This Week: Kinetics and Photochemistry

Reading: Chapter 9 of text and handout on numerical methods

Rate laws for homogeneous gas-phase reactions

- Unimolecular
- Bimolecular $A + B \rightarrow C + D$
- Termolecular
- Rate constants

Photolysis Rate Constants $A + h\nu \rightarrow C + D$

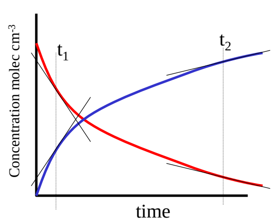
- Solar radiation spectrum and bond breaking
- Actinic flux, absorption cross sections, quantum yields

Mechanisms and Overall Reactions

Chemical Kinetics (Reaction Rates)

Rate of reaction at any time, t, is the slope of the tangent to curve describing change in concentration with time

$A + B \rightarrow C + D$



Rates can change w/time because reactant concentrations can change w/time. Note this is just the concept of *mass balance*

$d[A]/dt = d[B]/dt = -d[C]/dt = -d[D]/dt$ (by mass conservation)

Rate Expressions for Gas-phase Reactions

Unimolecular: $A \longrightarrow B$ $$-\frac{d[A]}{dt} = k^{I}[A] = \frac{d[B]}{dt}$$

First order process

Lifetime = 1/k; k has units of s^{-1}

Examples - decomposition: $N_2O_5 \rightarrow NO_3 + NO_2$

photolysis: $O_3 + h\nu \rightarrow O_2 + O$

Bimolecular: $A + B \longrightarrow C$ $$-\frac{d[A]}{dt} = k^{II}[A][B] = -\frac{d[B]}{dt} = \frac{d[C]}{dt}$$

k^{II}, bimolecular rate constant, has units of cm^3 $molec^{-1}$ s^{-1}

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

Special cases:

1. *B=A, rate law becomes 2nd Order in [A]*
2. [B]>>[A] rate law becomes *pseudo-first order in [A]*

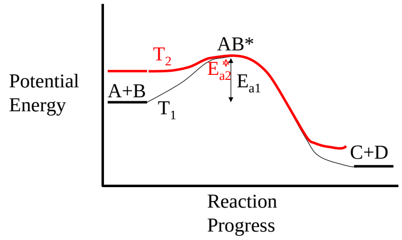
Termolecular: $A + B + M \longrightarrow C + M$

M is total air number density

AKA: Pressure dependent bimolecular reactions

Energy Requirements Affect Rates

Reaction rate constants are often functions of Temperature due to energy requirements



Energy barriers are common: higher T gives higher energy collisions, increasing the probability of a reaction

Termolecular (Pressure Dependent) Reactions

A bimolecular reaction which requires activated complex to be stabilized by collisions with surrounding gas molecules "M"

1. $A + B \rightarrow AB^*$ — k_1
2. $AB^* \rightarrow A + B$ — k_2
3. $AB^* + M \rightarrow C + M^*$ — k_3
4. $M^* \rightarrow M + \text{heat}$ — k_4

$$\frac{d[C]}{dt} = k_3[AB^*][M]$$

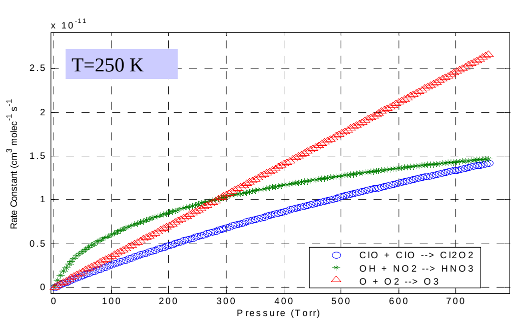
[M] is TOTAL AIR NUMBER DENSITY

Assume lifetime of AB* very short, reacts as soon as its formed (quasi steady state approximation):

$$\frac{d[AB^*]}{dt} \approx 0 \approx k_1[A][B] - k_2[AB^*] - k_3[AB^*][M]$$

$$[AB^*]_t = \frac{k_1[A][B]}{k_2 - k_3[M]} \longrightarrow \frac{d[C]}{dt} = \frac{k_3 k_1[A][B]}{k_2 - k_3[M]}[M]$$

Termolecular Rate Constants: Examples



$k_{ClO+ClO}$ and k_{O+O2} have been scaled

Questions

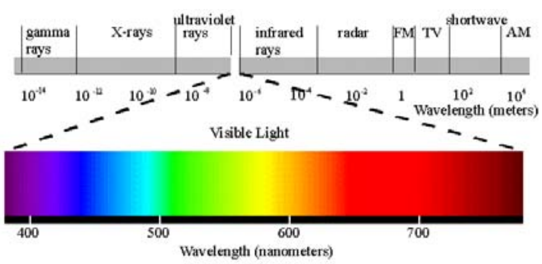
OH is produced in the atmosphere by the reaction of an energetically “hot” oxygen atom (we’ll talk about why its “hot” later) with H_2O

$$H_2O + O^* \rightarrow 2OH$$

1. What is the rate expression for the *loss* of O^* by this reactive process?
2. What is the rate expression for the *production* of OH by this reactive process?
3. Typically $[O^*]$ is << 1×10^6 molecules/cm^3, while $[H_2O]$ in the troposphere can be ~ 1×10^{15} molecules/cm^3. If the *bimolecular rate constant* for the above reaction is 1×10^{-11} cm^3 molec^{-1} s^{-1}, what is a typical lifetime for $[O^*]$ w.r.t this reaction in the troposphere?

Electromagnetic Spectrum

Radiation (light): Energy carried by oscillating electric and magnetic fields traveling through space at 3×10^8 m/s

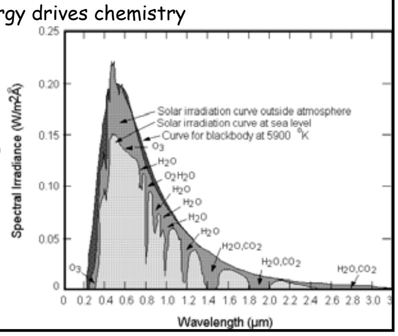


Solar Spectrum Modified by Atmosphere

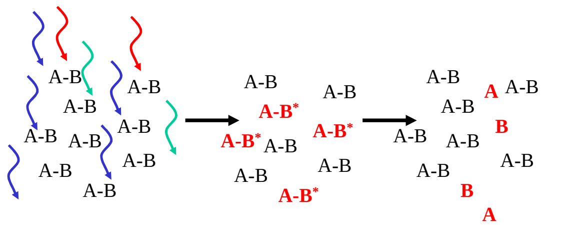
•Certain wavelengths of solar radiation are absorbed when traveling through the atmosphere.

•Some of this energy drives chemistry (photochemistry)

Sunlight with λ < 300 nm does not reach troposphere



Photolysis



Probability of photon-molecule collision × Probability of absorption of photon energy × Probability of bond-breaking given absorption

I (actinic flux)*[A-B] — **Absorption cross-section (σ)** — **Quantum Yield (ϕ)**

Actinic Flux vs. Altitude

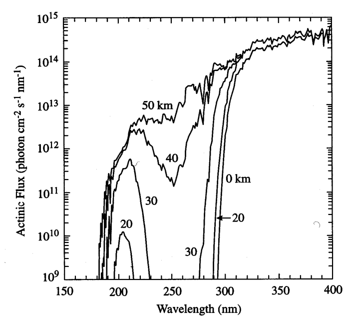


Fig. 10-2 Solar actinic flux at different altitudes, for typical atmospheric conditions and a 30° solar zenith angle. From DeMore, W. B., et al. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*. JPL Publication 97-4. Pasadena, Calif.: Jet Propulsion Lab, 1997.

Questions

1. At a single location on the ground, the photolysis of NO_2 begins earlier in the morning than the photolysis of O_3. Why might this temporal difference exist?

Questions

1. Which of the following are examples of first order reactions?
   a. Photolysis of stratospheric gases
   b. Dry deposition of gases to Earth's surface
   c. Uptake of CO_2 by plants