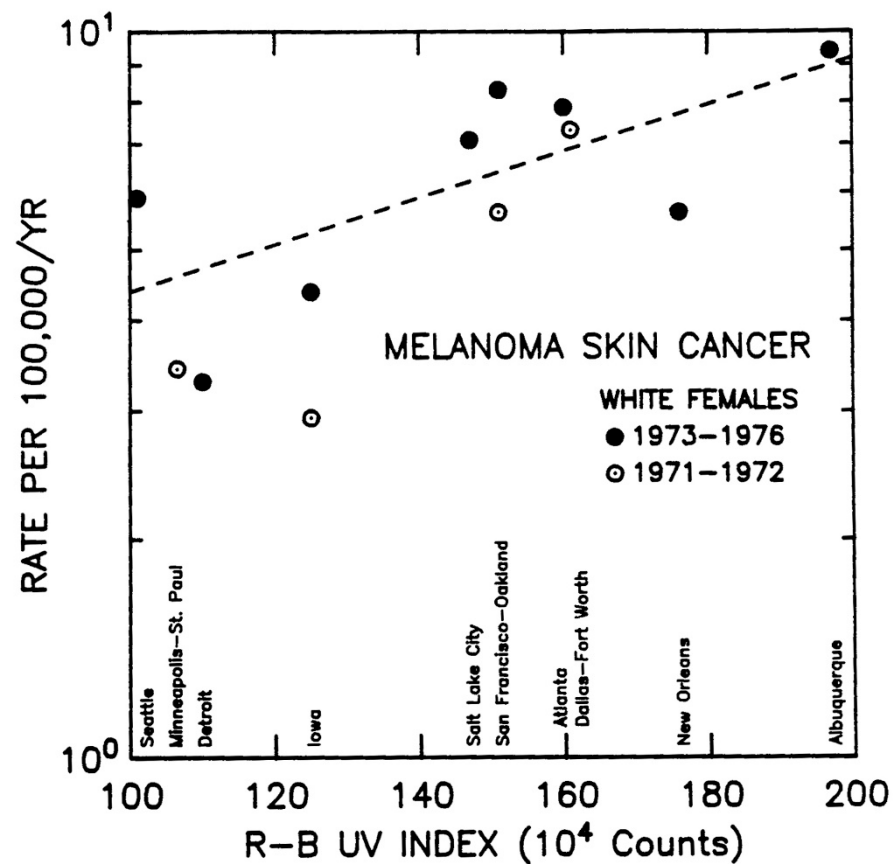
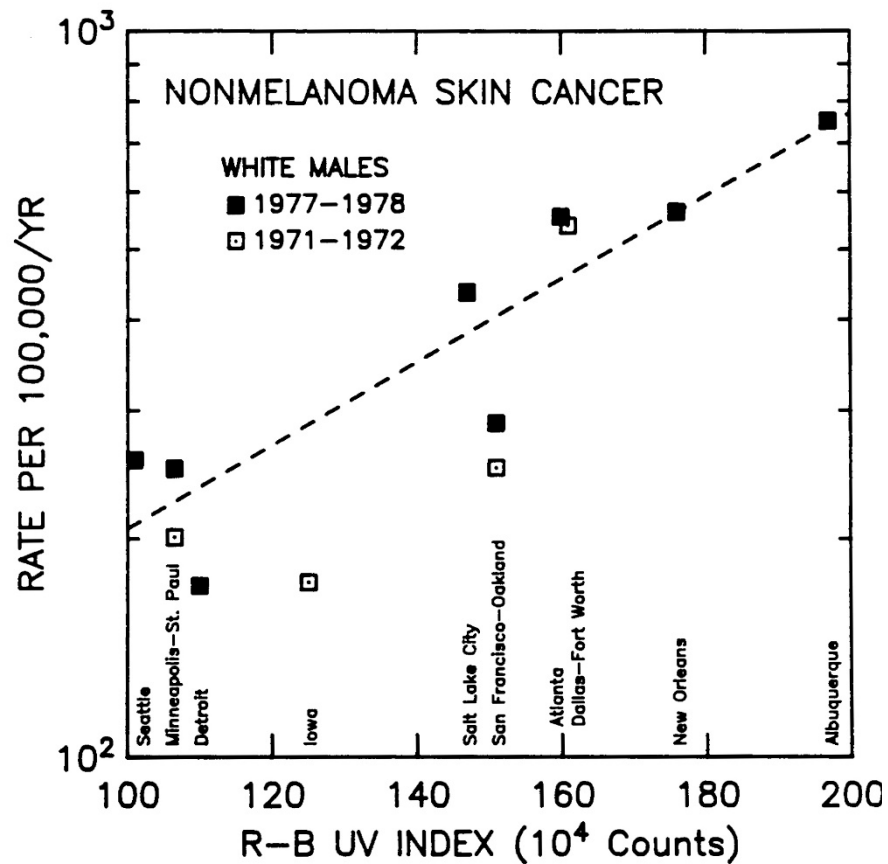


Fig. 2. Dependence of erythemal ultraviolet (UV) radiation at the Earth's surface on atmospheric ozone, measured on cloud-free days at various locations, at fixed solar zenith angles. Legend: South Pole [8]; Mauna Loa, Hawaii [9]; Lauder, New Zealand [10]; Thessaloniki, Greece (updated from Ref. [11]); Garmisch, Germany [12]; and Toronto, Canada (updated from Ref. [13]).

Madronich et al., *J. of Photochemistry and Photobiology B*, Vol. 46, 5–19, 1998.

Relationship Between Cancer and UV

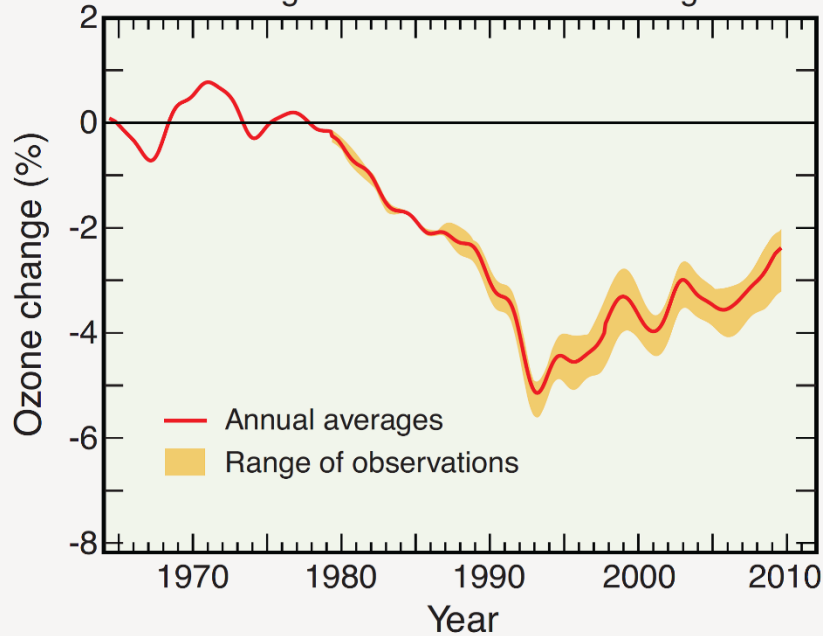


Scotto and Fraumeni, *Cancer Epidemiology*, W. B. Saunders and Co, Philadelphia, 1982.

Depletion of the Ozone Layer, Global

Global Total Ozone Changes

Changes from 1964–1980 average



Changes between 1964–1980
and 2005–2009 averages

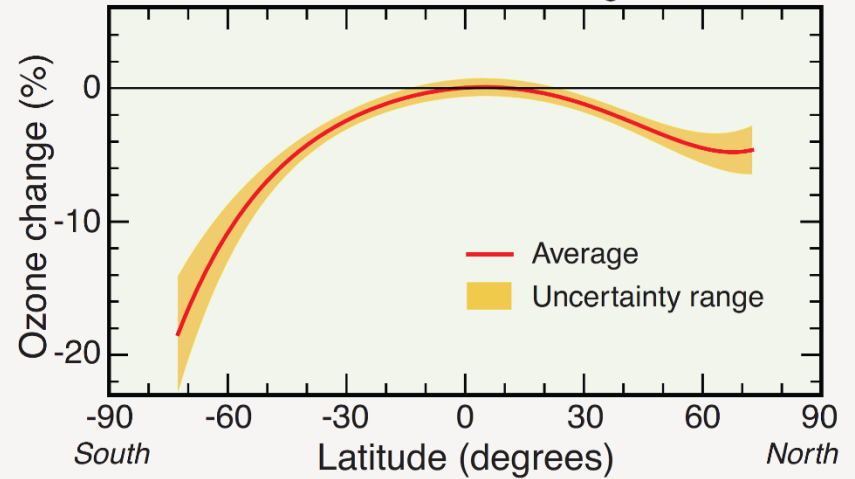


Figure Q13-1, WMO/UNEP Twenty Question and Answers

http://www.atmos.umd.edu/~rjs/class/spr2015/readings/WMO_Ozone_2010_QAs.pdf

Skin Cancer / Australia

Skin cancer occurs when skin cells are damaged, for example, by overexposure to ultraviolet (UV) radiation from the sun.

Every year, in Australia:

- skin cancers account for around 80% of all newly diagnosed cancers
- between 95 and 99% of skin cancers are caused by exposure to the sun
- GPs have over 1 million patient consultations per year for skin cancer
- the incidence of skin cancer is one of the highest in the world, two to three times the rates in Canada, the US and the UK.

There are three main types of skin cancer:

- **melanoma** – the most dangerous form of skin cancer
- **basal cell carcinoma***
- **squamous cell carcinoma***

Incidence and mortality

Two in three Australians will be diagnosed with skin cancer by the time they are 70.

Over the past decades, the incidence of skin cancer has risen in Australia. From 1982 to 2010 melanoma diagnoses increased by around 60%. From 1998 to 2007, GP consultations to treat non-melanoma skin cancer increased by 14%, to reach 950,000 visits each year.

Non-melanoma skin cancer is the most common type of skin cancer. This type of skin cancer is more common in men, with almost double the incidence compared to women. Over 434,000 people are treated for one or more non-melanoma skin cancers in Australia each year.

Excluding non-melanoma skin cancer, melanoma is the third most common cancer in both Australian women and men, and the most common cancer in Australians aged 15-44 years. In 2010, 11,405 people in Australia were diagnosed with melanoma.

In 2011, 2087 people died from skin cancer in Australia. The majority of these deaths were due to melanoma, with 1544 deaths from melanoma that year, compared with 543 deaths from non-melanoma skin cancers. The five-year relative survival rate for melanoma is 90% for Australian men and 94% for Australian women.

<http://www.cancer.org.au/about-cancer/types-of-cancer/skin-cancer.html>

- 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***

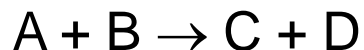
Types of Reactions

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

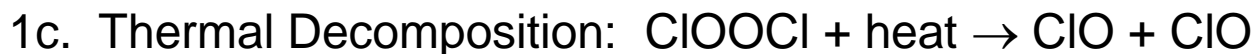
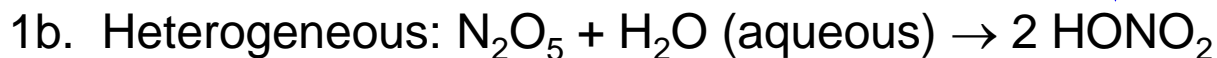
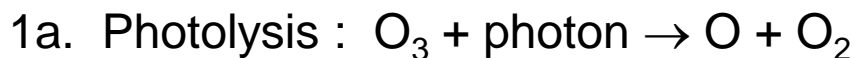
Types of Reactions

Atmospheric Chemistry:

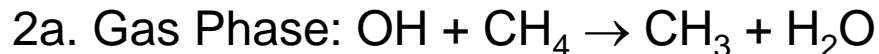
HONO₂ same as HNO₃ (nitric acid)
We'll use both notations interchangeably



1. Unimolecular



2. Bimolecular



3. Termolecular



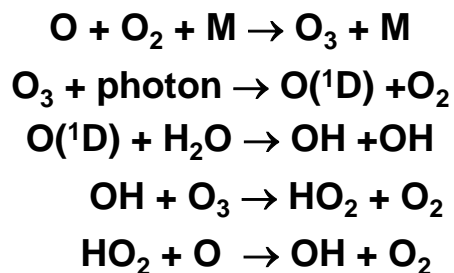
Importance of Radicals

- 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

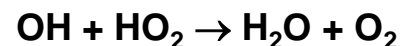
Initiation



Propagation



Termination



Radicals

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

Count the electrons:

HNO_3 : $1 + 7 + 3 \times 8 = 32$ electrons \Rightarrow no

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

NO_2 : 23 electrons \Rightarrow yes

Other radicals: OH, HO₂, 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 but last orbital empty:

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

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

Admission Ticket Lecture 11

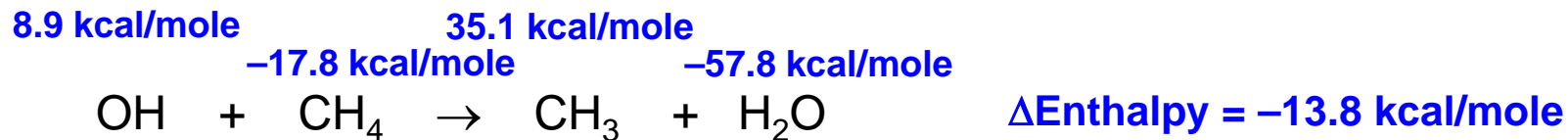
Gibbs Free energy involves both enthalpy and entropy. Briefly describe the relative roles of the change in enthalpy and entropy in affecting the rate of a chemical reaction.

Under what conditions will enthalpy dominate the rate?

Under what conditions will entropy dominate the rate?

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

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:

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

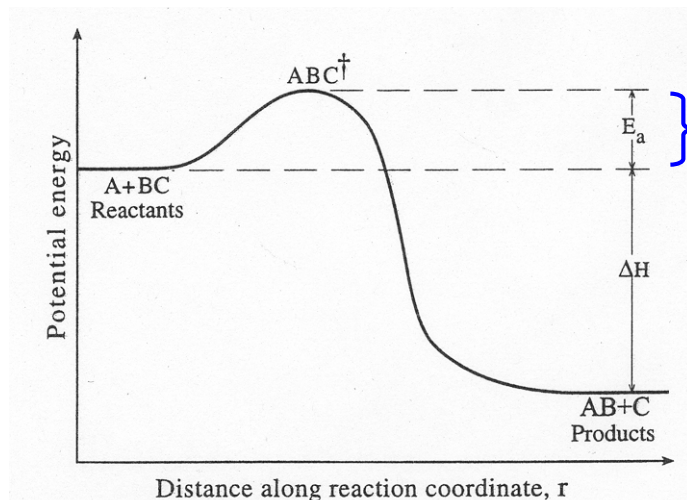
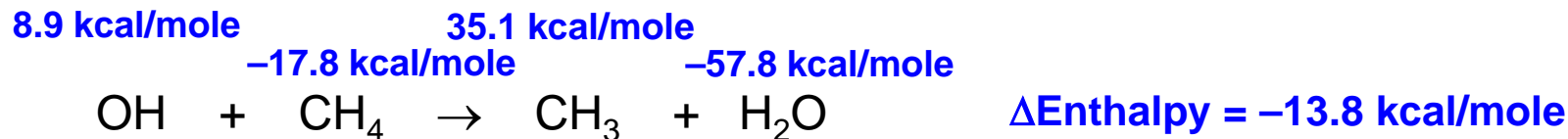


Figure 3.3 Barrier energies for the forward reaction (E_a) and the reverse reaction ($E_a + \Delta H$).

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

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

Bimolecular Gas Phase Reactions



Exothermic !

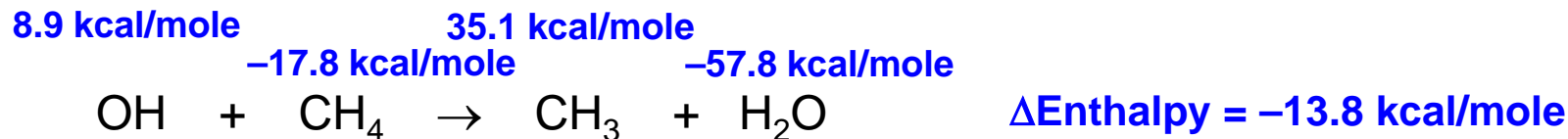
$$\text{Rate of Reaction} = \frac{d\text{CH}_4}{dt} = k [\text{OH}][\text{CH}_4]$$

Arrhenius Expression for rate constant:

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

$\text{OH} + \text{CH}_4 \rightarrow \text{CH}_3 + \text{H}_2\text{O}$	2.45×10^{-12}	1775	6.3×10^{-15}	1.1	100	<u>D12</u>
$\text{OH} + {}^{13}\text{CH}_4 \rightarrow {}^{13}\text{CH}_3 + \text{H}_2\text{O}$	(See Note)					<u>D13</u>
$\text{OH} + \text{CH}_3\text{D} \rightarrow \text{products}$	3.5×10^{-12}	1950	5.0×10^{-15}	1.15	200	<u>D14</u>
$\text{OH} + \text{H}_2\text{CO} \rightarrow \text{H}_2\text{O} + \text{HCO}$	5.5×10^{-12}	-125	8.5×10^{-12}	1.15	50	<u>D15</u>
$\text{OH} + \text{CH}_3\text{OH} \rightarrow \text{products}$	2.9×10^{-12}	345	9.1×10^{-13}	1.10	60	<u>D16</u>
$\text{OH} + \text{CH}_3\text{OOH} \rightarrow \text{products}$	3.8×10^{-12}	-200	7.4×10^{-12}	1.4	150	<u>D17</u>

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:

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

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

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

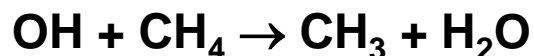
and contains the following information:

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.

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

Bimolecular Gas Phase Reactions



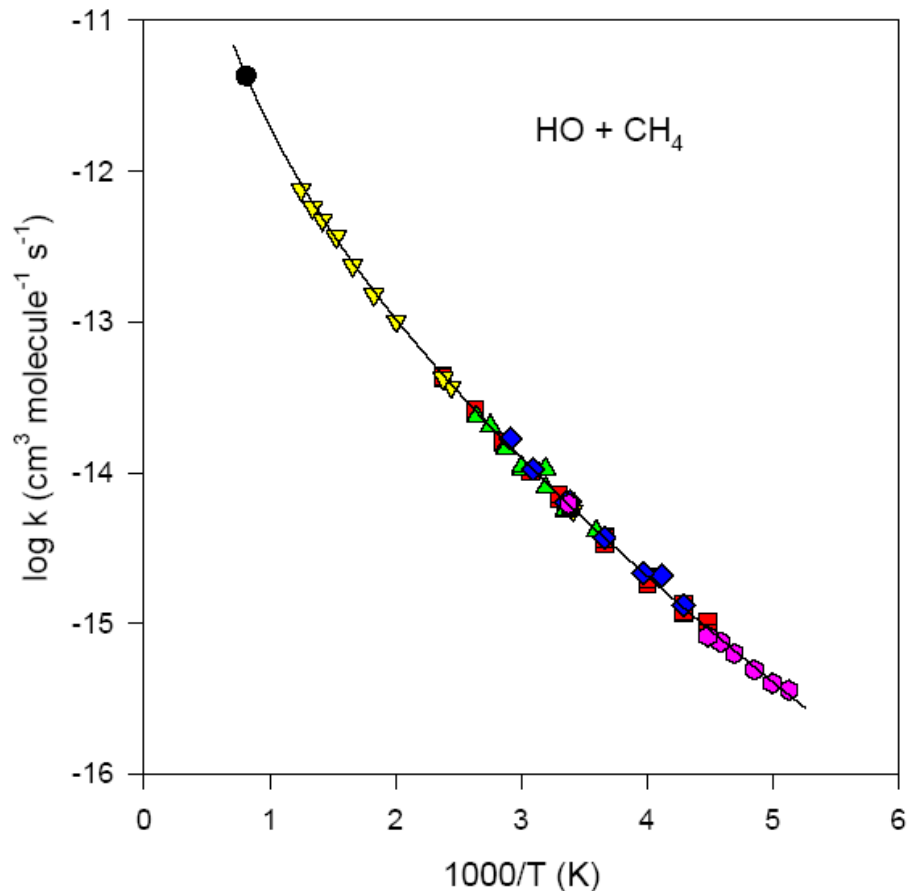
$$k = 2.45 \times 10^{-12} \times e^{-1775/T} \text{ cm}^3 \text{ sec}^{-1}$$

D12. OH + CH₄. 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

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

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

Photolytic Production of OH

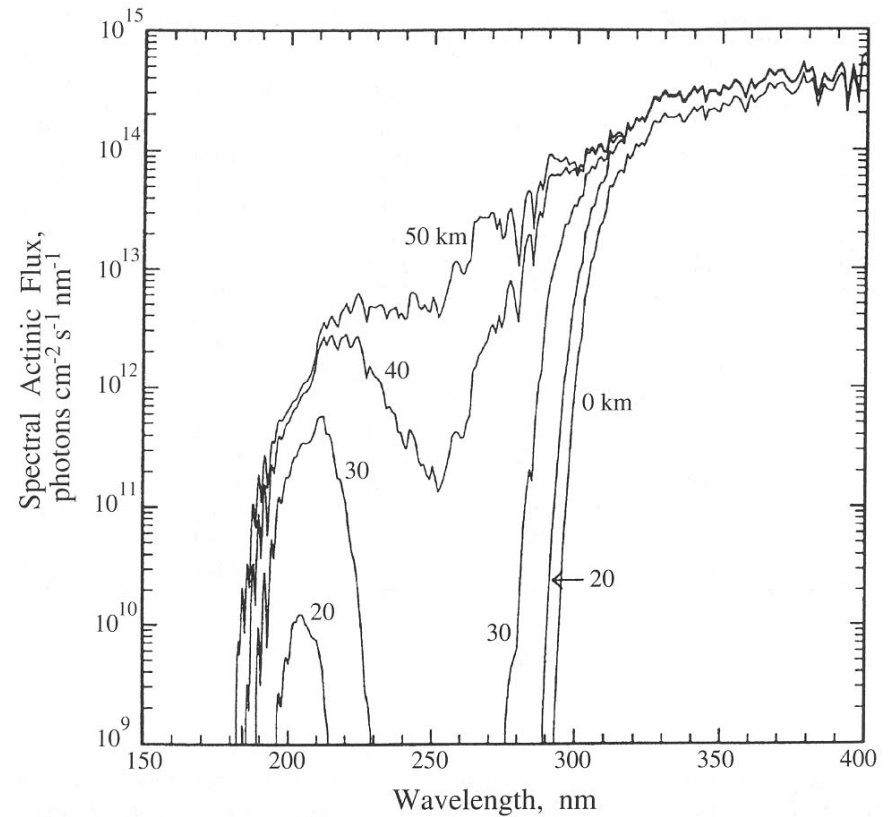
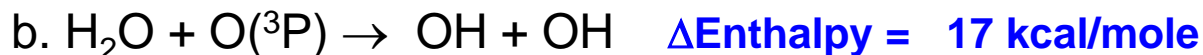
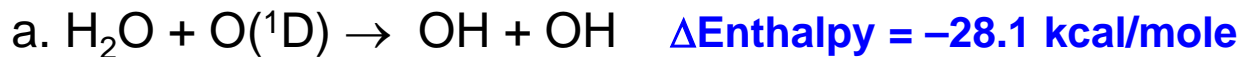


Figure 4.11, Seinfeld and Pandis, 2006
(from DeMore et al., 1994)

Bimolecular Production of OH



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

$$k_b = 0.0$$

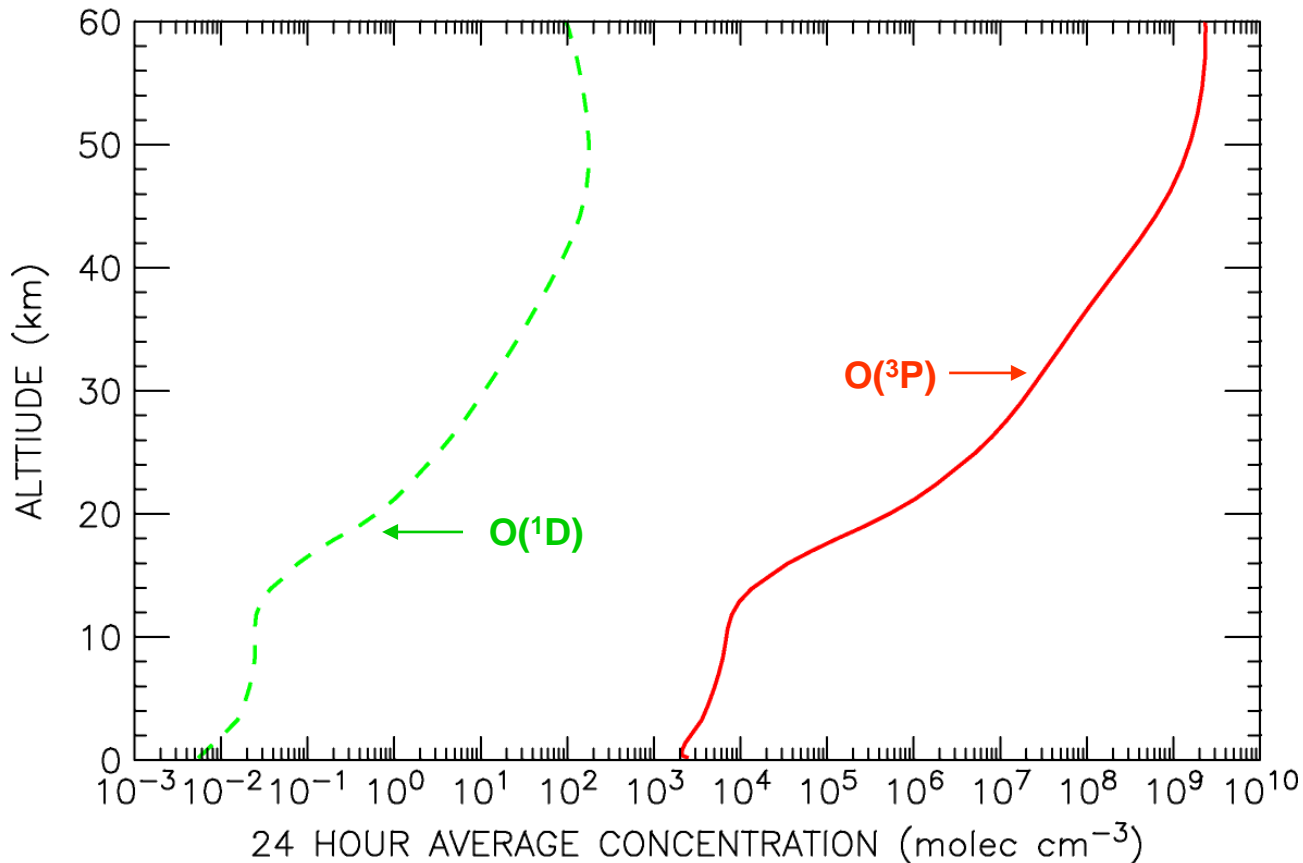
$$k_c = 1.1 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$$

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

Bimolecular Production of OH

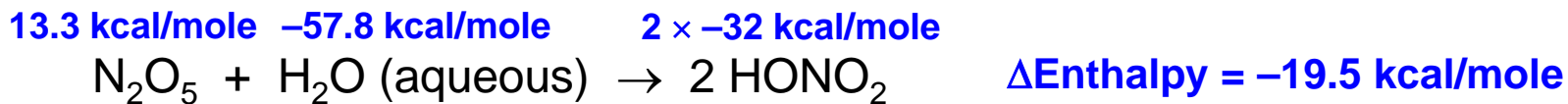
NCAR WACCM Output

35°N, Sept



At surface, [O^{1D}] ≈ 10⁻⁵ [O^{3P}]

Heterogeneous Reactions “Pseudo Uni-Molecular”



HONO₂ same as HNO₃ (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 H₂O 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 s^{-1}

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

γ = *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 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”



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

γ = *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:

γ will depend on temperature and aerosol type

γ depends on partial pressure (e.g., gas phase abundance) of HCl

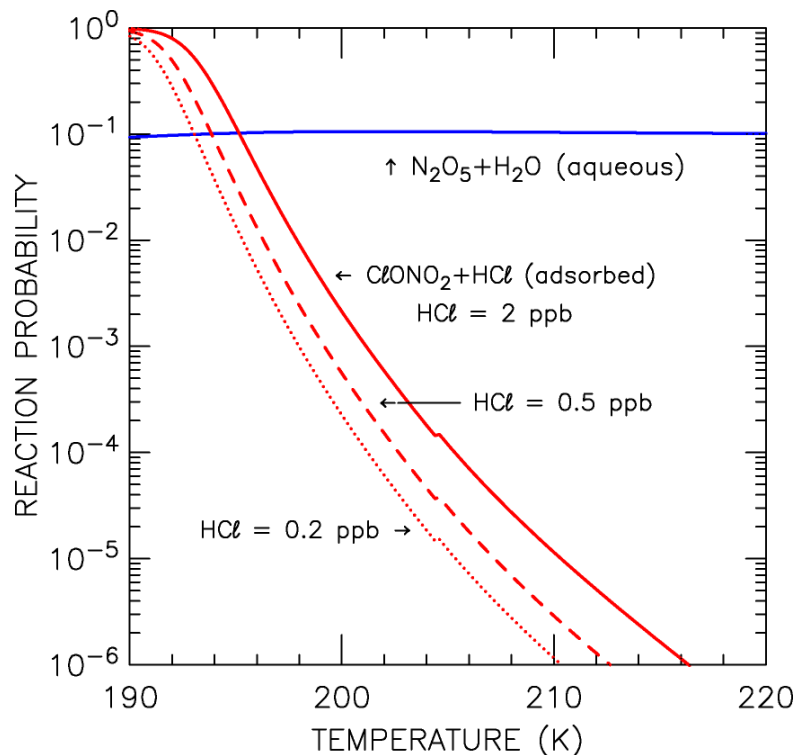
because, reacting surface is not primarily composed of HCl

Gas phase $\text{H}_2\text{O} \gg$ gas phase N_2O_5

$\text{N}_2\text{O}_5 + \text{H}_2\text{O}(\text{aqueous})$ 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



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

Rate of Reaction = $k_{\text{THERMAL}} [\text{ClOOCI}]$; Units of k_{THERMAL} 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

30.5 kcal/mole

2 × 24.3 kcal/mole



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

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:

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

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

- 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.

