

## Extra Slides for Kinetics Lectures

### Atmospheric Chemistry 5151

#### Why do we care about gas phase reactions?

- Atmosphere is primarily gas phase medium
  - Pollution emissions often in gas phase
- Consider the lonely OH molecule here in Boulder...
  - Number of photons seen per second
    - Assume  $1360 \text{ W m}^{-2}$ , all radiation is 500 nm, and OH molecule has cross section of  $0.5 \text{ nm}^2$
    - Answer ~ 2000 photons per second
  - Number of heterogeneous collisions per second
    - Assume  $\sim 10^5$  particles  $\text{cm}^{-3}$  with average diameter of 500 nm
    - $\sim 50$  collisions per second
    - We will derive this later
  - Number of gas phase collisions
    - Use 630 Torr, 298 K
    - $\sim 8 \times 10^9$  collisions per second!!
    - We will derive this later

Extra

## Before we start...

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- Where do molecules hide all of their energy?
  - Translations – just moving → related to temperature
  - Rotations – spinning, right round, like a record baby, right round
  - Vibrations – within molecule, atoms changing inter-atomic distances
  - Electronic – electrons within molecule occupying different orbitals, for lack of a better analogy, think of electrons as little planets orbiting the sun (nucleus) and orbits are different distances from center
- Good concepts to keep in mind

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## “Practical Thermo”

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- Example 1:  $\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$ 

–	$\Delta H_f$ (kcal mol <sup>-1</sup> )	$S_f$ (cal K <sup>-1</sup> mol <sup>-1</sup> )
– OH	8.89	43.91
– CH <sub>4</sub>	-17.80	44.55
– H <sub>2</sub> O	-57.798	45.133
– CH <sub>3</sub>	35.05	46.36

  - $\Delta H_{\text{rxn}} = -13.8 \text{ kcal mol}^{-1}$ ,  $\Delta S_{\text{rxn}} = 3.0 \text{ cal K}^{-1} \text{ mol}^{-1}$ , &  $\Delta G_{\text{rxn}} = -14.7 \text{ kcal mol}^{-1}$  for 298 K
- Example 2:  $\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$ 

–	$\Delta H_f$ (kcal mol <sup>-1</sup> )	$S_f$ (cal K <sup>-1</sup> mol <sup>-1</sup> )
– N <sub>2</sub> O <sub>5</sub>	3.18	85.01
– NO <sub>2</sub>	8.17	57.40
– NO <sub>3</sub>	17.6	61.76

  - $\Delta H_{\text{rxn}} = +22.6 \text{ kcal mol}^{-1}$ ,  $\Delta S_{\text{rxn}} = 34.15 \text{ cal K}^{-1} \text{ mol}^{-1}$ , &  $\Delta G_{\text{rxn}} = +12.4 \text{ kcal mol}^{-1}$  for 298 K
  - $\Delta G = 0$  at 662 K; change from spontaneous to non-spontaneous reaction
- Note: we have not included change in  $\Delta H_f$ 's with respect to temperature
  - Often these are small – for initial order-of-magnitude type guesses, do not worry about

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## What are chances of truly termolecular collision?

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- How long is collision vs how long is time between collisions?
  - Collisions last  $\sim 10^{-13}$  s to  $10^{-12}$  s
    - For argument's sake, say  $10^{-12}$  s
  - Time between collisions  $\sim 10^{-9}$  s
    - Remember, we already said  $\sim 8 \times 10^9$  collisions  $s^{-1}$
  - Means collision duration / total time  $\sim 0.001$ 
    - Chance of 3 molecules colliding simultaneously  $\sim 0.001^2 = 10^{-6}$
    - To have truly termolecular collision, fighting factor of a million in probability
      - Much more likely if process occurs as a series of bimolecular collisions

Extra

## Rate Laws

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- Rate of reaction: change of concentration with respect to time
- Example:  $\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$
- How do you express the rate of this reaction?
  - $-\text{d}[\text{OH}]/\text{dt} = -\text{d}[\text{CH}_4]/\text{dt} = \text{d}[\text{H}_2\text{O}]/\text{dt} = \text{d}[\text{CH}_3]/\text{dt}$
- What does this rate depend on?
  - $-\text{d}[\text{OH}]/\text{dt} = k * [\text{OH}] * [\text{CH}_4]$
  - $k$  = rate coefficient
    - $k$  is essentially a probability that a collision between reactants will lead to products
    - Can vary with temperature and pressure

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## Reaction Order

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- Rate =  $k[A]^a[B]^b$
- Reaction order =  $a + b$ 
  - $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$
  - Rate =  $k[\text{NO}]^1 [\text{O}_3]^1 = k[\text{NO}][\text{O}_3]$
  - Second order reaction
  - Reaction is “first order in NO”
- “Pseudo-first order”
  - If  $[\text{O}_3] \gg [\text{NO}]$ ,  $[\text{O}_3]$  essentially constant
  - Rate =  $-\text{d}[\text{NO}]/\text{dt} = k [\text{O}_3] [\text{NO}] \approx k'[\text{NO}]$
  - Spot the atmospheric reaction that could easily be approximated as a pseudo-first order reaction:
    - A:  $\text{CH}_3\text{OO}\bullet + \text{NO} \rightarrow \text{CH}_3\text{O} + \text{NO}_2$
    - B:  $\text{CH}_3\text{O}\bullet + \text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{HO}_2$
    - C:  $\text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2 \text{O}_2$

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## Example: CFC's and HCFC's

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- Info:
  - Old CFC = CFC-11 =  $\text{CFCl}_3$
  - New HCFC = HCFC-21 =  $\text{CHFCl}_2$
- Assumptions:
  - Lifetimes determined by reaction with hydroxyl radical (OH)
  - Typical concentration of OH in troposphere  $\sim 1 \times 10^6$  molecule  $\text{cm}^{-3}$
  - Rate coefficient at room temp
    - $k_{\text{CFC-11}} < 5.0 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
    - $k_{\text{HCFC-21}} = 2.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
- Lifetimes
  - $\tau_{\text{CFC-11}} = 1 / k[\text{OH}] = 1 / (5.0 \times 10^{-18} * 1 \times 10^6) = 2 \times 10^{11} \text{ s} = 6340 \text{ years}$
  - $\tau_{\text{HCFC-21}} = 1 / k[\text{OH}] = 1 / (2.5 \times 10^{-14} * 1 \times 10^6) = 4 \times 10^7 \text{ s} = 1.2 \text{ years}$
- We are better off with HCFC's, but Wormtail is not

Extra

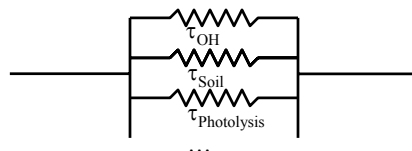
## Example: What can possibly happen to methane in the troposphere?

- Transport to stratosphere –  $\tau \sim 8$  yrs (taken from Homework #1)
- Loss to soil –  $\tau \sim 100$  yrs
  - Very uncertain, just grabbed someone else’s estimate for this
- Photolysis –  $\tau \sim 300$  yrs
  - Absorption cross section in UV  $\sim 10^{-24}$  cm<sup>2</sup>; compare to  $\sim 10^{-17}$  cm<sup>2</sup> for O<sub>3</sub>
  - $\sim 10^{14}$  photons cm<sup>-2</sup> s<sup>-1</sup> in UV; O<sub>3</sub> has photolytic lifetime of  $\sim 1000$  s
  - Lifetime of CH<sub>4</sub> would be 10<sup>7</sup> times longer based on smaller cross section
- Rainout/particle uptake -  $\tau \sim$  very long (didn’t get around to making estimate)
  - Methane not very soluble or sticky
- Reaction with OH –  $\tau \sim 5$  yrs
  - $k = 6 \times 10^{-15}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>
  - [OH]  $\sim 1 \times 10^6$  molecule cm<sup>-3</sup> (Note: this is an assumed global [OH])
- Reaction with NO<sub>3</sub> –  $\tau \sim 30$  yrs
  - $k < 1 \times 10^{-18}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>
  - [NO<sub>3</sub>] up to 400 ppt  $\sim 10^{10}$  molecule cm<sup>-3</sup>, use 10<sup>9</sup> molecule cm<sup>-3</sup>
- Reaction with Cl atoms –  $\tau \sim 300$  yrs
  - $k = 1 \times 10^{-13}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>
  - [Cl] maybe 10<sup>5</sup> molecule cm<sup>-3</sup> at most in marine areas, use 10<sup>3</sup> molecule cm<sup>-3</sup>
- Reaction with O<sub>3</sub> –  $\tau = 250$  yrs
  - Guess  $k \sim 10^{-22}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup> based on  $k$  for O<sub>3</sub> + C<sub>2</sub>H<sub>2</sub> of 10<sup>-20</sup>
  - [O<sub>3</sub>]  $\sim 50$  ppb =  $1.3 \times 10^{12}$  molecule cm<sup>-3</sup>

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## Lifetime for Multiple Loss Processes

- CH<sub>4</sub> loss to reaction with OH, NO<sub>3</sub>, photolysis, ...
- Total loss rate coefficient adds:
  - $k_{\text{Total}} = k_1' + k_2' + k_3' + \dots$
  - These must be all first order processes (units = s<sup>-1</sup>)
- Lifetimes adds as equivalent resistor network



- $\tau_{\text{Total}} = 1/\tau_{\text{OH}} + 1/\tau_{\text{NO}_3} + 1/\tau_{\text{Trans2strat}} + \dots$
- $\tau_{\text{Total}} = 1/(5.2 \text{ yrs}) + 1/(30 \text{ yrs}) + 1/(8 \text{ yrs}) = 2.9 \text{ yrs}$

Extra

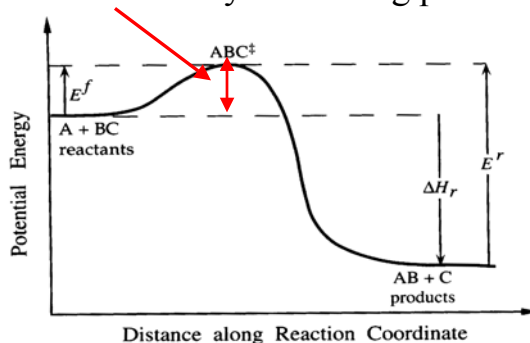
## Magnitude of Termolecular Rate Coefficients

- Remember  $k_0$  units are  $\text{cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$
- Examples:
  - $\text{O} + \text{O}_2 \rightarrow \text{O}_3$   $k_0 = 6.0 \times 10^{-34}$
  - $\text{NO}_2 + \text{NO}_3 \rightarrow \text{N}_2\text{O}_5$   $k_0 = 2.0 \times 10^{-30}$
  - $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{O}_2 + \text{NO}_2 \rightarrow \text{CH}_3\text{CH}_2\text{C}(\text{O})\text{O}_2\text{NO}_2$   
 PPN  $k_0 = 9.0 \times 10^{-28}$
- Note difference of 6 orders of magnitude
- Larger molecules have larger termolecular rate coefficients because there are more ways for them to hide excess energy
  - Thus an excited complex can exist for longer without falling apart, allowing more time for the forward reaction to proceed to products

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## Activation Energy for Reaction

Activation energy  $\sim$  amount of energy for reactants to overcome barrier on way to forming products



From Seinfeld and Pandis

FIGURE 3.14 Potential energy surface along the reaction coordinate for a bimolecular reaction.

Negative activation energy possible  
 Often result of intermediate complex formation

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## “Maximum” Rate Coefficient

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- We just said collision rate coefficient is:
  - $k = P * \sigma_{AB} * (8kT / \pi\mu)^{1/2} * e^{-E_0/kT}$
- Typical collision cross section
  - $r \sim 0.2 \text{ nm} \rightarrow \sigma = 0.5 \text{ nm}^2 = 5 \times 10^{-15} \text{ cm}^2$
- Mean molecular velocity
  - Use  $m_A$  &  $m_B = 50 \text{ g mol}^{-1}$
  - $c = (8kT / \pi\mu)^{1/2} \approx 5 \times 10^4 \text{ cm s}^{-1}$
- Calculate maximum rate coefficient
  - $E_0 = 0$
  - $P = 1$
  - Max  $k = 5 \times 10^{-15} \text{ cm}^2 * 5 \times 10^4 \text{ cm s}^{-1} = 2.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
  - If  $k_{\text{example}} = 2.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ , approximate probability of a reaction during one collision is  $\sim 1$  in 1000 chance, or 0.1%

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## Transition State Theory (cont.)

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- Continuation of example  $A + BC \rightarrow AB + C$
- Reaction rate =  $v[ABC^\ddagger]$ 
  - $v$  = frequency of break up of  $ABC^\ddagger$  into products
  - Substitute in from previous slide
  - Rate =  $vK^\ddagger [A][BC]$ 

$$= v \left( e^{\frac{\Delta S^\ddagger_{0^\ddagger}}{R}} \right) \left( e^{-\frac{\Delta H^\ddagger_{0^\ddagger}}{RT}} \right) [A][BC]$$
  - “Loose” transition state  $\rightarrow$  larger  $\Delta S^\ddagger \rightarrow$  larger rate
  - $\Delta H^\ddagger$  related to activation energy, larger  $\Delta H^\ddagger \rightarrow$  smaller rate
- $v$  can be approximated as  $kT / h$ 
  - $\sim 6 \times 10^{12} \text{ s}^{-1}$  (energy of  $\sim 50 \mu\text{m}$  radiation)
  - Vibration – in particular B -- C stretching

Extra

## How does one measure a rate coefficient?

- $A + B \rightarrow \text{Products}$ 
  - Rate =  $-d[A]/dt = k [A][B]$
- Make life simpler
  - Typical procedure to work with large excess of B and follow time rate of change of A (pseudo-first order)
  - $[B]_t \sim \text{constant} = [B]_0$
  - Integrate :  $\ln \frac{[A]}{[A]_0} = -k[B]_0 t$
- Note: do not need to know absolute [A]
  - Only need to know relative  $[A]/[A]_0$
  - Precision with which you can measure k depends on how well you can measure three things:  $[A]/[A]_0$ ,  $[B]_0$ , and time
  - For  $\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$ , easier to have excess of  $\text{CH}_4$ 
    - Can be obtained easily, can create stable concentration of it readily by simply flowing it from a cylinder; Cannot buy a bottle of OH!

Extra

## Diffusion-Controlled Reactions in Solution

- For uncharged non-polar species
- Fick's first law  $J = \frac{dn}{dt} = -DE \frac{\delta[N_A]}{\delta x}$ 
  - J = rate of diffusion of species A across area E along x axis
  - dn is amount of A crossing area E ( $\text{cm}^2$ ) in dt
  - D = diffusion coefficient ( $\text{cm}^2 \text{s}^{-1}$ )
  - $\delta[N_A] / \delta x$  = concentration gradient in x direction
- Leads to rate coefficient:  $k = 4\pi r_{AB} D_{AB} (6.02 \times 10^{20})$ 
  - $r_{AB}$  = distance between centers of molecules  $\sim 0.4 \text{ nm}$
  - $D_{AB} = D_A + D_B \sim 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$
  - Typical rate coefficient  $\sim 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$ 
    - $\sim 5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
    - Close to gas phase values
- Little interaction between reactants and solvent
  - Determines solubility of reactive species & cage effects

Extra



## “Practical” Aside: Number of collisions with surfaces

- $k = \frac{1}{4} * \gamma * v * (\pi * r_a^2 * N_a)$ 
  - $\gamma$  = uptake coefficient = unitless = number of collisions that lead to reaction  $v$  = mean molecular speed =  $(8 kT / \pi m)^{1/2}$ 
    - $\sim 500 \text{ m s}^{-1}$  at room temperature
  - $r_a$  = average radius of aerosol that gas molecule is colliding with
  - $N_a$  = number density of aerosol
  - $v \text{ (m s}^{-1}\text{)} * r_a^2 \text{ (m}^2\text{)} * N_a \text{ (# m}^{-3}\text{)} \rightarrow \text{s}^{-1}$
- Can replace  $(\pi * r_a^2 * N_a)$  with  $A$ 
  - $k_{\text{het}} = \frac{1}{4} * \gamma * v * A$ 
    - Where  $A$  = surface area per unit volume
    - Real aerosols have size distributions, so using an “average radius” is not necessarily a good approximation

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## Resistance Model (cont.)

- Conductance of diffusion of gas to surface ( $\Gamma_g$ )
  - Start by assuming small Knudson # (ratio of mean free path to radius of particle =  $K_n$ )
  - $\sim 10^{10}$  collisions  $\text{s}^{-1} \rightarrow 10^{-10}$  s between collisions @  $500 \text{ m s}^{-1} \rightarrow 50 \text{ nm}$
  - Atmospheric particles in accumulation mode  $\sim 100 \text{ nm} \rightarrow$  Not valid!!
  - Rate of gas molecules diffusing to surface =  $2\pi d D_g N_g$
  - =  $2D_g N_g / d$  normalized to particle surface area
    - $d$  = particle diameter
  - Normalize to rate of collisions:  $\Gamma_g = \frac{8D_g}{u_{\text{avg}} d}$
  - Distortion of Boltzmann velocity distribution near surface due to rapid uptake
 
$$\frac{\Gamma_g}{u_{\text{avg}} d} = \frac{8D_g}{8D_g} - \frac{1}{2}$$
- Free molecular regime ( $d_{\text{part}} \ll$  mean free path),  $K_n$  large
  - Rate of gas molecules diffusing to surface =  $\pi a^2 \alpha_c u_{\text{avg}} N_g$
  - $\alpha$  = probability of uptake at the surface,  $u_{\text{avg}}$  = velocity
- For intermediate regimes of  $K_n$ 
  - Rate of gas molecules diffusing to surface =  $2\pi d D_g N_g / (1 + \lambda K_n)$
  - Where  $\lambda = \frac{1.33 + 0.71 / K_n}{1 + 1 / K_n}$

Extra