

Kinetics and Atmospheric Chemistry

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Atmospheric Chemistry

CHEM-5151/ATOC-5151

Required reading: Finlayson-Pitts and Pitts
Chapter 5

Recommended reading: Jacob, Chapter 9

Other reading: Seinfeld and Pandis 3.5

General Outline of Next 3 Lectures

- Intro = General introduction
 - Quick review of thermodynamics
- Finlayson-Pitts & Pitts, Chapter 5
 - A. Fundamental Principles of Gas-Phase Kinetics
 - B. Laboratory Techniques for Determining Absolute Rate Constants for Gas-Phase Reactions
 - C. Laboratory Techniques for Determining Relative Rate Constants for Gas-Phase Reactions
 - D. Reactions in Solution
 - E. Laboratory Techniques for Studying Heterogeneous Reactions
 - F. Compilations of Kinetic Data for Atmospheric Reactions

Kinetics and Atmospheric Chemistry

- What we're doing here...
 - Photochemistry already covered
 - We will cover gas phase kinetics and heterogeneous reactions
 - Introductions to a few techniques used for measuring kinetic parameters
- What kind of information do we hope to get out of "atmospheric kinetics"?
 - Predictive ability over species emitted into atmosphere
 - Which reactions will actually proceed to products?
 - Which products will they form?
 - How long will emitted species remain before they react? Competition with photolysis, wash out, etc.
 - Pare down list of thousands of possible reactions to the ones that really matter
 - Aiming towards idea practical predictive abilities
 - Use look up tables to decide if reaction is likely to proceed and determine an "atmospheric lifetime" (= amount of time required for concentration of species to decrease by $1/e$, we'll get to this...)

Intro

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 W m^{-2} , all radiation is 500 nm, and OH molecule has cross section of 0.5 nm^2
 - You tell me...
 - Number of heterogeneous collisions per second
 - Assume $\sim 10^5 \text{ particles cm}^{-3}$ with average diameter of 500 nm
 - ~ 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!!
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 - Answer ~ 2000 photons per second
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Extra

Before we start...

- Where do molecules hide all of their energy?

Intro

Before we start...

- 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

Extra

Quick Refresher on Thermodynamics

- Gibbs free energy

$$\Delta G = \Delta H - T \Delta S$$
 - Gibbs free energy ~ energy available for chemical reaction
 - Negative ΔG = spontaneous reaction
 - ΔH = change in enthalpy from reactants to products
 - Lower ΔH leads to lower ΔG
 - ΔS = change in entropy from reactants to products
 - Higher ΔS leads to lower ΔG
- No need to reinvent the wheel, you can look up ΔH and ΔS values
 - Idea is be able to calculate which reactions will occur
 - From there, we can spend time figuring out how fast they occur

Intro

Enthalpy

- Enthalpy = internal energy + pressure-volume state
- $\Delta H_{\text{rxn}} > 0 \rightarrow$ endothermic; $\Delta H_{\text{rxn}} < 0 \rightarrow$ exothermic
- Always trying to minimize energy – go “downhill”

Example of
exothermic
reaction

$$E_{\text{prod}} < E_{\text{react}}$$

From Seinfeld
and Pandis

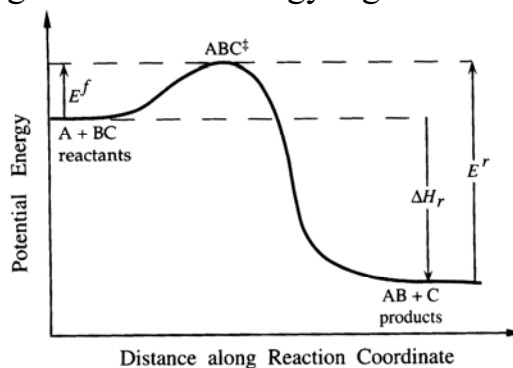


FIGURE 3.14 Potential energy surface along the reaction coordinate for a bimolecular reaction.

Intro

Entropy

- Entropy = amount of disorder
- 2nd Law of Thermodynamics = nature tends to increase in entropy
- For gas phase reactions, big entropy changes driven by number of compounds involved in reaction
 - Two reactants \rightarrow two products = $\Delta S \sim 0$
 - Association and dissociation reactions have $\Delta S \sim 30$ entropy units ($\text{cal K}^{-1}\text{mol}^{-1}$) per compound lost/gained
 - ~ 10 entropy units per degree of freedom lost/gained
 - Entropy can be calculated from a more first principles approach
 - Only necessary in practice for transient species such as reaction intermediates

Intro

“Practical Thermo”

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

–	ΔH_f (kcal mol ⁻¹)	S_f (cal K ⁻¹ mol ⁻¹)
– OH	8.89	43.91
– CH ₄	-17.80	44.55
– H ₂ O	-57.798	45.133
– CH ₃	35.05	46.36

 - Calculate ΔH_{rxn} , ΔS_{rxn} , & ΔG_{rxn} for room temp?
- Example 2: $\text{N}_2\text{O}_5 \rightarrow \text{NO}_2 + \text{NO}_3$

–	ΔH_f (kcal mol ⁻¹)	S_f (cal K ⁻¹ mol ⁻¹)
– N ₂ O ₅	3.18	85.01
– NO ₂	8.17	57.40
– NO ₃	17.6	61.76

 - Calculate ΔH_{rxn} , ΔS_{rxn} , & ΔG_{rxn} for room temp?
 - At what temp does $\Delta G = 0$?
- Note: we have not included change in ΔH_f 's with respect to temperature
 - Often these are small – for initial order-of-magnitude type guesses, do not worry about

Intro

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

–	ΔH_f (kcal mol ⁻¹)	S_f (cal K ⁻¹ mol ⁻¹)
– N ₂ O ₅	3.18	85.01
– NO ₂	8.17	57.40
– NO ₃	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 ΔH_f 's with respect to temperature
 - Often these are small – for initial order-of-magnitude type guesses, do not worry about

Extra

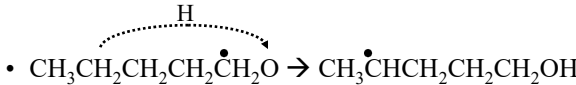
Elementary vs Overall Reactions

- Overall = sum of more than one elementary reaction
 - $\text{OH} + \text{CO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO}_2$
- Elementary = simplest reaction, cannot be broken down, cannot have more than 3 reactants
 - $\text{OH} + \text{CO} \rightarrow \text{H} + \text{CO}_2$
 - $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2$
- We like to deal with elementary reactions
 - Which reaction is “bottle neck”?
 - Which concentrations will affect rate of reaction?
 - Something to be aware of, very intuitive though
 - Much of atmospheric chemistry literature deals in elementary reactions anyway

A

Molecularity of Reactions

- Unimolecular
 - Gas phase decompositions, isomerizations
 - Example 1,6 H shift in alkoxy radical (P&P p.189)



$$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\overset{\text{H}}{\text{C}}\text{H}_2\text{O}\cdot \rightarrow \text{CH}_3\cdot\text{CHCH}_2\text{CH}_2\text{CH}_2\text{OH}$$
- Bimolecular
 - Basic two body reactions
 - $\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$
- Trimolecular
 - Three body reactions, association reactions
 - Classic example: $\text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M}$
 - M = usually N_2 or O_2 for atmosphere

A

What are chances of truly termolecular collision?

- How long is collision vs how long is time between collisions?
 - Just looking for guesses here...

A

What are chances of truly termolecular collision?

- 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 ~ 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

“Everything boils down to bimolecular reactions”

- Bimolecular reactions are well, bimolecular
 - $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$
- Unimolecular and termolecular reactions need collisions too
 - For thermal decompositions, energy to overcome barrier to dissociation provided by collisions with other gas phase molecules
 - $\text{N}_2\text{O}_5 + \text{M} \leftrightarrow \text{N}_2\text{O}_5^* + \text{M}$
 - $\text{N}_2\text{O}_5^* \rightarrow \text{NO}_2 + \text{NO}_3$
 - Exact definitions of what constitutes a chemical species depends on what you are doing
 - Association reactions thought of as series of two bimolecular reactions
 - $\text{OH} + \text{NO}_2 \leftrightarrow \text{OH}\bullet\text{NO}_2$
 - $\text{OH}\bullet\text{NO}_2 + \text{M} \rightarrow \text{HNO}_3$
 - Complex formation, excess energy removed by collision with 3rd body
 - Further info: Lindemann, RRK and RRKM theories, Troe’s method ...
 - Reactants are found at ppm levels – 10^6 more collisions with N_2 and O_2 will establish equilibrium quickly between interactions
- Truly unimolecular process = spontaneous radiative deactivation
 - $\text{NO}_2^* \rightarrow \text{NO}_2 + h\nu$

A

Rate Laws

- 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?
- What does this rate depend on?

A

Rate Laws

- 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?
 - $-\text{d}[\text{OH}]/\text{dt} = k * [\text{OH}] * [\text{CH}_4]$
 - $k = \text{rate coefficient}$
 - k is essentially a probability that a collision between reactants will lead to products
 - Can vary with temperature and pressure

Extra

Rate Laws

- General form
 - $a\text{A} + b\text{B} \rightarrow c\text{C} + d\text{D}$
 - $\text{Rate} = - (1/a) * (\text{d}[\text{A}]/\text{dt}) = (1/c) * (\text{d}[\text{C}]/\text{dt}) = \dots$
- Rate expressed in terms of concentrations
 - For non-elementary reactions:
 - $\text{Rate} = k[\text{A}]^m[\text{B}]^n[\text{C}]^p[\text{D}]^q$
 - m, n, p & q generally determined empirically
 - Not necessarily = a, b, c & d
 - May be zero, integers or fractions
 - For elementary reactions ($a + b \leq 3$)
 - $\text{Rate} = k[\text{A}]^a[\text{B}]^b$
 - Reactions must occur during a single collision
 - But probability of reaction $<$ unity

A

Reaction Order

- 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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Extra

Rate Coefficient

- Gas phase perspective
- Rate = molecule cm⁻³ s⁻¹
- First order
 - Rate = k[A]
 - Units: s⁻¹
- Second order
 - Rate = k[A][B]
 - Units: cm³ molecule⁻¹ s⁻¹
- Third order
 - Rate = k[A][B][C]
 - Units: cm⁶ molecule⁻² s⁻¹
- Rate coefficients vary with temperature and pressure
 - More on this later

TABLE 5.1 Some Common Conversion Factors for Gas-Phase Reactions

Concentrations ^a	
1 mol L ⁻¹	= 6.02 × 10 ²⁰ molecules cm ⁻³
1 ppm	= 2.46 × 10 ¹³ molecules cm ⁻³
1 ppb	= 2.46 × 10 ¹⁰ molecules cm ⁻³
1 ppt	= 2.46 × 10 ⁷ molecules cm ⁻³
1 atm	= 760 Torr = 4.09 × 10 ⁻² mol L ⁻¹ = 2.46 × 10 ¹⁹ molecules cm ⁻³
Second-order rate constants	
cm ³ molecule ⁻¹ s ⁻¹	× 6.02 × 10 ²⁰ = L mol ⁻¹ s ⁻¹
ppm ⁻¹ min ⁻¹	× 4.08 × 10 ⁵ = L mol ⁻¹ s ⁻¹
ppm ⁻¹ min ⁻¹	× 6.77 × 10 ⁻¹⁶ = cm ³ molecule ⁻¹ s ⁻¹
atm ⁻¹ s ⁻¹	× 4.06 × 10 ⁻²⁰ = cm ³ molecule ⁻¹ s ⁻¹
Third-order rate constants	
cm ⁶ molecule ⁻² s ⁻¹	× 3.63 × 10 ⁴¹ = L ² mol ⁻² s ⁻¹
ppm ⁻² min ⁻¹	× 9.97 × 10 ¹² = L ² mol ⁻² s ⁻¹
ppm ⁻² min ⁻¹	× 2.75 × 10 ⁻²⁹ = cm ⁶ molecule ⁻² s ⁻¹

^a The concentrations ppm, ppb, and ppt are relative to air at 1 atm and 25°C, where 1 atm = 760 Torr total pressure.

From Finlayson-Pitts and Pitts

A

Half-Lives & Lifetimes

- Half-life = $t_{1/2}$ = time for concentration of species to fall to 1/2 present value
- Natural lifetime = “lifetime” = τ = time for concentration of species to fall to 1/e of present value
- Note that lifetime of species does not depend on its own concentration
 - Exceptions obviously for self reactions
- Examples to explain this further

TABLE 5.2 Relationships between the Rate Constant, Half-Lives, and Lifetimes for First-, Second-, and Third-Order Reactions

Reaction order	Reaction	Half-life of A	Lifetime of A
First	(1) A $\xrightarrow{k_1}$ Products	$t_{1/2}^A = 0.693/k_1$	$\tau^A = 1/k_1$
Second	(2) A + B $\xrightarrow{k_2}$ Products	$t_{1/2}^A = 0.693/k_2[B]$	$\tau^A = 1/k_2[B]$
Third	(3) A + B + C $\xrightarrow{k_3}$ Products	$t_{1/2}^A = 0.693/k_3[B][C]$	$\tau^A = 1/k_3[B][C]$

From Finlayson-Pitts and Pitts

Remember, chemical lifetime always in competition with transport, photolysis, heterogeneous reactions, etc.

A

Problem to Solve in Class

- Lord Voldemort is back. He has decided that in order to make life miserable for us muggles, he is going to unleash the magic of chlorofluorocarbons (CFC's) to destroy the stratospheric ozone layer. He has an old stockpile of CFC-11 (CFCl_3), but his faithful servant Wormtail has told him that this new-fangled compound, HCFC-21 (CHFCl_2) is more effective at destroying stratospheric ozone. Voldemort assigns Lucius Malfoy to determine which compound will be better at reaching the stratosphere. Malfoy quickly uses a *hydroxy concentratum* spell to determine that a typical concentration of OH in troposphere is $\sim 1 \times 10^6$ molecule cm^{-3} , followed by a *doublecheckium* spell to confirm that the lifetimes of these compounds are indeed determined by their reaction with OH. Malfoy then uses a Polyjuice potion to disguise himself as Dr. A.R. Ravishankara and breaks into the Ministry of Magical Rate Coefficients data base to find the following numbers for hydroxyl radical reactions:
 - $k_{\text{CFC-11}} < 5.0 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
 - $k_{\text{HCFC-21}} = 2.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
- The question is, will Malfoy tell Voldemort to follow Wormtail's advice or punish him severely?

A

Example: CFC's and HCFC's

- **Info:**
 - Old CFC = CFC-11 = CFCl_3
 - New HCFC = HCFC-21 = CHFCl_2
- **Assumptions:**
 - Lifetimes determined by reaction with hydroxyl radical (OH)
 - Typical concentration of OH in troposphere $\sim 1 \times 10^6$ molecule 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**
 - $\tau_{\text{CFC-11}} = 1 / k[\text{OH}] = 1 / (5.0 \times 10^{-18} * 1 \times 10^6) = 2 \times 10^{11} \text{ s} = 6340 \text{ years}$
 - $\tau_{\text{HCFC-21}} = 1 / k[\text{OH}] = 1 / (2.6 \times 10^{-14} * 1 \times 10^6) = 4 \times 10^7 \text{ s} = 1.2 \text{ years}$
- We are better off with HCFC's, but Wormtail is not

Extra

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

- Suggestions from the peanut gallery...
 - (that means you)

A

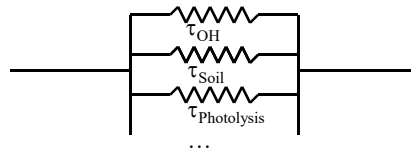
Example: What can possibly happen to methane in the troposphere?

- 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 $\sim 10^{-24}$ cm²; compare to $\sim 10^{-17}$ cm² for O₃
 - $\sim 10^{14}$ photons cm⁻² s⁻¹ in UV; O₃ has photolytic lifetime of ~ 1000 s
 - Lifetime of CH₄ would be 10⁷ 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
 - $k = 6 \times 10^{-15}$ cm³ molecule⁻¹ s⁻¹
 - [OH] $\sim 1 \times 10^6$ molecule cm⁻³ (Note: this is an assumed global [OH])
- Reaction with NO₃ – $\tau \sim 30$ yrs
 - $k < 1 \times 10^{-18}$ cm³ molecule⁻¹ s⁻¹
 - [NO₃] up to 400 ppt $\sim 10^{10}$ molecule cm⁻³, use 10^9 molecule cm⁻³
- Reaction with Cl atoms – $\tau \sim 300$ yrs
 - $k = 1 \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹
 - [Cl] maybe 10^5 molecule cm⁻³ at most in marine areas, use 10^3 molecule cm⁻³
- Reaction with O₃ – $\tau = 250$ yrs
 - Guess $k \sim 10^{-22}$ cm³ molecule⁻¹ s⁻¹ based on k for O₃ + C₂H₂ of 10^{-20}
 - [O₃] ~ 50 ppb = 1.3×10^{12} molecule cm⁻³

Extra

Lifetime for Multiple Loss Processes

- CH₄ loss to reaction with OH, NO₃, 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⁻¹)
- Lifetimes adds as equivalent resistor network

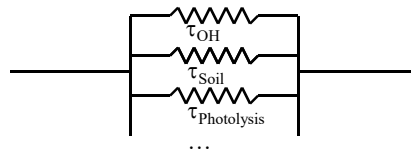


- $1/\tau_{\text{Total}} = 1/\tau_{\text{OH}} + 1/\tau_{\text{NO}_3} + 1/\tau_{\text{Trans2strat}} + \dots$
- **What is the overall lifetime for CH₄? (from last slide)**

A

Lifetime for Multiple Loss Processes

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- Total loss rate coefficient adds:
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 - These must be all first order processes (units = s⁻¹)
- 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

Steady State Approximation

- Short-lived species where $[X]$ can be assumed as constant
 - Make approximation that $d[X] / dt \approx 0$
 - $d[X]/dt = \text{Production} - \text{Loss} \approx 0$
 - So $\text{Production} \approx \text{Loss}$
- Example
 - Assume production of OH dominated by $O(^1D) + H_2O$ reaction
 - Assume loss of OH dominated by CH_4 reaction
 - $d[OH]/dt = 2 \cdot k_1 [O(^1D)][H_2O] - k_2 [OH][CH_4] \approx 0$
 - Rearrange : $[OH] \approx 2 \cdot k_1 [O(^1D)][H_2O] / k_2 [CH_4]$
 - Note: Can obtain approximation of $[OH]$ without measuring it directly

A

Termolecular Reactions & Pressure Dependence of Rate Constants

- $O + O_2 + M \rightarrow O_3 + M$
 - For atmospheric purposes $M = N_2$ or O_2
- $\text{Rate} = k [O][O_2][M] = + d[O_3]/dt$
 - $[M]$ not changed by reaction – assumed constant
 - $\text{Rate} = k' [O] [O_2]$
 - Two limits to this: high pressure and low pressure
 - $[M] \propto \text{pressure}$ (remember ideal gas law)
 - Think of as two step process:
 - $O + O_2 \leftrightarrow O_3^*$ $O_3^* = \text{excited } O-O_2 \text{ adduct}$
 - $O_3^* + M \rightarrow O_3 + M$ $M \text{ removes excess energy}$
 - If no M present O_3^* will fall apart back to reactants

A

Lindemann-Hinshelwood

- What is rate coefficient for termolecular reaction?
 - $O + O_2 \rightleftharpoons O_3^*$ k_f and k_r
 - $O_3^* + M \rightarrow O_3 + M$ k_p
 - Steady-state assumed for $[O_3^*]$:
 - $d[O_3^*]/dt \sim 0 = k_f [O][O_2] - k_r [O_3^*] - k_p [O_3^*][M]$
 - $[O_3^*] \sim k_f [O][O_2] / (k_r - k_p [M])$
 - Rate of product formation in second step:
 - $d[O_3]/dt = k_p [O_3^*][M]$
 - Substitute in for O_3^*
 - $d[O_3]/dt = k_f k_p [O][O_2][M] / (k_r - k_p [M])$
 - Rate = $k[O][O_2]$
 - Overall rate coefficient: $k = k_f k_p [M] / (k_r - k_p [M])$

A

Termolecular Reactions – Low Pressure Limit

- $k = k_f k_p [M] / (k_r - k_p [M])$
- Low pressure : $k_r \gg k_p [M]$
 - $k \sim k_f k_p [M] / k_r$
 - Rate depends on pressure!
 - From our example, in low pressure limit, O_3^* dissociates back to reactants much more frequently than collisions with bath gas (M) remove energy from O_3^*
 - Thus, rate limiting step is how often energy is removed from O_3^* and overall rate coefficient depends on $[M]$

A

Termolecular Reactions – High Pressure Limit

- $k = k_f k_p [M] / (k_r + k_p [M])$
- High pressure : $k_p [M] \gg k_r$
 - $k \sim k_f$
 - Rate independent of pressure!
 - In high pressure limit, (lots of M around) collisions with bath gas (M) remove energy from O_3^* much more frequently than O_3^* dissociation
 - Thus formation of O_3^* is rate limiting step and overall rate coefficient \sim rate coefficient for that step

A

Fall-Off Region

- What about the not-so-high and not-so-low pressures
- Transition between linear dependence on pressure and no dependence on pressure

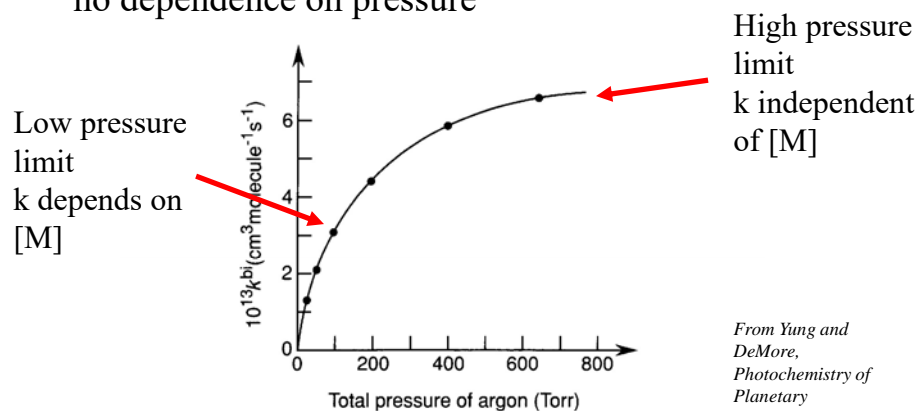


FIGURE 5.2 Plot of k_0^{bi} against total pressure for M = Ar for the reaction of OH with SO_2 (adapted from Atkinson *et al.*, 1976).

A

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

Extra

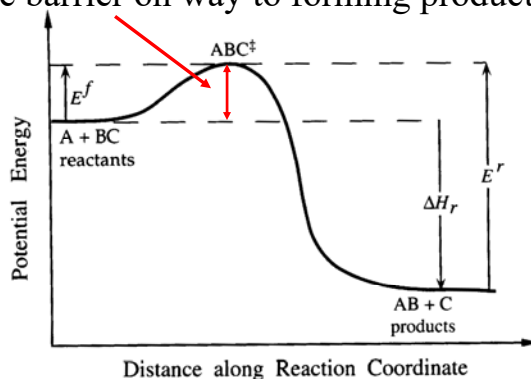
Temperature Dependence of Rate Coefficients

- Arrhenius Expression
 - Temp dependence of rate coefficient over narrow temp range described by:
 - $k = A e^{-E_a / RT}$
 - A = “pre-exponential factor”
 - Usually considered temperature independent
 - Will look at this in collision theory and transition state theory later
 - E_a = activation energy
 - R = gas constant
 - Plot $\ln k$ vs T^{-1}
 - Slope = E_a / R
 - Intercept = $\ln A$
 - Discussion of collision rate should illuminate a little of where this comes from (coming up in several slides)

A

Activation Energy for Reaction

Activation energy ~ amount of energy for reactants to overcome barrier on way to forming products



From Seinfeld and Pandis

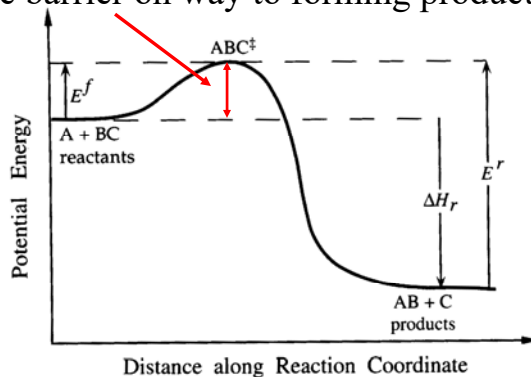
FIGURE 3.14 Potential energy surface along the reaction coordinate for a bimolecular reaction.

Could you have a negative activation energy?
If so, what mechanism would explain this?

A

Activation Energy for Reaction

Activation energy ~ amount of energy for reactants to overcome barrier on way to forming products



From Seinfeld and Pandis

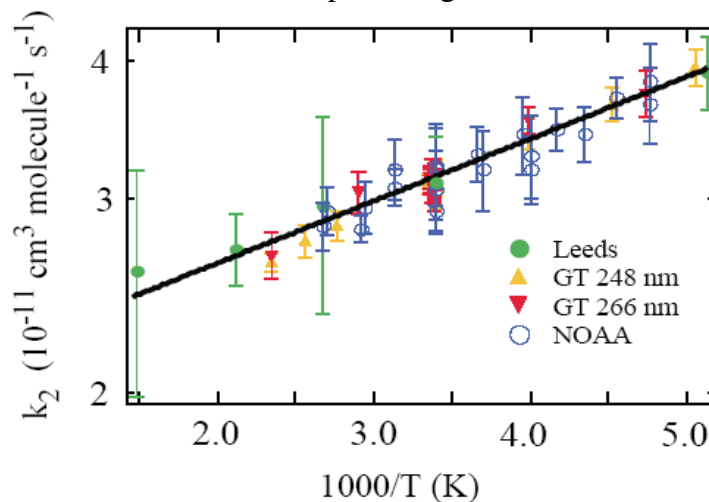
FIGURE 3.14 Potential energy surface along the reaction coordinate for a bimolecular reaction.

Negative activation energy possible
Often result of intermediate complex formation

Extra

Example of Arrhenius Plot

Measurements of rate coefficient for $O(^1D) + N_2$
 Plotted on log scale, so fit to Arrhenius expression appears as line
 Note that this is example of negative activation energy



From
 Ravishankara
 et al., *GRL*,
 VOL. 29, NO.
 15, 1745,
 2002

A

Collision Theory

- Collision rate for molecules A & B
- $Z_{AB} = \pi (r_A + r_B)^2 * (8kT / \pi\mu)^{1/2} * N_A N_B$
 - r_A & r_B = radii of molecules
 - k = Boltzmann constant = $1.38 \times 10^{-23} \text{ J K}^{-1}$
 - μ = reduced mass = $m_A m_B / (m_A + m_B)$
 - N_A & N_B = concentrations
 - Define σ_{AB} as collision cross section = $\pi (r_A + r_B)^2$
 - Assumes all collisions \rightarrow reaction
- As we have seen, reactions usually require some minimum activation energy in order to go on to products
 - For $E < E_0 \rightarrow$ no reaction
 - For $E > E_0 \rightarrow$ increasing probability of reaction with increasing energy $(1 - E_0/E)$
 - Integrate \rightarrow get factor of $e^{-E_0/kT}$
 - Note similarity to Boltzmann distribution, $N_i / N_j = e^{-(E_i - E_j)/kT}$

A

Collision Theory (cont.)

- Collision rate :
 - $Z_{AB} = \sigma_{AB} * (8kT / \pi\mu)^{1/2} * e^{-E_0/kT} N_A N_B$
- But what about orientation?
 - If molecules not aligned properly, no reaction
 - Insert steric factor, P
 - $Z_{AB} = P * \sigma_{AB} * (8kT / \pi\mu)^{1/2} * e^{-E_0/kT} N_A N_B$
- Compare to reaction rate
 - Rate = $k [A][B]$, or $k * N_A * N_B$
 - So, $k = P * \sigma_{AB} * (8kT / \pi\mu)^{1/2} * e^{-E_0/kT}$
- Compare this to Arrhenius expression
 - $k = A e^{-E_a / RT}$
 - $A = P * \sigma_{AB} * (8kT / \pi\mu)^{1/2}$
 - Pre-exponential factor has $T^{1/2}$ dependence
 - Over narrow range of temps, this is often dwarfed by $e^{-E_a / RT}$ factor

A

“Maximum” Rate Coefficient

- 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
 - $E_0 = ?$
 - $P = ?$
 - Max $k = ?$
 - If some rate coefficient = $2.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, what is the approximate probability of a reaction during one collision

A

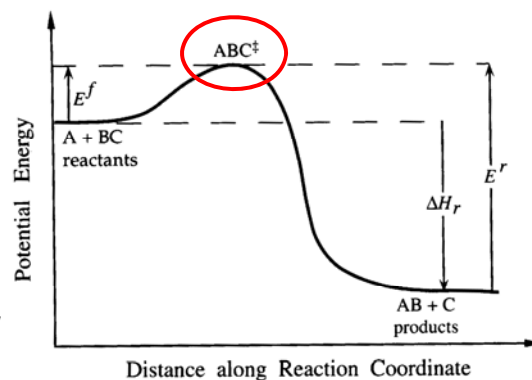
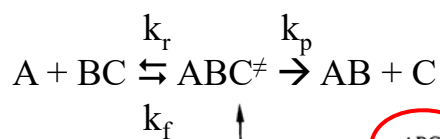
“Maximum” Rate Coefficient

- 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 ~ 1 in 1000 chance, or 0.1%

Extra

Transition State Theory

ABC^\ddagger complex formed at top of energy hill
 Referred to as transition state



From Seinfeld
and Pandis

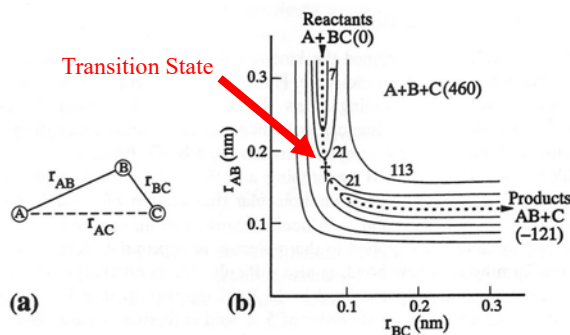
FIGURE 3.14 Potential energy surface along the reaction coordinate for a bimolecular reaction. A

Potential Energy Surface

From Yung and DeMore

64 Photochemistry of Planetary Atmospheres

Reaction of $A + BC \rightarrow AB + C$



Energy contours plotted as function of internuclear distances

Lowest energy path goes through saddle point – this is the transition state

Figure 3.1 (a) Schematic diagram showing the distances between the atoms A, B, and C. (b) Typical potential energy surface for a particular ABC angle. The lowest-energy path for the reaction to proceed from $A + BC$ to $AB + C$ is indicated by the dotted line, which represents the reaction coordinate. On this path, the highest energy is reached at the transition state, marked by the cross. This potential surface is computed for the reaction $F + H_2 \rightarrow H + HF$. The numerical values are energies in kJ mole^{-1} . After Muckerman, J. T., *J. Chem. Phys.* **54**, 115, 1971.

Transition State Theory (cont.)

- Still looking at :
$$A + BC \xrightleftharpoons[k_f]{k_r} ABC^\ddagger \xrightarrow{k_p} AB + C$$
- Assume equilibrium between reactants and transition state

$$K^\ddagger = \frac{k_f}{k_r} = \frac{[ABC^\ddagger]}{[A][BC]}$$

- Use thermodynamic relationship $\Delta G = -RT \ln K$

$$K^\ddagger = e^{-\frac{\Delta G^{0\ddagger}}{RT}} = \left(e^{-\frac{\Delta H^{0\ddagger}}{RT}} \right) \left(e^{\frac{\Delta S^{0\ddagger}}{R}} \right)$$

- Where $\Delta H^{0\ddagger}$ and $\Delta S^{0\ddagger}$ refer to changes from reactants up to transition state (not products)
- These can be estimated/calculated
- Crux of calculations is how well can transition state be approximated

A

Transition State Theory (cont.)

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

$$= \nu \left(e^{\frac{\Delta S^\ddagger}{R}} \right) \left(e^{-\frac{\Delta H^\ddagger}{RT}} \right) [A][BC]$$

- How do ΔS^\ddagger and ΔH^\ddagger affect overall rate?
- ν can be approximated as kT / h
 - How fast is that?
 - What molecular motion would be associated with this step?

A

Transition State Theory (cont.)

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

$$= \nu \left(e^{\frac{\Delta S^\ddagger}{R}} \right) \left(e^{-\frac{\Delta H^\ddagger}{RT}} \right) [A][BC]$$

- “Loose” transition state \rightarrow larger $\Delta S^\ddagger \rightarrow$ larger rate
- ΔH^\ddagger related to activation energy, larger $\Delta H^\ddagger \rightarrow$ smaller rate
- ν 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

Transition State Theory (cont.)

- In total:

$$k = \frac{k_B T}{h} \left(e^{\frac{\Delta S^{0\ddagger}}{R}} \right) \left(e^{-\frac{\Delta H^{0\ddagger}}{RT}} \right)$$
- Statistical mechanical approach to estimating k
 - Use partition functions, q
 - From Atkins *Physical Chemistry* text book
 - “The molecular partition function gives an indication of the average number of states that are thermally accessible to a molecule at the temperature of the system.”
 - Partition functions broken down into contributions from translational, rotational, vibrational, and electronic degrees of freedom
 - $q = q_{\text{trans}} q_{\text{rot}} q_{\text{vib}} q_{\text{elec}}$
 - Why do we care?
 - Can estimate a rate coefficient from basic information about the reactants (geometries, masses & vibrational frequencies) and educated guesses about transition state

A

Summary of Topics Up to This Point

- What have we just covered...
 - Review of “practical” thermodynamics
 - Rates and rate coefficients
 - Atmospheric chemical lifetimes
 - Pressure dependence of rate coefficients
 - Temperature dependence of rate coefficients
 - Collision and transition state theories
 - How to calculate rate coefficients
- Homework will review some of these concepts and explore new concepts
- Moving on to rest of Chapter 5...

A

Laboratory Techniques for Determining Absolute Rate Constants for Gas-Phase Reactions

- Our second section here
- After all these years, atmospheric chemical kinetics is still empirical
 - Theory is still behind measurements
 - Can use theory to estimate unmeasured rate coefficients (& judge measured ones!), extrapolate measured results to conditions not reached by measurements
- We will cover the basics on common features for any rate coefficient measurement
- Major techniques you should have a basic understanding of
 - Fast – Flow Systems *
 - Flash – Photolysis Systems *
 - Pulse Radiolysis
 - Cavity Ring Down Systems *
 - Static techniques

B

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
- In this example: $\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$, which species would you measure?

B

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 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

Exponential Decay Plots for OH Reaction

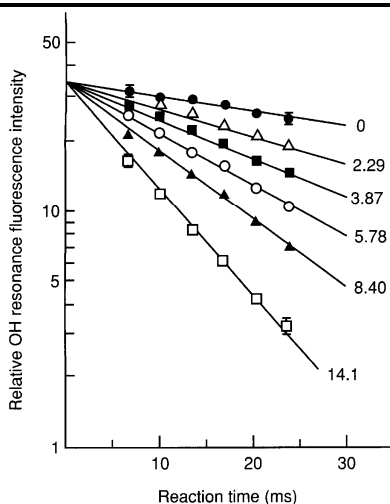


FIGURE 5.5 Typical plot of OH resonance fluorescence intensity as a function of reaction time in the presence of increasing concentrations of CINO (in units of 10^{13} molecules cm^{-3}) at 373 K (adapted from Finlayson-Pitts *et al.*, 1986).

From Finlayson-Pitts and Pitts

- Exponential decays appear as lines on log scale
- Increasing concentration of excess reactant increases loss rate of OH
 - Note there is measurable loss rate of OH in absence of excess reactant
- Time scale is less than 30 ms!
 - First points are at $t > 5$ ms so that production of OH can go to completion

B

First Order Rate Coefficient vs [Reactant]

- Remember:
 - $\ln[A]/[A]_0 = -k[B]_0 t$
- Measure $k^*[B]_0$
 - Call this $k' = k^*[B]_0$
- Plot of k' vs $[B]_0$
 - Slope = k
- Requires multiple measurements at various $[B]_0$
 - Best if you can span an order of magnitude in variation of $[B]_0$
 - Done for one temperature at a time

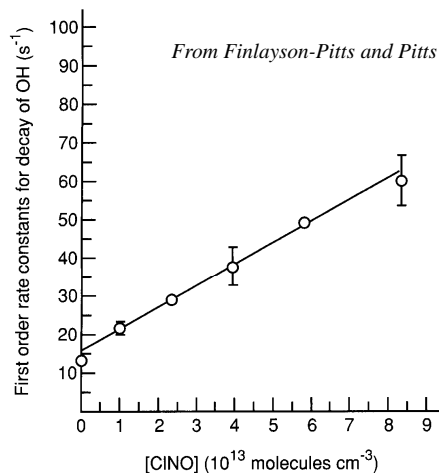


FIGURE 5.6 Typical plot of observed first-order rate constants for the decay of OH as a function of the initial ClNO concentration at 373 K (adapted from Finlayson-Pitts *et al.*, 1986).

B

From Finlayson-Pitts & Pitts

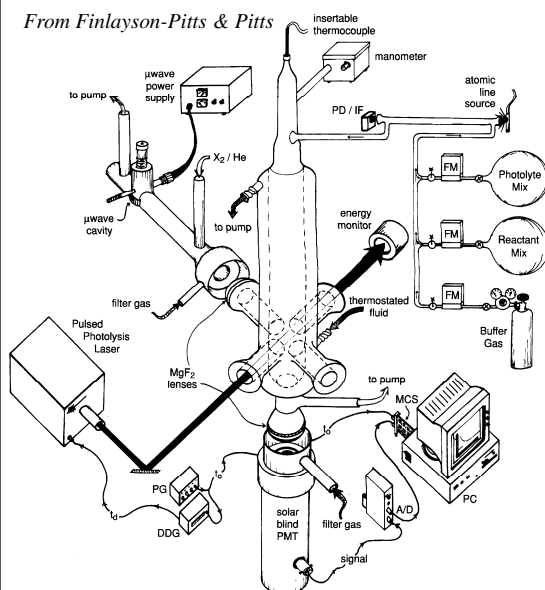


FIGURE 5.7 Laser photolysis resonance fluorescence apparatus for studying the kinetics of gas-phase reactions of H, O, Cl, and Br atoms with atmospheric trace gases. A/D, amplifier/discriminator; DDG, digital delay generator; FM, flow meter; IF, interference filter; MCS, multichannel scaler; PD, photodiode array detector; PG, pulse generator; PMT, photomultiplier. (Graciously provided by J. M. Nicovich and P. H. Wine, Georgia Institute of Technology).

Laser Photolysis Resonance Fluorescence System

- Generally, mix excess reactant and radical precursors together, then produce radicals (or start chemistry somehow)
 - Should be on short time scale relative to how fast reaction occurs
 - Here, chemistry started with laser
 - Example: $\text{H}_2\text{O}_2 + h\nu \rightarrow 2 \text{OH}$
- Here, temporal profile of radical followed with lamp / PMT system

B

Other important things to think about in measuring a rate coefficient

- Method of following change in time of one reactant means you do not see what products are
 - Determining what products are involves other types of experiments
- How fast do reactions happen though?
 - Depends on product of concentration of excess reactant and rate coefficient (lifetime!)
 - Can possibly guess this beforehand - some combination of previous experience and theory
- What is a discernable change in the concentration?
 - Depends how sensitive your detection technique is
- Ideally want to avoid loss of reactive species on walls of reactor

B

Transition Slide

- | | |
|--|---|
| <ul style="list-style-type: none"> • Parting shots from Ed: <ul style="list-style-type: none"> – A lot of work has already gone into measuring important gas phase reaction rate coefficients <ul style="list-style-type: none"> • Stratosphere very well covered • Troposphere still being actively worked on – There is still much active research in this area, but not as wide open as other areas within atmospheric chemistry – Boulder has been very active place for rate coefficient measurements over the years and still is – If you have the chance, visit labs that do this kind of research | <ul style="list-style-type: none"> • Not spending lecture time on sections C • Section C: Laboratory Techniques for Determining Relative Rate Constants for Gas-Phase Reactions <ul style="list-style-type: none"> – Will have homework question(s) on this section, so be sure to read |
|--|---|

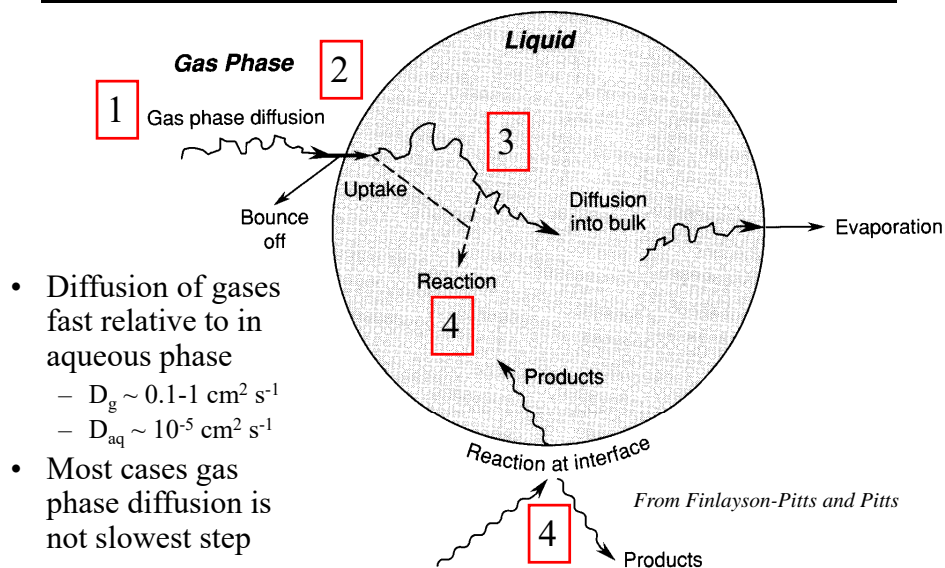
B & C

Reactions in Solution

- Atmosphere contains aqueous phase material
 - Clouds, fogs, rain, particulate matter
 - Aqueous solutions or film of water surrounding insoluble core
 - More on this stuff later in course
- For now, we will look at how gases interact with these particles
 1. Gas phase diffusion to surface of droplet
 2. Transport across air-water interface
 3. Diffusion of solvated species into bulk phase of droplet
 4. Reaction of species in aqueous phase or at interface

D

Uptake and Reaction of Gases in Liquids



- Diffusion of gases fast relative to in aqueous phase
 - $D_g \sim 0.1\text{-}1 \text{ cm}^2 \text{ s}^{-1}$
 - $D_{aq} \sim 10^{-5} \text{ cm}^2 \text{ s}^{-1}$
- Most cases gas phase diffusion is not slowest step

FIGURE 5.12 Schematic diagram of uptake and reaction of gases in liquids.

D

Henry's Law

- $[X] = H_X P_X$
 - $[X]$ = concentration of species in aqueous phase (mol L⁻¹)
 - H_X = Henry's law constant (mol L⁻¹ atm⁻¹)
 - P_X = partial pressure (atm)
- Describes equilibrium conditions
 - Assumes no fast irreversible reactions in solution
 - Assumes unimpeded air-water interface
 - Needs to be altered for solutions of high ionic strength

TABLE 5.6 Henry's Law Coefficients (H) of Some Atmospheric Gases Dissolving in Liquid Water at 25°C

Gas	H (mol L ⁻¹ atm ⁻¹)	Reference ^e
O ₂	1.3×10^{-3}	Loomis, 1928
NO	1.9×10^{-3}	Loomis, 1928
C ₂ H ₄	4.9×10^{-3}	Loomis, 1928
NO ₂ ^a	1×10^{-2}	Schwartz and White, 1983
O ₃	$(0.82-1.3) \times 10^{-2}$	Briner and Perrottet, 1939
N ₂ O	2.5×10^{-2}	Loomis, 1928
CO ₂ ^b	3.4×10^{-2}	Loomis, 1928
SO ₂ ^b	1.22	Maahs, 1982
HONO ^b	49	Schwartz and White, 1981
NH ₃ ^b	62	Van Krevelen <i>et al.</i> , 1949
H ₂ CO	6.3×10^3	Blair and Ledbury, 1925
H ₂ O ₂	$(0.7-1.0) \times 10^5$	Martin and Damschen, 1981
	1.4×10^5 ^c	Yoshizumi <i>et al.</i> , 1984
	6.9×10^4 ^d	Hwang and Dasgupta, 1985
HNO ₃	2.1×10^5	Schwartz and White, 1981
HO ₂	$(1-3) \times 10^3$	Schwartz, 1984b
OH	30	Golden <i>et al.</i> , 1990; Hanson <i>et al.</i> , 1992
PAN	5	Holdren <i>et al.</i> , 1984
CH ₃ SCH ₃	0.48-0.56	Dacey <i>et al.</i> , 1984

Source: Adapted from Schwartz (1984a).

^a Physical solubility; reacts with liquid water.

^b Physical solubility exclusive of acid-base equilibria.

^c At 20°C.

^d Temperature dependence also reported as $H = \exp[7.92 \times 10^3 / T (K) - 15.44]$.

^e See Table 8.1 for references and additional data.

From Finlayson-Pitts and Pitts

D

Solution Phase Collisions

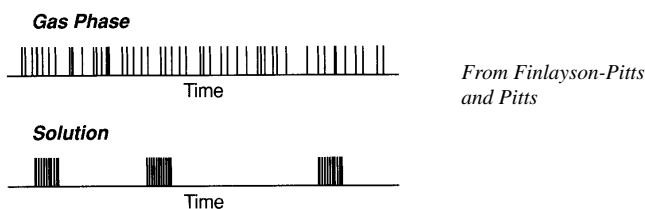


FIGURE 5.13 Patterns of A-B collisions expected in the gas phase and in solution (adapted from Adamson, 1973).

- Reactants in solution phase exist in solvent “cage”
 - Many collisions involved in an “encounter”
 - Promotes recombination of highly reactive
 - Longer diffusion times between encounters than between collisions in gas phase, but series of collisions during an encounter
 - Result for neutral non-polar reactants is rate coefficients in solution ~ equal to those in gas phase

D

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 (cm²) in dt
 - D = diffusion coefficient (cm² 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 ~ 0.4 nm
 - $D_{AB} = D_A + D_B \sim 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$
 - Typical rate coefficient ~ $10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$
 - One bonus point on the homework to the person who can translate that to gas phase units the fastest
- Little interaction between reactants and solvent
 - Determines solubility of reactive species & cage effects

D

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
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- Leads to rate coefficient: $k = 4\pi r_{AB} D_{AB} (6.02 \times 10^{20})$
 - r_{AB} = distance between centers of molecules ~ 0.4 nm
 - $D_{AB} = D_A + D_B \sim 2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$
 - Typical rate coefficient ~ $10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$
 - $\sim 5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
 - Close to gas phase values
- Little interaction between reactants and solvent
 - Determines solubility of reactive species & cage effects

Extra

Reactions of Charged Species in Solution

- Electrostatic attractions and repulsions between ions significantly alter rate coefficients from diffusion controlled values
- Electrostatic force between ions in solution $F = \frac{Z_A Z_B e^2}{4\pi\epsilon_0\epsilon r^2}$
 - $Z_A e$ and $Z_B e$ are charges on A and B
 - $\epsilon =$ permittivity of vacuum = $8.85 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$
 - $\epsilon =$ dielectric constant of solvent
 - $r =$ distance between ions
- Calculate change in free energy in bringing ions together to distance d_{AB} where they can react $\Delta G_{es} = \frac{(6.02 \times 10^{23}) Z_A Z_B e^2}{4\pi\epsilon_0\epsilon d_{AB}}$
- Results in rate coefficient that depends on nature of solvent

$$\ln k = \ln k_0 + \frac{Z_A Z_B e^2}{4\pi\epsilon_0\epsilon d_{AB} kT}$$

- $k_0 =$ rate coefficient for reaction in solvent where $\epsilon = \infty$, i.e., electrostatic forces are zero

D

Ionic Strength of Solution

- Ionic strength : $I = \frac{1}{2} \sum C_i Z_i^2$
 - Replace C with activity, $a = C\gamma$,
 - Where $\gamma =$ activity coefficient
 - Accounts for non-ideal behavior due to ion-solvent and ion-ion interactions
- Debye-Huckel limiting law predicts
 - $\log \gamma = -B Z^2 I^{1/2}$
 - $B =$ constant, depends on properties of solution
 - For water, $B = 0.51 \text{ L}^{1/2} \text{ mol}^{-1/2}$
 - Only for solutions of low ionic strength
- Insert into Transition State Theory
 - $\log k = \log k_0 + 1.02 Z_A Z_B I^{1/2}$
 - Deviations at higher ionic strengths – see Benson text book, 1960
- Be aware: Atmospheric aerosols have range of ionic strengths!
 - $\sim 10^{-3} \text{ M}$ for cloud and rain water
 - $\sim 10 \text{ M}$ for aerosol in polluted urban areas

D

Experimental Techniques for Solution Reactions

- Analogous to gas phase kinetics techniques
 - Follow concentration in time of one species in presence of large excess of another species
- UV-visible spectroscopy is primary tool
- Generation of free radicals
 - OH, HO₂, NO₃ and halogens, such as Cl₂⁻
 - Flash photolysis with flash lamps or lasers
 - Pulse radiolysis using high energy ionizing radiation
- See later chapters (7, 8 & 9) for more info on chemistry going on in aqueous phase

D

“Practical” Aside: Number of collisions with surfaces

- $k = \frac{1}{4} * \gamma * v * (\pi * r_a^2 * N_a)$
 - γ = 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
 - **What are units on k?**
- 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

E

“Practical” Aside: Number of collisions with surfaces

- $k = \frac{1}{4} * \gamma * v * (\pi * r_a^2 * N_a)$
 - γ = 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

Extra

Heterogeneous Reactions

- Reactions of gases with either solids or liquids
- Very active field of research, less mature than gas phase kinetics, but rapidly growing
- Some terms
 - γ_{rxn} – surface reaction probability = net fraction of gas-condensed phase collisions that leads to irreversible uptake of gas due to chemical reaction
 - α – mass accommodation coefficient = fraction of gas-condensed phase collisions that result in uptake of gas by condensed phase
 - γ_{net} – net collisional uptake probability = net rate of uptake of gas normalized to rate of gas-surface collisions
 - $\gamma_{\text{net}} = \gamma_{\text{meas}}$ because this is quantity measured in lab
- Great reference
 - C.E. Kolb et al., “Laboratory Studies of Atmospheric Heterogeneous Chemistry”, in *Progress and Problems in Atmospheric Chemistry*, J.R. Barker Ed., Chapter 18, Advanced Series in Physical Chemistry (C.-Y. Ng, Ed.), Vol. 3, World Scientific, Singapore, 1995.

E

Breaking Down Heterogeneous Reactions

1. Transport of gas to surface + initial interaction
 - Gas phase diffusion
2. Uptake at the interface
 - Mass accommodation coefficient
3. Diffusion into the bulk
 - Liquid phase diffusion (much slower than gas phase)
4. Henry's Law equilibrium
 - If reaction slow compared to diffusion, species can evaporate out of liquid
 - Dynamic equilibrium between gas and liquid phases eventually established – uptake still occurring!
5. Reaction in the bulk
 - If reaction occurring in bulk, speed of reaction dependent on particle volume
 - If reaction occurring at/near surface, speed of reaction dependent on particle surface area
6. Reactions at the interface
 - “Fourth phase” – not well understood at present
 - Reactions in this layer may be very important

E

Resistance Model

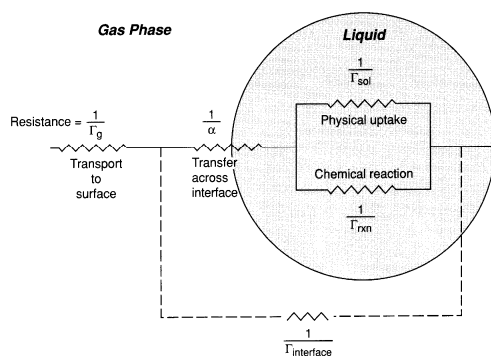


FIGURE 5.16 Schematic of resistance model for diffusion, uptake, and reaction of gases with liquids. Γ_g represents the transport of gases to the surface of the particle, α the mass accommodation coefficient for transfer across the interface, Γ_{sol} the solubilization and diffusion in the liquid phase, Γ_{rxn} the bulk liquid-phase reaction, and $\Gamma_{interface}$ the reaction of the gas at the interface.

From Finlayson-Pitts and Pitts

$$\frac{1}{\gamma_{net}} = \frac{1}{\Gamma_g} + \frac{1}{\alpha} + \frac{1}{\Gamma_{rxn} + \Gamma_{sol}}$$

- Look at “conductance” of each step, Γ
 - Rate of individual step normalized to rate of gas-surface collisions
 - Number of collisions per unit area second:

$$= \frac{N_g u_{avg}}{4} = N_g \sqrt{\frac{RT}{2\pi M}}$$
 - Note that g_{net} is the parameter actually measured in experiments
 - Will examine each conductance individually in next few slides

E

Resistance Model (cont.)

- Conductance of diffusion of gas to surface (Γ_g)
 - Start by assuming small Knudson # (ratio of mean free path to radius of particle = K_n)
 - Is this valid for troposphere?
 - 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: $\Gamma_g = \frac{8D_g}{u_{avg} d}$
 - Distortion of Boltzmann velocity distribution near surface due to rapid uptake

$$\frac{1}{\Gamma_g} = \frac{u_{avg} d}{8D_g} - \frac{1}{2}$$
- Free molecular regime ($d_{part} \ll$ mean free path), K_n large
 - Rate of gas molecules diffusing to surface = $\pi a^2 \alpha_c u_{avg} N_g$
 - α = probability of uptake at the surface, u_{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 $\lambda = \frac{1.33 + 0.71 / K_n}{1 + 1 / K_n}$

E

Resistance Model (cont.)

- Conductance of diffusion of gas to surface (Γ_g)
 - Start by assuming small Knudson # (ratio of mean free path to radius of particle = K_n)
 - $\sim 10^{10}$ collisions $s^{-1} \rightarrow 10^{-10}$ s between collisions @ 500 m $s^{-1} \rightarrow 50$ nm
 - Atmospheric particles in accumulation mode ~ 100 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: $\Gamma_g = \frac{8D_g}{u_{avg} d}$
 - Distortion of Boltzmann velocity distribution near surface due to rapid uptake

$$\frac{1}{\Gamma_g} = \frac{u_{avg} d}{8D_g} - \frac{1}{2}$$
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 - Rate of gas molecules diffusing to surface = $\pi a^2 \alpha_c u_{avg} N_g$
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 - 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

Resistance Model (cont.)

- Solubility and diffusion in liquid phase (Γ_{sol})

- Flux into particle center depends on concentration gradient
- Concentration gradient changes with time as uptake occurs – influence of re-evaporation back to gas phase

$$Rate = (c_{l,interface} - c_{l,bulk}) \sqrt{\frac{D_l}{\pi}}$$

- When $c_{l,bulk} = 0$

$$Rate = (c_{l,interface}) \sqrt{\frac{D_l}{\pi}}$$

- Note: rate is time dependent
- Assume dissolved species in thin layer of thickness $(D_l t)^{1/2}$ in equilibrium with gas phase

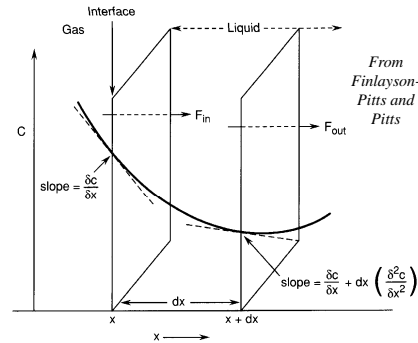


FIGURE 5.17 Schematic diagram for treatment of diffusion of a species in one dimension in a liquid.

$$Rate = N_g HRT \sqrt{\frac{D_l}{\pi}}$$

Normalize to gas-surface collision rate

$$\Gamma_{sol} = \frac{4HRT}{u_{avg}} \sqrt{\frac{D_l}{\pi}}$$

E

Resistance Model (cont.)

- Reaction in liquid phase (Γ_{rxn})

- Consider irreversible, first-order reaction, rate constant = k (s^{-1})
- Assume $c_{l,bulk} = 0$ at $t = 0$

$$Rate = c_{l,interface} \sqrt{D_l k}$$

- Normalized for gas-surface collisions

$$\Gamma_{rxn} = \frac{4HRT}{u_{avg}} \sqrt{D_l k}$$

- Define diffusio-reactive length

$$l = \sqrt{\frac{D_l}{k}}$$

- Diffuso-reactive parameter

$$q = a \sqrt{\frac{k}{D_l}} = \frac{a}{l} \quad a = \text{particle radius}$$

- To extrapolate lab measurements of uptake coefficient on thick films, γ_{meas} , to small droplets, γ_c :

$$\frac{1}{\gamma_c} = \frac{1}{\alpha} + \frac{1}{\gamma_{meas}} \cdot \frac{1}{(\coth q - 1/q)}$$

- For large a , use

$$\gamma_c \approx \gamma_{meas} (\coth q - 1/q)$$

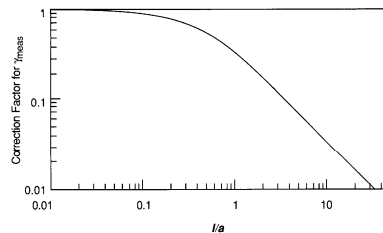


FIGURE 5.18 Correction factors for the measured uptake coefficient, γ_{meas} , as a function of the ratio of the diffusio-reactive length (l) to the droplet radius (a) (adapted from Hanson *et al.*, 1994).

From Finlayson-Pitts and Pitts

E

Final Equation & Limiting Cases

$$\frac{1}{\gamma_{net}} = \frac{1}{\Gamma_g} + \frac{1}{\alpha} + \frac{1}{\frac{4HRT}{u_{avg}} \left(\sqrt{\frac{D_l}{\pi t}} + \sqrt{D_l k} \right)}$$

- Fast gas transport, high solubility and/or fast reaction $\longrightarrow \frac{1}{\gamma_{net}} \approx \frac{1}{\alpha}$
- Fast gas transport, low solubility and fast reaction $\longrightarrow \frac{1}{\gamma_{net}} = \frac{1}{\gamma_{meas}} = \frac{1}{\alpha} + \frac{u_{avg}}{4HRT\sqrt{D_l k}}$
- High solubility (and/or short exposure times), no reaction $\longrightarrow \frac{1}{\gamma_{net}} = \frac{1}{\gamma_{meas}} = \frac{1}{\Gamma_g} + \frac{1}{\alpha}$
- Gas transport and mass accommodation fast, solubility low, and slow reaction $\longrightarrow \gamma_{net} = \gamma_{meas} = \frac{4HRT\sqrt{D_l}}{u_{avg}} \left(\sqrt{\frac{1}{\pi t}} + \sqrt{k} \right)$
- Low solubility and no reaction $\longrightarrow \frac{1}{\gamma_{net}} = \frac{1}{\gamma_{meas}} = \frac{1}{\Gamma_g} + \frac{1}{\alpha} + \frac{u_{avg}\sqrt{\pi t}}{4HRT\sqrt{D_l}}$
- There is evidence that some reactions occur at the interface
 - Requires additional resistance term or new approach (Hanson, 1997, 1998) E

Lab Techniques for Heterogeneous Reactions

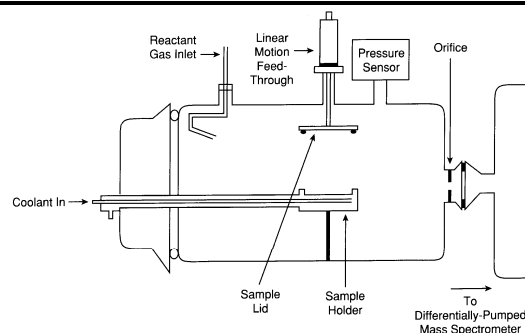
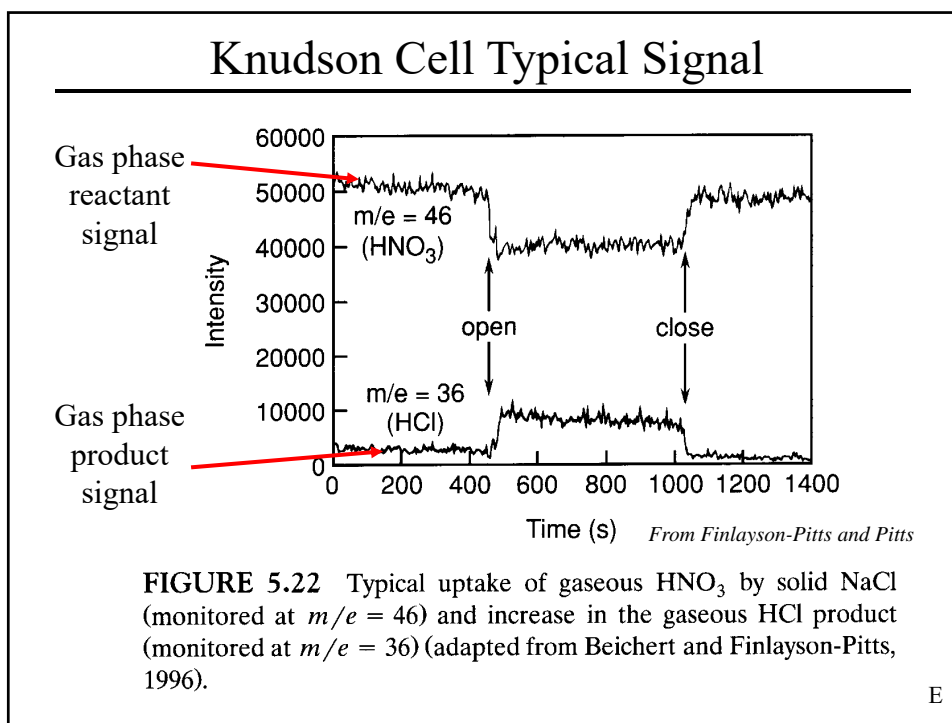


FIGURE 5.21 Schematic of a Knudsen cell.

From Finlayson-Pitts and Pitts

- Quick intro to Knudsen cell
 - Gases flowed through chamber
 - Sample lid is lifted to expose gas to temperature controlled surface
 - Monitor decrease in gas signal at exit of chamber due to uptake on surface
 - Can calculate uptake coefficient

E



E

Lab Techniques for Heterogeneous Reactions

- List of other techniques described in chapter
 - Flow tubes
 - Falling-droplet apparatus
 - Bubble apparatus
 - Aerosol chambers
 - Liquid jet apparatus
 - DRIFTS
 - Surface science techniques
 - XPS, UPS, TEM, ...
 - Other techniques
 - Cloud chambers, fluidized bed reactors, ...
- Boulder has a very active heterogeneous chemistry community
 - Reading up on these techniques will help with understanding seminars and journal articles!!

E

Compilations of Kinetic Data for Atmospheric Reactions

- NASA-JPL
 - Sander et al., Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies
 - <http://jpldataeval.jpl.nasa.gov/>
- IUPAC
 - Roger Atkinson et al., Atmos. Chem. Phys., 4, 1461–1738, 2004
 - www.atmos-chem-phys.org/acp/4/1461/; SRef-ID: 1680-7324/acp/2004-4-1461
- NIST
 - Amongst other NIST databases, Chemical Kinetics data
 - <http://www.nist.gov/srd/chemkin.htm>
- Notre Dame
 - Radiation Chemistry Data Center
 - Aqueous phase data
 - www.rcdc.nd.edu

F

Posted on the class website

- Excel spread sheet showing some calculations for these lectures, will post some of homework solutions as well (after homework is due of course)
- “Extra” slides
- Link to Centennial issue of Journal of Physical Chemistry
 - <http://pubs3.acs.org/acs/journals/toc.page?incoden=jpchax&indecade=0&involume=100&inissue=31>

Some parting shots...

- Terms symbols / selection rules from photochemistry
→ driven by conservation of angular momentum
- Want to know what O₃ smells like – photocopy something with the lid open
- Great number to memorize : 1 atm = 760 Torr = 2.5 x 10¹⁹ molecule cm⁻³ * 295 / Temp
- In chemistry (as in life), there are very few absolutes
 - We have already seen several examples of this:
 - Spin “forbidden” transitions
 - Dissociation “thresholds”
 - “Irreversible” reactions
 - These are all convenient ways of saying that something has an extremely low probability

Enthalpy Table

Table 3.1 Enthalpies of simple molecules

Species	$\Delta H_f(298\text{ K})$ (Kcal mole ⁻¹)	Species	$\Delta H_f(298\text{ K})$ (Kcal mole ⁻¹)	Species	$\Delta H_f(298\text{ K})$ (Kcal mole ⁻¹)
H	52.1	C ₂ H ₄	12.45	PNi ₂	-26.2 ± 2
H ₂	0.0	C ₂ H ₆	26.4	PO ₂	-64.3
O	59.57	CH ₄	17.9	CF ₂ Cl	-117.9
O ₂	0.0	CH ₃ CN	57.6 ± 2	CF ₃ Cl	-169.2
O ₃	34.1	CH ₃ CO	15.6	CF ₃ I	-112 ± 1
HO	9.3	CH ₃ CHO	-11 ± 3	CH ₂ Cl ₂	-68.1
H ₂ O	3 ± 1	CH ₃ CO ₂	-5.8	CH ₂ F ₂	-115.4
H ₂ O ₂	-57.81	CH ₃ CHOH	-39.7	CH ₂ Br ₂	-43.2
N	-32.60	CH ₃ CO ₂ H	-84.7 ± 2	CH ₂ BrCl	-107.2
N ₂	0.0	CH ₃ CO ₂ OH	10 ± 3	CH ₂ BrF	-17 ± 2
NH ₃	-85.3	CH ₃ CO ₂ CH ₃	-56.2	CH ₂ Br ₂	-124 ± 2
NH ₄ ⁺	-19.98	CH ₃ CO ₂ CH ₂ CH ₃	-6 ± 2	CH ₂ Br ₂	-120 ± 1
NO	21.97	CH ₃ CO ₂ CH ₂ CH ₂ CH ₃	-41 ± 5	CH ₂ Br ₂	-71 ± 2
NO ₂	17.2 ± 2	CH ₃ CO ₂ CH ₂ CH ₂ CH ₂ CH ₃	39.4	CH ₂ Br ₂	-213 ± 2
N ₂ O	19.61	n-C ₄ H ₁₀	4.8	CH ₂ Br ₂	-264 ± 2
N ₂ O ₄	19.8	n-C ₄ H ₈	22.6 ± 2	CH ₂ Br ₂	-127 ± 2
N ₂ O ₅	2.2	l-C ₄ H ₁₀	19 ± 2	CH ₂ Br ₂	-30
N ₂ O ₅	27 ± 2	l-C ₄ H ₈	24.8	CH ₂ Br ₂	-34.0
HNO	-19.8	CH ₃ CHO	-17.9	CH ₂ Br ₂	-26.8
HNO ₂	-19.8	CH ₃ CO ₂ H	-81.9	CH ₂ Br ₂	22 ± 2
HNO ₃	-32.3	CH ₃ CO ₂ NO ₂	-62 ± 5	CH ₂ Br ₂	17.6 ± 1
HO ₂ NO ₂	-11 ± 2	S	66.22	CH ₂ Br ₂	23 ± 2
C	170.9	HS	34 ± 1	CH ₂ Br ₂	27.99
CH ₄	142.0	H ₂ S	-4.9	CH ₂ Br ₂	15.7
CH ₂	35 ± 0.2	SO ₂	1.3	CH ₂ Br ₂	-8.67
CH ₃	-17.88	SO ₃	-70.96	CH ₂ Br ₂	-19 ± 2
CN	104 ± 3	H ₂ O	-94.6	CH ₂ Br ₂	30
HCN	32.3	H ₂ O ₂	-1 ± 3	CH ₂ Br ₂	19.5
CH ₃ NH ₂	-5.5	H ₂ SO ₄	-92 ± 2	CH ₂ Br ₂	31 ± 3
CO	-26.42	CS ₂	17.8	CH ₂ Br ₂	34 ± 3
CO ₂	-94.07	CS ₂ OH	67 ± 2	CH ₂ Br ₂	18 ± 2
CH ₃ OH	-10 ± 1	CH ₃ S	28.0	CH ₂ Br ₂	12.36
CH ₂ O	-26.0	CH ₃ SO ₂	31 ± 2	CH ₂ Br ₂	3.5
COOH	-53 ± 2	CH ₃ SO ₃	26.4	CH ₂ Br ₂	40 ± 2
HCOOH	-94.3	CH ₃ SO ₃ H	0.0	CH ₂ Br ₂	6 ± 2
CH ₃ O	4 ± 2	CH ₃ SC ₂ H ₅	-5.5	CH ₂ Br ₂	48 ± 2
CH ₃ O ₂	-8.2	CH ₃ SSC ₂ H ₅	-5.8	CH ₂ Br ₂	44 ± 2
CH ₃ OH	-62	OCS	-34	CH ₂ Br ₂	-2.6 ± 2
CH ₃ OOH	-31.3	F	19.8	CH ₂ Br ₂	-8.5
CH ₃ ONO	-15.86	HF	-65.34	CH ₂ Br ₂	-14.8
CH ₃ ONO ₂	-29.8	HO ₂ F	-23.4 ± 1	CH ₂ Br ₂	32 ± 2
CH ₃ NO ₂	-29.8	FO	59 ± 0.4	CH ₂ Br ₂	25.2
CH ₃ O ₂ NO ₂	-10.6 ± 2	F ₂ O	9 ± 1	CH ₂ Br ₂	24.52
C ₂ H ₂	-133 ± 2	PO ₂	34.35	CH ₂ Br ₂	6.3
C ₂ H ₄	-15.7	PO ₃	15 ± 1	CH ₂ Br ₂	3.5
C ₂ H ₆	-20.2	PNi ₂	-16 ± 2	CH ₂ Br ₂	14.92
C ₂ H ₄	72 ± 3	PNi ₂	-16 ± 2	CH ₂ Br ₂	14.92

Taken from Yung and DeMore, Photochemistry of Planetary Atmospheres

Entropy Table

Table 3.2. Entropies of simple molecules

Species	$S^{\circ}(298\text{ K})$ ($\text{cal}^{-1}\text{ mole}^{-1}\text{ deg}^{-1}$)	Species	$S^{\circ}(298\text{ K})$ ($\text{cal}^{-1}\text{ mole}^{-1}\text{ deg}^{-1}$)	Species	$S^{\circ}(298\text{ K})$ ($\text{cal}^{-1}\text{ mole}^{-1}\text{ deg}^{-1}$)	Species	$S^{\circ}(298\text{ K})$ ($\text{cal}^{-1}\text{ mole}^{-1}\text{ deg}^{-1}$)
H	27.4	C ₂ H ₄	52.5	NO ₂	62.3	CFC ₃	74.0
H ₂	31.2	C ₂ H ₆	38.0	FONO ₂	70.0	CF ₂ Cl	68.7
O	38.5	C ₂ H ₂	54.9	CF	50.9	CF ₂ Cl ₂	71.8
O ₂	49.0	CH ₂ N	58.0	CF ₂	57.5	CHCl	68.3
O ₃	57.0	CH ₃ N	58.8	CF ₃	62.1	CH ₂ Cl	70.1
HO	41.9	CH ₃ CO	57.8	CF ₄	62.4	CH ₃ Cl	67.2
HO ₂	54.4	CH ₃ CO	64.5	CHF ₃	62.0	COFCl	66.2
H ₂ O	45.1	CH ₃ CHO	63.2	CHF ₂	61.7	CH ₂ CHF	63.3
H ₂ O ₂	36.6	CH ₃ CHOH	65.3	CH ₂ F ₂	58.9	CH ₂ CF ₃	71.8
N	43.8	CH ₃ COOH	67.5	CH ₃ F	55.9	CH ₂ CF ₂	67.6
N ₂	45.8	CH ₃ COOH	67.5	CH ₃ OF	59.4	CH ₂ CF ₂	69.9
NH ₃	46.3	C ₂ H ₂ O ₂	75.0	COF ₂	61.9	CH ₂ CF ₂	68.6
NH ₄	46.0	CH ₃ COO ₂	74.1	CF ₂ O	61.9	CF ₂ CF ₃	81.6
NO	50.3	CH ₃ COOCH ₃	74.1	CF ₂ O ₂	68.7	CH ₂ CF ₂ CF ₃	68.7
NO ₂	57.3	C ₂ H ₆	62.1	CF ₃ OH	68.7	CH ₂ CF ₂ CF ₂ Cl	81.4
NO ₃	60.3	C ₂ H ₄	63.8	CF ₃ OOCH ₃	77.1	C ₂ Cl ₄	81.4
N ₂ O	52.6	n-C ₃ H ₇	68.5	CF ₃ OOH	77.1	CH ₂ Cl ₂	79.5
N ₂ O ₂	72.9	C ₂ H ₄	64.5	Cl	39.5	CH ₂ Cl ₃	80.6
N ₂ O ₅	82.8	C ₂ H ₄	72.8	Cl ₂	53.3	CH ₂ Cl ₃	76.4
HNO	52.7	C ₂ H ₄ CHO	70.5	HCl	44.6	CH ₂ Cl ₂ Cl	65.9
HONO	29.6	CH ₃ COOCH ₃	70.5	ClO	54.1	CH ₂ Cl ₂ Cl	65.9
HNO ₂	63.7	S	40.1	COO	64.0	CH ₂ ClCl	41.8
HO ₂ NO ₂	57.8	S ₂	54.5	OCIO	61.5	Br	41.8
CH	47.9	H ₂ S	49.2	CO ₂	73.0	HBr	47.4
CH ₂	46.3	H ₂ S	49.2	CO ₃	67.0	HOBr	59.2
CH ₃	46.4	SO ₂	53.0	CO ₃	64.0	HO	56.8
CH ₄	44.5	SO ₂	59.3	Cl ₂ O	72.2	BrNO	65.3
CN	48.4	HSO	61.3	Cl ₂ O ₂	56.5	BrONO	65.3
HCN	48.2	HSO ₂	69.1	HOCl	62.2	BrNO ₂	65.3
HCNO	55.0	HSO ₂	69.1	ClO	62.2	BrONO ₂	65.3
NCO	55.0	HSO ₂	69.1	ClONO	65.1	CH ₂ Br	79.1
CO	47.3	CS ₂	56.9	ClONO ₂	65.1	CHBr ₂	79.1
CO ₂	51.1	CS ₂ OH	57.6	ClONO ₂	65.1	CHBr ₃	80.0
HCO	53.7	CH ₃ S	61.0	ClONO ₂	65.1	CH ₂ Br ₂	70.1
CH ₂ O	52.3	CH ₃ SOO	61.0	ClONO ₂	65.1	CH ₂ Br ₂	70.1
COOH	61.0	CH ₃ SO ₂	61.0	Cl ₂	52.1	CH ₂ Br ₂	70.1
HCOOH	59.4	CH ₃ SH	68.4	CCl ₄	63.4	CH ₂ Br	58.7
CH ₂ OH	65.3	CH ₃ SH	68.4	CCl ₂	71.0	CH ₂ Br ₂	68.6
CH ₂ O ₂	65.3	CH ₃ SSCH ₃	80.5	C ₂ Cl ₄	81.4	CH ₂ CHBr	68.6
CH ₂ OH	58.8	CH ₃ SSCH ₃	80.5	C ₂ Cl ₆	81.4	CH ₂ CHBr	68.6
CH ₂ OOH	57.3	OCS	55.3	CHCl ₃	70.7	I	43.2
CH ₂ OOH	67.5	F	37.9	CHCl ₂	66.5	I ₂	62.3
CH ₃ ONO	68.0	F ₂	48.5	CHCl ₂	58.2	HI	49.3
CH ₃ NO ₂	65.7	HF	41.5	CH ₂ Cl	64.6	CHI ₃	60.6
CH ₃ NO ₂	71.1	HO ₂ F	54.4	CH ₂ Cl ₂	65.3	CHI ₃	60.6
CH ₃ NO ₂	78.1	FO	51.8	COCl ₂	63.3	IO ₂	58.8
CH ₃ O ₂ NO ₂	49.6	FO	59.1	COCl ₂	67.8	INO	67.6
C ₂ H ₂	48.0	FO ₂	61.9	CHCl ₂	63.3	INO ₂	70.3
C ₂ H ₄ OH	62.2	FONO	66.3	CH ₂ FCl	62.0		
C ₂ H ₆	56.3	FNO	59.3	CFCl ₂	71.5		

Taken from Yung and DeMore, Photochemistry of Planetary Atmospheres