

# Focus 18: Reaction Dynamics

## From Collisions to Electron Transfer

Physical Chemistry Course

Mindanao State University – Iligan Institute of Technology

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# Outline

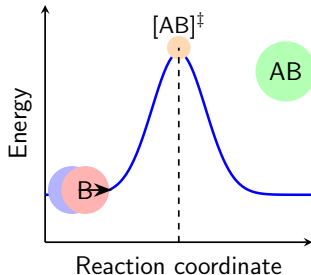
- 1 Introduction
- 2 Topic 18A: Collision Theory
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- 4 Topic 18C: Transition-State Theory
- 5 Topic 18D: Molecular Collision Dynamics
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# What is Reaction Dynamics?

**Reaction Dynamics** studies the **detailed molecular mechanisms** of chemical reactions

## Beyond traditional kinetics:

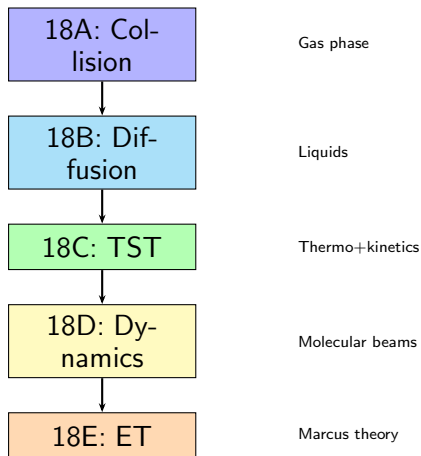
- How do molecules collide?
- What happens during collision?
- Where does energy go?
- What is the reaction path?
- How fast can reactions be?



## Time scales:

- Bond vibrations: fs ( $10^{-15}$  s)
- Reactions: ps-ns ( $10^{-12}$ - $10^{-9}$  s)
- Diffusion: ns- $\mu$ s

# The Journey Through Focus 18



# Learning Objectives

By the end of this topic, you should be able to:

- 1 Calculate collision frequencies and reaction cross-sections from molecular properties
- 2 Distinguish between diffusion-controlled and activation-controlled reactions
- 3 Apply transition-state theory to calculate rate constants from thermodynamic parameters
- 4 Interpret kinetic isotope effects and quantum tunneling in chemical reactions
- 5 Analyze molecular beam experiments and potential energy surfaces
- 6 Apply Marcus theory to electron transfer reactions and predict rates

# Prerequisites - Quick Reminder

**From earlier topics, you should know:**

## **Kinetic Theory:**

- Maxwell-Boltzmann distribution
- Mean speeds:  $\bar{v} = \sqrt{8kT/\pi m}$
- Collision frequency

## **Chemical Kinetics:**

- Rate laws and rate constants
- Arrhenius equation:  $k = Ae^{-E_a/RT}$
- Reaction mechanisms

## **Thermodynamics:**

- Gibbs energy:  $\Delta G = \Delta H - T\Delta S$
- Equilibrium constants
- Standard states

## **Statistical Mechanics:**

- Partition functions
- Boltzmann distribution
- Energy levels

# Topic 18A: Collision Theory

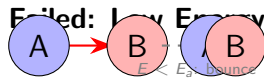
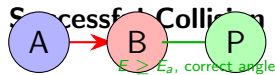
## The Simplest Model:

Reactions occur when molecules collide *if*:

- 1 They collide with sufficient frequency
- 2 They have enough kinetic energy ( $\geq E_a$ )
- 3 They have correct orientation (steric factor)

## Learning Objectives:

- Derive collision rate from kinetic theory
- Connect to Arrhenius equation
- Understand steric factors
- Apply to unimolecular reactions



# Kinetic Molecular Theory Background

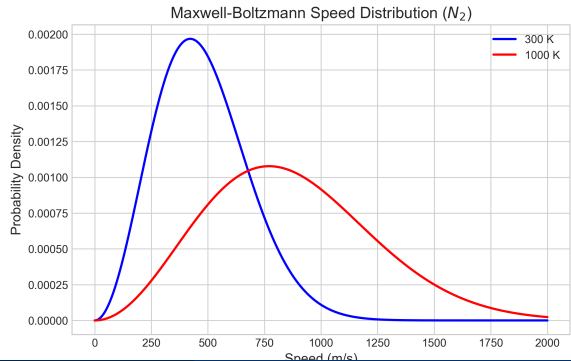
## Maxwell-Boltzmann Distribution of Speeds:

The fraction of molecules with speeds between  $v$  and  $v + dv$ :

$$f(v) = 4\pi \left( \frac{m}{2\pi k_B T} \right)^{3/2} v^2 e^{-mv^2/2k_B T}$$

### Key Quantities:

- Mean speed:  $\bar{v} = \left( \frac{8k_B T}{\pi m} \right)^{1/2}$
- Root-mean-square:  $v_{rms} = \left( \frac{3k_B T}{m} \right)^{1/2}$
- Most probable:  $v_p = \left( \frac{2k_B T}{m} \right)^{1/2}$





# Collision Cross-Section - Hard Sphere Model

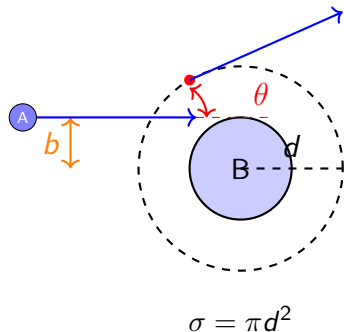
## Geometric Definition:

- Treat molecules as hard spheres
- Radii  $r_A$  and  $r_B$
- Collision occurs when centers approach within  $d = r_A + r_B$
- Target area:  $\sigma = \pi d^2$

$$\sigma = \pi d^2 = \pi(r_A + r_B)^2$$

## Impact Parameter $b$ :

- Perpendicular distance between trajectories



# Derivation of Collision Rate (Part 1)

**Setup:** Consider molecule A moving through gas of B molecules.

## Step 1: Collision Cylinder

- In time  $\Delta t$ , A sweeps volume  $V = \sigma v_{rel} \Delta t$
- Number of B molecules in cylinder:  $N_B = \mathcal{N}_B \cdot \sigma v_{rel} \Delta t$
- Collision rate for one A:  $\sigma v_{rel} \mathcal{N}_B$

## Step 2: Average Over Velocity Distribution

- Must average over Maxwell-Boltzmann distribution of  $v_{rel}$
- For two species:  $\bar{v}_{rel} = \left( \frac{8k_B T}{\pi \mu} \right)^{1/2}$
- Reduced mass:  $\mu = \frac{m_A m_B}{m_A + m_B}$

# Derivation of Collision Rate (Part 2)

## Step 3: Total Collision Density

Total collisions per unit volume per unit time between A and B molecules:

$$Z_{AB} = \sigma \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} \mathcal{N}_A \mathcal{N}_B$$

## Physical Interpretation:

- $\sigma$  = collision cross-section (geometric factor)
- $\bar{v}_{rel} = \left( \frac{8k_B T}{\pi \mu} \right)^{1/2}$  = mean relative speed
- $\mathcal{N}_A, \mathcal{N}_B$  = number densities (molecules per unit volume)
- $Z_{AB}$  has units: collisions  $\text{m}^{-3} \text{s}^{-1}$

# Special Case: Identical Molecules

For collisions between identical molecules  $A + A$ :

## Modified Formula:

- Must avoid double-counting (each collision counted twice)
- Factor of  $1/2$  correction

$$Z_{AA} = \frac{1}{2} \sigma \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} \mathcal{N}_A^2$$

## For identical molecules:

- $\mu = m_A/2$  (reduced mass)
- $\bar{v}_{rel} = \sqrt{2}\bar{v}$  where  $\bar{v}$  is mean speed of one molecule
- Collision frequency is  $\sqrt{2}$  times what you'd naively expect

# Worked Example: Collision Rate for N<sub>2</sub> (Part 1)

**Problem:** Calculate  $Z_{N_2-N_2}$  for nitrogen gas at 298 K and 1 bar. Given:  $\sigma \approx 0.43 \text{ nm}^2 = 4.3 \times 10^{-19} \text{ m}^2$

## Step 1: Number density from ideal gas law

$$\mathcal{N} = \frac{P}{k_B T} = \frac{10^5 \text{ Pa}}{(1.381 \times 10^{-23} \text{ J K}^{-1})(298 \text{ K})} = 2.43 \times 10^{25} \text{ m}^{-3}$$

## Step 2: Mean relative speed

Mass of N<sub>2</sub>:  $m = 28 \text{ amu} = 4.65 \times 10^{-26} \text{ kg}$

Reduced mass:  $\mu = m/2 = 2.32 \times 10^{-26} \text{ kg}$

$$\bar{v}_{rel} = \sqrt{\frac{8 \times 1.381 \times 10^{-23} \times 298}{\pi \times 2.32 \times 10^{-26}}} = 670 \text{ m s}^{-1}$$

# Worked Example: Collision Rate for N<sub>2</sub> (Part 2)

## Step 3: Calculate collision density

Using the formula:  $Z_{N_2-N_2} = \frac{1}{2} \sigma \bar{v}_{rel} \mathcal{N}^2$

$$Z_{N_2-N_2} = \frac{1}{2} \times 4.3 \times 10^{-19} \times 670 \times (2.43 \times 10^{25})^2$$

$$Z_{N_2-N_2} \approx 5 \times 10^{34} \text{ collisions m}^{-3} \text{ s}^{-1}$$

**Interpretation:** This enormous collision rate shows why most gas reactions require activation energy - if every collision reacted, all reactions would be instantaneous!

# Energy Requirements: Not All Collisions React

## The Problem:

- $Z_{AB} \sim 10^{34} \text{ collisions m}^{-3} \text{ s}^{-1}$  is enormous!
- If every collision led to reaction, all reactions would be over in nanoseconds
- Reality: Most reactions have measurable rates (seconds to hours)

## The Solution: Activation Energy

- Only collisions with kinetic energy  $\varepsilon \geq E_a$  along line of centers react
- Fraction of molecules with energy  $> E_a$  from Boltzmann distribution:

$$f(E > E_a) = \int_{E_a}^{\infty} f(E) dE = e^{-E_a/RT}$$

**The exponential factor dramatically reduces the reactive collision rate**

# Maxwell-Boltzmann Energy Distribution

The fraction of molecules with translational energy between  $\varepsilon$  and  $\varepsilon + d\varepsilon$ :

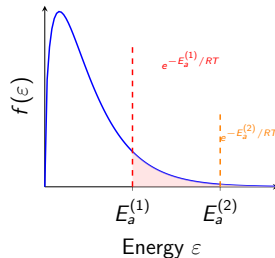
$$f(\varepsilon) = \frac{2\pi}{(\pi k_B T)^{3/2}} \varepsilon^{1/2} e^{-\varepsilon/k_B T}$$

## Key Features:

- Maximum at  $\varepsilon = k_B T/2$
- Mean energy:  $\langle \varepsilon \rangle = \frac{3}{2} k_B T$
- High-energy tail decays exponentially
- Fraction with  $\varepsilon > E_a$ :

$$\int_{E_a}^{\infty} f(\varepsilon) d\varepsilon = e^{-E_a/k_B T}$$

**Higher  $E_a \Rightarrow$  Smaller reactive fraction  $\Rightarrow$  Slower reaction**





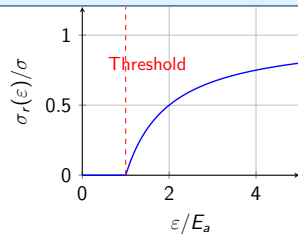
# Reactive Cross-Section: Energy Dependence

The collision cross-section depends on collision energy  $\varepsilon$ :

$$\sigma_r(\varepsilon) = \begin{cases} 0 & \varepsilon < E_a \\ \sigma \left(1 - \frac{E_a}{\varepsilon}\right) & \varepsilon \geq E_a \end{cases}$$

## Physical Interpretation:

- Below  $E_a$ : No reaction possible ( $\sigma_r = 0$ )
- At  $E_a$ : Reaction just becomes possible ( $\sigma_r = 0$ )
- Well above  $E_a$ : Approaches geometric  $\sigma$
- The factor  $(1 - E_a/\varepsilon)$  represents the "likelihood" of having enough energy in the right direction



The linear rise from threshold is a simplified model; real reactions may have different energy dependencies.

# Derivation of the Collision Theory Rate Constant

**Starting Point:** Reactive collision rate per unit volume

$$\text{Rate} = \int_0^{\infty} \sigma_r(\varepsilon) v_{\text{rel}}(\varepsilon) \mathcal{N}_A \mathcal{N}_B f(\varepsilon) d\varepsilon$$

**Key Steps:**

- 1 Insert  $\sigma_r(\varepsilon) = \sigma(1 - E_a/\varepsilon)$  for  $\varepsilon \geq E_a$
- 2 Use  $v_{\text{rel}} = \sqrt{2\varepsilon/\mu}$  (relation between speed and energy)
- 3 Integrate over Boltzmann distribution  $f(\varepsilon) \propto e^{-\varepsilon/k_B T}$

**Result after integration:**

$$k_r = N_A \sigma \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} e^{-E_a/RT}$$

**In terms of molar concentrations  $[A]$ ,  $[B]$ :**

# Connection to Arrhenius Equation

## Collision Theory Result:

$$k_r = N_A \sigma \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} e^{-E_a/RT}$$

## Arrhenius Empirical Form:

$$k = A e^{-E_a/RT}$$

## Identification of Pre-exponential Factor:

$$A_{theory} = N_A \sigma \left( \frac{8k_B T}{\pi \mu} \right)^{1/2}$$

- Typical values:  $A \sim 10^{10} - 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  for bimolecular gas reactions
- Temperature dependence:  $A \propto T^{1/2}$  (weak, often ignored)
- For Arrhenius plots ( $\ln k$  vs  $1/T$ ): slope =  $-E_a/R$ , intercept =  $\ln A$

# Numerical Calculation of A-factor (Part 1)

**Example:** Calculate  $A$  for  $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$  at 600 K

**Given:**

- $\sigma = 0.30 \text{ nm}^2 = 3.0 \times 10^{-19} \text{ m}^2$
- $m_{\text{H}_2} = 2.016 \text{ amu} = 3.35 \times 10^{-27} \text{ kg}$
- $m_{\text{I}_2} = 253.8 \text{ amu} = 4.22 \times 10^{-25} \text{ kg}$

**Step 1: Reduced mass**

$$\mu = \frac{m_{\text{H}_2} \cdot m_{\text{I}_2}}{m_{\text{H}_2} + m_{\text{I}_2}} = \frac{3.35 \times 10^{-27} \times 4.22 \times 10^{-25}}{3.35 \times 10^{-27} + 4.22 \times 10^{-25}} \approx 3.32 \times 10^{-27} \text{ kg}$$

(Since  $m_{\text{I}_2} \gg m_{\text{H}_2}$ , the denominator  $\approx 4.22 \times 10^{-25} \text{ kg}$ )

**Step 2: Mean relative speed**

$$\bar{v}_{\text{rel}} = \sqrt{\frac{8 \times 1.381 \times 10^{-23} \times 600}{3.14159 \times 3.32 \times 10^{-27}}} = 2520 \text{ m s}^{-1}$$

# Numerical Calculation of A-factor (Part 2)

## Step 3: Calculate A-factor

Using the formula:  $A = N_A \sigma \bar{v}_{rel}$

$$A = 6.022 \times 10^{23} \times 3.0 \times 10^{-19} \times 2520$$

$$A = 4.6 \times 10^8 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Converting to  $\text{dm}^3$  (multiply by  $10^3$ ):

$$A = 4.6 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

**Interpretation:** This is in the typical range  $10^{10} - 10^{11}$  for bimolecular gas reactions, consistent with collision theory predictions!

# The Steric Factor Problem

**Experiment vs Theory:** Does  $A_{\text{exp}}$  match  $A_{\text{theory}}$ ?

Reaction	$A_{\text{exp}}$ ( $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )	$A_{\text{theory}}$ ( $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )	$P = A_{\text{exp}}/A_{\text{theory}}$
$2\text{NOCl} \rightarrow 2\text{NO} + \text{Cl}_2$	$9.4 \times 10^9$	$5.9 \times 10^{10}$	0.16
$2\text{ClO} \rightarrow \text{Cl}_2 + \text{O}_2$	$6.3 \times 10^7$	$2.5 \times 10^{10}$	0.0025
$\text{H}_2 + \text{C}_2\text{H}_4 \rightarrow \text{C}_2\text{H}_6$	$1.2 \times 10^6$	$7.3 \times 10^{10}$	$1.7 \times 10^{-5}$
$\text{K} + \text{Br}_2 \rightarrow \text{KBr} + \text{Br}$	$1.0 \times 10^{12}$	$2.1 \times 10^{11}$	4.8

## Observations:

- **Usually**  $P < 1$ : Not all orientations are reactive (steric hindrance)
- **Complex molecules:** Smaller  $P$  (need precise alignment)
- **Sometimes**  $P > 1$ : Long-range forces extend reactive range (Harpoon mechanism)

# The Steric Factor: Modified Collision Theory

## Modified Collision Theory:

$$k_r = P \cdot N_A \sigma \left( \frac{8k_B T}{\pi \mu} \right)^{1/2} e^{-E_a/RT}$$

## What is P?

- **Steric factor:** Fraction of collisions with proper orientation
- Effective reactive cross-section:  $\sigma_r = P\sigma$
- Depends on molecular geometry and reaction mechanism
- Accounts for orientation requirements

## Examples:

- **Atoms:**  $P \approx 1$  (spherically symmetric)
- **Linear molecules:**  $P \sim 0.1 - 1$  (need end-on approach)
- **Complex molecules:**  $P \sim 10^{-6} - 10^{-2}$  (specific reactive site)

# The Steric Factor: Reactive Geometry

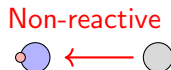
## Orientation Matters:

Only certain collision geometries lead to reaction:

- **Reactive:** Attack at reactive site
- **Non-reactive:** Wrong orientation or glancing collision

The steric factor  $P$  quantifies the fraction of properly oriented collisions.

## Reactive Geometry:



Red dot = reactive site



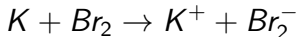
# Case Study: The Harpoon Mechanism ( $P > 1$ )

**Reaction:**  $\text{K} + \text{Br}_2 \rightarrow \text{KBr} + \text{Br}$  ( $P \approx 4.8!$ )

**Why does  $P > 1$ ?** Long-range electron transfer!

**Mechanism:**

- 1 K has low ionization energy ( $I_K = 4.34 \text{ eV}$ )
- 2  $\text{Br}_2$  has high electron affinity ( $E_{ea} = 2.55 \text{ eV}$ )
- 3 At critical distance  $R^*$ , electron transfer becomes favorable:



- 4 Coulombic attraction pulls ions together (like throwing a harpoon!)
- 5  $R^* \gg d$  (geometric), so  $\sigma_{\text{reactive}} > \sigma_{\text{geometric}}$

**Estimate of  $R^*$ :**

$$I_K - E_{ea} = \frac{e^2}{4\pi\epsilon_0 R^*}$$

$$R^* \approx 0.8 \text{ nm} \quad (\text{vs } d \approx 0.2 \text{ nm})$$

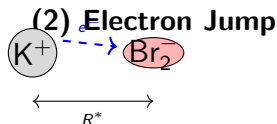
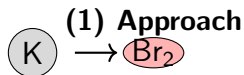
# The Harpoon Mechanism: Visualization

## Three-Step Process:

**(1) Approach:** K and Br<sub>2</sub> approach as neutrals

**(2) Electron Jump:** At  $R^*$ , electron transfers to Br<sub>2</sub>

**(3) Harpoon:** Coulombic attraction pulls ions together



**Reactive cross-section much larger than geometric!**

# Temperature Dependence of Reaction Rates

From collision theory:  $k = AT^{1/2}e^{-E_a/RT}$

**Taking logarithm:**

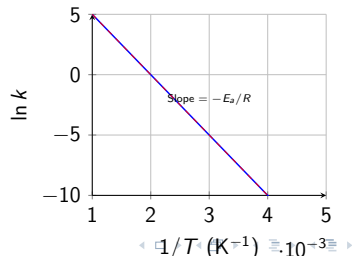
$$\ln k = \ln A + \frac{1}{2} \ln T - \frac{E_a}{RT}$$

**Arrhenius plot** ( $\ln k$  vs  $1/T$ ) assumes  $A$  is constant:

$$\ln k = \ln A - \frac{E_a}{RT}$$

**In practice:**

- The  $T^{1/2}$  factor is weak
- Over typical experimental ranges (50-100 K), the exponential dominates
- Arrhenius plots are nearly linear
- Slope gives  $E_a/R$



# Unimolecular Reactions: The Lindemann Mechanism

**Problem:** How can  $A \rightarrow P$  be explained by collision theory?

**Lindemann-Hinshelwood Mechanism (1922):**

- ① **Activation:**  $A + M \xrightarrow{k_a} A^* + M$
- ② **Deactivation:**  $A^* + M \xrightarrow{k'_a} A + M$
- ③ **Reaction:**  $A^* \xrightarrow{k_b} P$

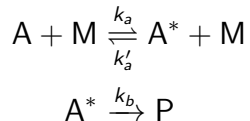
**Key Idea:**

- $A^*$  = high-energy form of A
- M = any collision partner
- Competition: deactivation vs. reaction

**Two limiting regimes: high pressure and low pressure**

# Lindemann Mechanism: Deriving the Rate Law

**Mechanism:**



**Rate of product formation:**  $\frac{d[\text{P}]}{dt} = k_b[\text{A}^*]$

**Steady-state approximation for  $\text{A}^*$ :**

$$\frac{d[\text{A}^*]}{dt} = k_a[\text{A}][\text{M}] - k'_a[\text{A}^*][\text{M}] - k_b[\text{A}^*] = 0$$

**Solve for  $[\text{A}^*]$ :**

$$[\text{A}^*] = \frac{k_a[\text{A}][\text{M}]}{k'_a[\text{M}] + k_b}$$

**Overall rate:**

$$\frac{d[\text{P}]}{dt} = \frac{k_a k_b [\text{A}][\text{M}]}{k'_a[\text{M}] + k_b}$$

# Lindemann Mechanism: High Pressure Limit

## General Rate Law:

$$\frac{d[P]}{dt} = \frac{k_a k_b [M]}{k'_a [M] + k_b} [A] = k_{uni} [A]$$

**High Pressure Limit:**  $k'_a [M] \gg k_b$  (fast deactivation)

$$k_{uni} \approx \frac{k_a k_b}{k'_a} = K_{eq} k_b$$

## Characteristics:

- First-order in  $[A]$
- Independent of pressure
- Rate-determining step:  $A^* \rightarrow P$
- Equilibrium established between  $A$  and  $A^*$
- Collisions are frequent enough to maintain equilibrium

# Lindemann Mechanism: Low Pressure Limit

## General Rate Law:

$$k_{uni} = \frac{k_a k_b [M]}{k'_a [M] + k_b}$$

**Low Pressure Limit:**  $k'_a [M] \ll k_b$  (slow activation)

$$k_{uni} \approx k_a [M]$$

## Characteristics:

- Pseudo-second-order (depends on  $[M]$ )
- Proportional to pressure
- Rate-determining step:  $A + M \rightarrow A^*$
- Every  $A^*$  formed reacts immediately ( $k_b$  is fast)
- Collisions are rare, activation is limiting

# Lindemann Mechanism: Graphical Representation

Rearrange to Lindemann form:

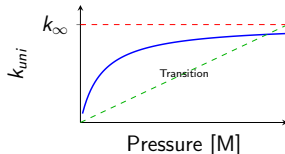
$$\frac{1}{k_{uni}} = \frac{1}{k_{\infty}} + \frac{k'_a}{k_a k_b [M]} = \frac{1}{k_{\infty}} + \frac{1}{k_a [M]}$$

where  $k_{\infty} = \frac{k_a k_b}{k'_a}$  is the high-pressure limit.

**Lindemann Plot:**  $1/k_{uni}$  vs  $1/[M]$

- Linear relationship
- Intercept =  $1/k_{\infty}$
- Slope =  $1/k_a$

**Experimental verification:** Many unimolecular reactions show exactly this behavior!





# RRK Theory: Energy Distribution in Molecules (Part 1)

## Rice-Ramsperger-Kassel (RRK) Theory:

Refines Lindemann by considering *how* energy is distributed within  $A^*$ .

### Key Assumptions:

- Molecule has  $s$  equivalent oscillators (vibrational modes)
- Energy  $E$  is distributed randomly among these modes (statistical)
- Reaction occurs when energy  $E_0$  accumulates in the reactive bond
- Energy flows freely between modes (ergodic hypothesis)

**Key Question:** What is the probability that the reactive bond has enough energy to break?

# RRK Theory: Energy-Dependent Rate Constant (Part 2)

Probability that reactive bond has energy  $\geq E_0$ :

$$P(E_0|E) = \left(1 - \frac{E_0}{E}\right)^{s-1} \quad \text{for } E \geq E_0$$

Energy-dependent rate constant:

$$k_b(E) = k_b^0 \left(1 - \frac{E_0}{E}\right)^{s-1}$$

**Physical Interpretation:**

- Higher  $s$  (more oscillators): Energy more diluted, slower reaction
- Larger molecules: Smaller  $k_b(E)$  at given  $E$
- Explains why large molecules fall off more rapidly in Lindemann plots

# Summary: Collision Theory

## Achievements:

- ✓ Derived rate constant from first principles (kinetic theory)
- ✓ Explained Arrhenius form:  $k = Ae^{-E_a/RT}$
- ✓ Calculated  $A$ -factors ( $\sim 10^{10} - 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ )
- ✓ Lindemann mechanism explains unimolecular reactions
- ✓ Qualitative understanding of steric effects

## Limitations:

- ✗ Steric factor  $P$  is empirical (must be measured)
- ✗ Hard-sphere model too simplistic
- ✗ Doesn't explain molecular details of reaction pathway
- ✗ No information about transition state structure

**Next: Transition-State Theory provides molecular-level insight**

# Practice Problems

**Problem 1:** Calculate the collision frequency  $Z_{O_2-O_2}$  for oxygen at 300 K and 1 atm. Use  $\sigma = 0.40 \text{ nm}^2$ .

**Problem 2:** For the reaction  $H_2 + I_2 \rightarrow 2HI$ ,  $E_a = 171 \text{ kJ mol}^{-1}$ . What fraction of collisions at 600 K have sufficient energy to react?

**Problem 3:** A reaction has  $A_{exp} = 2.5 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$  and  $A_{theory} = 5.0 \times 10^{11} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ . Calculate the steric factor  $P$ . What does this tell you about the reaction?

**Problem 4:** For a Lindemann mechanism with  $k_\infty = 1.0 \times 10^5 \text{ s}^{-1}$  and  $k_a = 1.0 \times 10^{-10} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ , at what pressure (in torr) does  $k_{uni} = k_\infty/2$ ? ( $T = 300 \text{ K}$ )

*Answers: (1)  $\sim 10^{35} \text{ m}^{-3} \text{ s}^{-1}$ ; (2)  $e^{-171000/(8.314 \times 600)} \approx 1.7 \times 10^{-15}$ ; (3)  $P = 0.005$ , highly orientation-dependent; (4)  $\sim 0.04 \text{ torr}$*

# Topic 18A: Key Takeaways

## Essential Equations:

- **Collision rate:**  $Z_{AB} = \sigma \sqrt{\frac{8k_B T}{\pi \mu}} \mathcal{N}_A \mathcal{N}_B$
- **Rate constant:**  $k_r = P \cdot N_A \sigma \bar{v}_{rel} e^{-E_a/RT}$
- **A-factor (theory):**  $A = N_A \sigma \bar{v}_{rel}$
- **Steric factor:**  $P = \frac{A_{exp}}{A_{theory}}$  (typically 0.001-1)

## When to use Collision Theory:

Gas-phase reactions

Order-of-magnitude estimates

Understanding steric effects & harpoon mechanisms

**NOT** for precise predictions (use TST instead)

**NOT** for solution reactions (diffusion matters)

**Key Insight:** Collisions are necessary but not sufficient - need energy + orientation!

# Interactive Learning: Topic 18A

## Explore Collision Theory Interactively!

### Interactive Jupyter Notebook Features:

- **Collision Calculator:** Adjust  $T$ ,  $P$ ,  $\sigma$  with sliders
- **Animated Collisions:** Watch molecules collide!
- **Energy-Dependent  $\sigma(\varepsilon)$ :** Interactive plots
- **Harpoon Mechanism Explorer:** See long-range ET
- **RRK Model:** Explore unimolecular decay
- **Practice Problems:** Code-based exercises

**Notebook:** 01\_Collision\_Theory.ipynb

Scan to Open:



Or navigate to:

Reaction\_Dynamics\_Interactive/

# Topic 18B: Diffusion-Controlled Reactions

## Moving from Gas to Liquid Phase

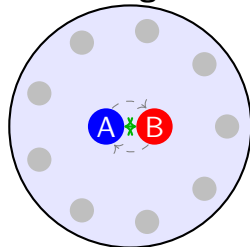
### Gas Phase:

- Molecules fly freely
- Single collisions
- Low density ( $\sim 10^{25} \text{ m}^{-3}$ )
- Long mean free path ( $\sim 100 \text{ nm}$ )
- Collision frequency  $\sim 10^{10} \text{ s}^{-1}$

### Liquid Phase:

- Molecules are crowded
- **Cage Effect** - trapped by solvent
- High density ( $\sim 10^{28} \text{ m}^{-3}$ )

### Solvent Cage Effect:



Trapped by solvent  
Multiple collisions

# The Concept of Encounter Pairs

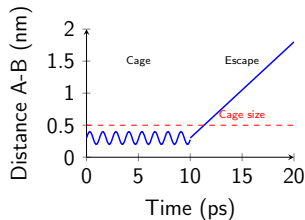
## Encounter Pair

When two reactants A and B meet in solution, they are temporarily trapped in a solvent cage and undergo multiple collisions before separating.

### Key Differences from Gas Phase:

- **Gas:** One collision per encounter
- **Liquid:**  $\sim 10^2 - 10^3$  collisions per encounter
- Collision frequency within cage:  $\sim 10^{13} \text{ s}^{-1}$
- Cage lifetime:  $\sim 10^{-11} \text{ s}$
- Effective "single" encounter

### Encounter Dynamics:





# Two Limiting Regimes

## Diffusion-Controlled

### Fast Reaction

- $k_a \gg k_{-d}$  (reaction faster than separation)
- Every encounter leads to reaction
- Rate limited by **transport** (diffusion)
- Low activation energy ( $E_a \approx E_{\text{viscosity}}$ )
- Examples: Radical recombination,  $\text{H}^+ + \text{OH}^-$

$$k \approx k_d \sim 10^{10} \text{ M}^{-1}\text{s}^{-1}$$

## Activation-Controlled

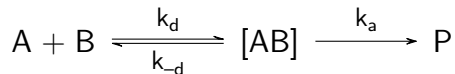
### Slow Reaction

- $k_a \ll k_{-d}$  (separation faster than reaction)
- Many encounters before reaction
- Rate limited by **energy barrier**
- High activation energy
- Behaves like gas-phase kinetics

$$k \propto e^{-E_a/RT}$$

# Mechanism: The Two-Step Model (Part 1)

## Reaction Scheme:



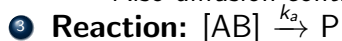
## Elementary Steps:



- $k_d$ : Diffusion rate constant
- Formation of encounter pair
- Limited by diffusion coefficient  $D$



- $k_{-d}$ : Separation rate constant
- Breakup of encounter pair
- Also diffusion-controlled



# Mechanism: Energy Diagram

## Free Energy Profile:

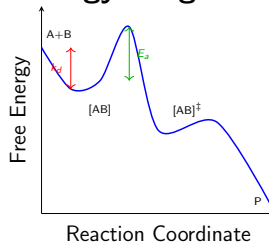
- $A + B \rightarrow [AB]$ : Diffusion barrier (small)

$AB \rightarrow [AB]^\ddagger$ : Activation barrier

$AB^\ddagger \rightarrow P$ : Reaction

The rate-limiting step depends on relative barrier heights!

## Energy Diagram:



# Steady-State Treatment (Part 1)

**Apply steady-state approximation to encounter pair [AB]:**

$$\frac{d[\text{AB}]}{dt} = k_d[\text{A}][\text{B}] - k_{-d}[\text{AB}] - k_a[\text{AB}] = 0$$

**Solve for [AB]:**

$$[\text{AB}] = \frac{k_d[\text{A}][\text{B}]}{k_{-d} + k_a}$$

**Rate of product formation:**

$$\text{Rate} = k_a[\text{AB}] = \frac{k_a k_d}{k_{-d} + k_a} [\text{A}][\text{B}]$$

# Steady-State Treatment (Part 2)

**Overall rate constant:**

$$k_{eff} = \frac{k_a k_d}{k_{-d} + k_a}$$

**Rearrange to resistance form:**

$$\frac{1}{k_{eff}} = \frac{1}{k_d} + \frac{1}{K k_a}$$

where  $K = k_d/k_{-d}$  is the equilibrium constant for encounter pair formation.

**Two resistances in series: diffusion and activation**

**Interpretation:** Like electrical resistances, the slower step dominates!

# Limiting Cases from the General Expression

## General Result:

$$k_{eff} = \frac{k_a k_d}{k_{-d} + k_a}$$

### Case 1: Diffusion Control

$k_a \gg k_{-d}$  (fast reaction)

$$k_{eff} = \frac{k_a k_d}{k_a} = k_d$$

- Rate independent of  $k_a$
- Maximum possible rate
- $k_{eff} \sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$
- Weak temperature dependence
- $E_a \approx E_{viscosity} \approx 10 - 20 \text{ kJ/mol}$

### Case 2: Activation Control

$k_a \ll k_{-d}$  (slow reaction)

$$k_{eff} = \frac{k_d}{k_{-d}} k_a = K k_a$$

- Rate proportional to  $k_a$
- Arrhenius behavior
- Strong temperature dependence
- $E_a$  = activation barrier
- Same as gas-phase kinetics

# Fick's First Law of Diffusion

## Foundation of Diffusion Theory:

### Fick's First Law (steady-state):

$$J = -D \frac{\partial c}{\partial x}$$

### Physical Interpretation:

- $J$ : Flux ( $\text{mol m}^{-2} \text{s}^{-1}$ ) - flow rate per unit area
- $D$ : Diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ )
- $\frac{\partial c}{\partial x}$ : Concentration gradient
- Negative sign: Flow from high to low concentration

**Typical Values:**  $D \sim 10^{-9} \text{ m}^2 \text{s}^{-1}$  in water (small molecules)

# Fick's Second Law of Diffusion

**Fick's Second Law** (time-dependent):

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}$$

**Physical Interpretation:**

- Describes how concentration evolves in time
- Parabolic partial differential equation (diffusion/heat equation)
- In 3D:  $\frac{\partial c}{\partial t} = D \nabla^2 c$
- Solution gives  $c(x, t)$  - concentration distribution

**These laws form the mathematical foundation for Smoluchowski theory**



# Stokes-Einstein Relation (Part 1)

## Connection between diffusion and molecular properties:

For a spherical particle of radius  $r$  moving through liquid of viscosity  $\eta$ :

$$D = \frac{k_B T}{6\pi\eta r}$$

## Physical Basis:

- Stokes drag force:  $F = 6\pi\eta r v$
- Einstein relation:  $D = \mu k_B T$  where  $\mu = 1/6\pi\eta r$
- Connects microscopic (diffusion) to macroscopic (viscosity)

## Key Dependencies:

- $D \propto T$  (faster at higher temperature)
- $D \propto 1/\eta$  (slower in viscous media)

# Stokes-Einstein Relation (Part 2)

## Typical Values at 25°C:

Species	$r$ (nm)	$D$ ( $10^{-9}$ m <sup>2</sup> /s)
H <sub>2</sub> O	0.14	2.3
Glycerol	0.3	1.0
Hemoglobin	3.1	0.069

## Viscosity of Water:

- 25°C:  $\eta = 0.89$  mPa·s
- 0°C:  $\eta = 1.79$  mPa·s
- Strong T-dependence!

## Observation:

- Larger molecules: smaller  $D$
- Size effect is dramatic (factor of 30!)

**Stokes-Einstein is remarkably accurate for molecules in solution**

# Smoluchowski Theory: Deriving $k_d$

**Goal:** Calculate the rate constant for diffusion-controlled encounter.

## Model Assumptions:

- 1 Molecule A is stationary at origin
- 2 B molecules diffuse toward A with diffusion coefficient  $D = D_A + D_B$
- 3 Reaction occurs when B reaches distance  $R^* = r_A + r_B$  (contact)
- 4 Steady-state concentration profile of B around A
- 5 B molecules are consumed at  $r = R^*$  (perfect sink)

## Boundary Conditions:

- At  $r = R^*$ :  $[B] = 0$  (instantaneous reaction)
- As  $r \rightarrow \infty$ :  $[B] = [B]_{bulk}$  (uniform far away)

**Solve Fick's law in spherical coordinates with these boundary conditions**

# Smoluchowski Derivation

**Fick's First Law in spherical coordinates (steady-state):**

$$J(r) = -D \frac{d[B]}{dr}$$

**Continuity equation (spherical):**

$$\frac{1}{r^2} \frac{d}{dr} (r^2 J) = 0$$

This gives:  $r^2 J = \text{constant}$

**Solution with boundary conditions:**

$$[B](r) = [B]_{bulk} \left( 1 - \frac{R^*}{r} \right)$$

**Flux at contact surface:**

$$J(R^*) = -D \left. \frac{d[B]}{dr} \right|_{r=R^*} = D \frac{[B]_{bulk}}{R^*}$$

# Smoluchowski Result for $k_d$

**From flux calculation:**

$$\text{Rate} = 4\pi R^* D[A][B]$$

**Compare with rate law:**  $\text{Rate} = k_d[A][B]$

$$k_d = 4\pi R^* D N_A$$

where  $N_A$  converts to molar units.

**Using Stokes-Einstein:**  $D = \frac{k_B T}{6\pi\eta r}$

For similar-sized molecules:  $R^* \approx 2r$  and  $D \approx \frac{k_B T}{6\pi\eta r}$

$$k_d \approx \frac{8RT}{3\eta}$$

**Remarkable Result:**

# Numerical Estimate of Diffusion Limit

**For water at 25°C:**

**Given:**

- $T = 298 \text{ K}$
- $\eta = 8.9 \times 10^{-4} \text{ Pa}\cdot\text{s}$
- $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$

**Calculation:**

$$k_d = \frac{8RT}{3\eta} = \frac{8 \times 8.314 \times 298}{3 \times 8.9 \times 10^{-4}}$$

$$k_d = \frac{19,830}{0.00267} = 7.4 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

$$k_d \approx 7 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1} = 7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

# Temperature Dependence of Diffusion-Controlled Reactions

**From Smoluchowski:**  $k_d = \frac{8RT}{3\eta}$

**Temperature dependence comes from:**

- 1 Direct  $T$  factor:  $k_d \propto T$
- 2 Viscosity:  $\eta(T)$  decreases with increasing  $T$

**Viscosity Temperature Dependence:**

$$\eta(T) = \eta_0 e^{E_\eta/RT}$$

Typical values:  $E_\eta \approx 10 - 20$  kJ/mol for liquids

**Combined effect:**

$$k_d \propto \frac{T}{\eta(T)} \propto T e^{-E_\eta/RT}$$

Taking logarithm and differentiating:

$$\frac{d \ln k_d}{d(1/T)} = -\frac{E_\eta}{R} + \frac{RT}{T^2} = -\frac{E_\eta - RT}{R}$$

# Experimental Verification

## Examples of Diffusion-Controlled Reactions:

Reaction	$k$ ( $\text{M}^{-1} \text{s}^{-1}$ )	$E_a$ (kJ/mol)
$\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O}$	$1.4 \times 10^{11}$	13
$\text{H}_3\text{O}^+ + \text{OH}^-$	$1.3 \times 10^{11}$	12
$\bullet \text{CH}_3 + \bullet \text{CH}_3$	$\sim 10^{10}$	8
$\text{Fe}^{2+} + \text{Fe}^{3+}$ (exchange)	$4 \times 10^3$	42
Sucrose hydrolysis	$5 \times 10^{-5}$	107

## Observations:

- $\text{H}^+/\text{OH}^-$  faster than predicted: Proton transfer via hydrogen bonding (Grotthuss mechanism)
- Radical recombination: Near diffusion limit
- $\text{Fe}^{2+}/\text{Fe}^{3+}$ : Electron transfer has barrier (Chapter 18E)

• Sucrose: High  $E_a$  clearly activation controlled



# Viscosity Effects on Reaction Rates

**Prediction:** For diffusion-controlled reactions,  $k \propto 1/\eta$

**Test:** Vary solvent viscosity (add glycerol, change solvent, vary T)

**Plot:**  $k$  vs  $1/\eta$

- **Linear:** Diffusion-controlled
- **Flat:** Activation-controlled
- **Curved:** Intermediate or mixed control

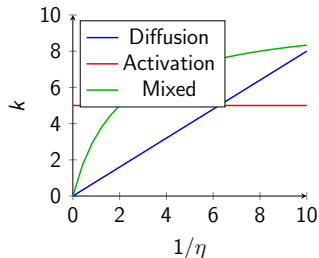
## Kramers Theory:

More sophisticated treatment including friction:

$$k \propto \frac{1}{\eta} \text{ (high } \eta \text{)}$$

$$k \propto \eta \text{ (low } \eta \text{)}$$

## Rate vs Viscosity:



Diffusion-controlled reactions slow down in viscous media

# The Material Balance Equation

**General equation for species J undergoing transport and reaction:**

$$\frac{\partial[J]}{\partial t} = D \frac{\partial^2[J]}{\partial x^2} - v \frac{\partial[J]}{\partial x} - k_r[J]$$

**Three contributions:**

- ① **Diffusion:**  $D \frac{\partial^2[J]}{\partial x^2}$ 
  - Spreading due to concentration gradients
  - Fick's second law
  - Always acts to smooth out concentration differences
- ② **Convection:**  $-v \frac{\partial[J]}{\partial x}$ 
  - Bulk flow of fluid
  - $v$  = flow velocity
  - Important in stirred reactors, flowing systems
- ③ **Reaction:**  $-k_r[J]$

# Coupled Diffusion and Reaction

**Simplified 1D case (no convection):**

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - kc$$

**Steady-state solution ( $\partial c / \partial t = 0$ ):**

$$D \frac{d^2 c}{dx^2} = kc$$

**General solution:**

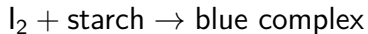
$$c(x) = Ae^{-x/\lambda} + Be^{x/\lambda}$$

where the **reaction-diffusion length** is:

$$\lambda = \sqrt{\frac{D}{k}}$$

# Example: Iodine Diffusion in Starch Solution

**Experiment:**  $\text{I}_2$  vapor diffuses into aqueous starch solution where it reacts:



## Observation:

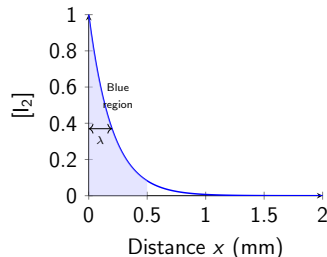
- Sharp blue front moves down column
- Front position:  $x_f \propto \sqrt{t}$
- Width of colored region  $\sim \lambda$

## Analysis:

With  $D = 2 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  and  $k = 0.1 \text{ s}^{-1}$ :

$$\lambda = \sqrt{\frac{D}{k}} = \sqrt{\frac{2 \times 10^{-9}}{0.1}} = 1.4 \times 10^{-4} \text{ m} = 0.14 \text{ mm}$$

## Concentration Profile:



# The Damköhler Number

**Dimensionless parameter comparing reaction and diffusion rates:**

$$Da = \frac{\text{reaction rate}}{\text{diffusion rate}} = \frac{kL^2}{D}$$

where  $L$  is characteristic length scale.

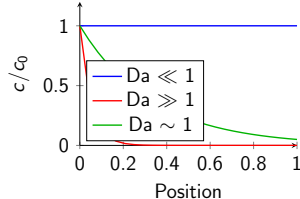
## Physical Interpretation:

**$Da \ll 1$ :** Diffusion-limited

- Reaction is slow
- Concentration uniform
- Well-mixed approximation valid
- Rate  $\propto k$

**$Da \gg 1$ :** Mass-transfer limited

## Concentration Profiles:



# Worked Example 1: Calculate $k_d$ for Specific Molecules

**Problem:** Calculate the diffusion-controlled rate constant for the reaction between two identical molecules with  $r = 0.5$  nm in water at 25°C.

**Given:**

- $r_A = r_B = 0.5$  nm =  $5 \times 10^{-10}$  m
- $T = 298$  K
- $\eta_{\text{water}} = 8.9 \times 10^{-4}$  Pa·s
- $k_B = 1.381 \times 10^{-23}$  J K<sup>-1</sup>
- $N_A = 6.022 \times 10^{23}$  mol<sup>-1</sup>

**Solution:**

1. **Contact distance:**  $R^* = r_A + r_B = 1.0$  nm =  $1.0 \times 10^{-9}$  m

2. **Diffusion coefficient for each molecule:**

$$D = \frac{k_B T}{6\pi\eta r} = \frac{1.381 \times 10^{-23} \times 298}{6\pi \times 8.9 \times 10^{-4} \times 5 \times 10^{-10}} = 4.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$$

# Worked Example 1 (continued)

## 3. Combined diffusion coefficient:

$$D_{rel} = D_A + D_B = 2D = 9.8 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$$

## 4. Smoluchowski rate constant:

$$k_d = 4\pi R^* D_{rel} N_A$$

$$k_d = 4\pi \times 1.0 \times 10^{-9} \times 9.8 \times 10^{-10} \times 6.022 \times 10^{23}$$

$$k_d = 7.4 \times 10^6 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Convert to  $\text{M}^{-1} \text{ s}^{-1}$ :

$$k_d = 7.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

**Answer:**  $k_d \approx 7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  - close to universal diffusion limit!

## Worked Example 2: Determine Reaction Control Regime

**Problem:** A reaction has  $k_{obs} = 5 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$  in water at 25°C. The activation energy is  $E_a = 25 \text{ kJ/mol}$ . Is this reaction diffusion-controlled or activation-controlled?

**Solution:**

1. Compare to diffusion limit:

$$k_d \approx 7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$
$$\frac{k_{obs}}{k_d} = \frac{5 \times 10^8}{7 \times 10^9} \approx 0.07 = 7\%$$

The observed rate is only 7% of diffusion limit.

2. Check activation energy:

- Diffusion-controlled:  $E_a \sim 10 - 20 \text{ kJ/mol}$
- Observed:  $E_a = 25 \text{ kJ/mol}$  (slightly higher)

**Conclusion: Mixed control with significant activation barrier.**



# Summary: Topic 18B

## Key Concepts:

- ① **Cage Effect:** Multiple collisions within solvent cage
  - Changes encounter dynamics vs gas phase
  - Effective single "encounter" event
- ② **Two-Step Mechanism:** Diffusion + Activation
  - $k_{\text{eff}}^{-1} = k_d^{-1} + (Kk_a)^{-1}$
  - Two resistances in series
- ③ **Smoluchowski Theory:**  $k_d = 4\pi R^* DN_A \approx \frac{8RT}{3\eta}$ 
  - Diffusion limit:  $\sim 10^{10} \text{ M}^{-1} \text{ s}^{-1}$  in water
  - Depends on  $T/\eta$ , nearly size-independent
- ④ **Fick's Laws:** Foundation of diffusion theory
  - First law: Flux proportional to gradient
  - Second law: Time evolution of concentration
- ⑤ **Material Balance:** Couples diffusion, convection, and reaction
  - Reaction-diffusion length:  $\lambda = \sqrt{D/k}$

# Practice Problems

**Problem 1:** Calculate the diffusion coefficient of a spherical protein with radius 3.0 nm in water at 25°C ( $\eta = 0.89 \text{ mPa}\cdot\text{s}$ ).

**Problem 2:** For a reaction with  $k_{obs} = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  at 25°C, estimate what fraction of encounters lead to reaction. Assume  $k_d = 7 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ .

**Problem 3:** A reaction rate triples when temperature increases from 15°C to 35°C. The viscosity decreases by a factor of 1.8 over this range. Is the reaction diffusion-controlled or activation-controlled? Estimate  $E_a$ .

**Problem 4:** Calculate the reaction-diffusion length  $\lambda$  for a first-order reaction with  $k = 1.0 \text{ s}^{-1}$  and  $D = 10^{-9} \text{ m}^2 \text{ s}^{-1}$ .

*Answers: (1)  $D \approx 7.3 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ ; (2)  $\sim 29\%$ ; (3) Activation-controlled,  $E_a \approx 35 \text{ kJ/mol}$ ; (4)  $\lambda \approx 30 \text{ }\mu\text{m}$*

# Applications and Modern Extensions

## Biological Systems:

- Enzyme-substrate encounter ( $k_{cat}/K_M$  often near diffusion limit)
- Signal transduction cascades
- Protein-protein interactions
- Morphogen gradient formation

## Chemical Engineering:

- Reactor design (stirring requirements)
- Catalysis in porous media
- Gas-liquid reactions
- Fast reactions in flow systems

## Modern Developments:

- Single-molecule tracking (fluorescence microscopy)
- Microfluidics and confinement effects
- Anomalous diffusion in crowded environments

# Topic 18B: Key Takeaways

## Essential Equations:

- **Diffusion-limited rate:**  $k_d = 4\pi RDN_A$  (Smoluchowski)
- **Overall rate:**  $\frac{1}{k} = \frac{1}{k_d} + \frac{1}{k_a}$  (encounter + activation)
- **Cage effect:**  $\eta = \frac{k_{\text{cage}}}{k_{\text{cage}} + k_{\text{sep}}}$  (geminate pairs)
- **Viscosity dependence:**  $k \propto \frac{T}{\eta}$  (Stokes-Einstein)

## When diffusion controls the rate:

Solution reactions (always important!)

Fast reactions ( $E_a < 20$  kJ/mol)

Radical recombinations (barrierless)

**NOT** for gas-phase (use collision theory)

**NOT** when  $k_a \ll k_d$  (activation-limited)

**Key Insight:** In solution, molecules must find each other before they can react!

# Interactive Learning: Topic 18B

## Explore Diffusion-Controlled Reactions Interactively!

### Interactive Jupyter Notebook Features:

- **Cage Effect Simulator:** Visualize solvent cage dynamics
- **Smoluchowski Calculator:** Compute diffusion-controlled rates
- **Encounter Pair Dynamics:** Animated trajectories
- **Viscosity Effects:** Interactive rate vs  $\eta$  plots
- **Activation vs Diffusion:** Regime comparison
- **Real Examples:** Radical recombination, enzyme kinetics

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# Topic 18C: Overview

## Transition-State Theory (TST) / Activated Complex Theory (ACT)

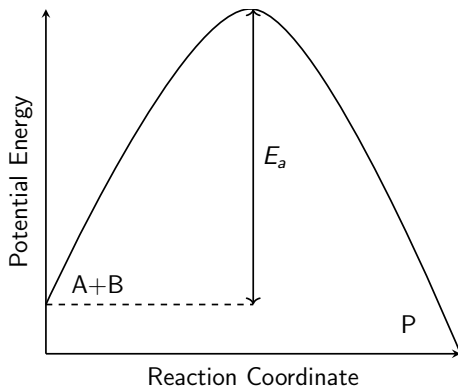
- The most sophisticated "classical" theory of reaction rates.
- Developed by Eyring, Evans, and Polanyi (1930s).
- **Key Concept:** Focus on the species at the top of the energy barrier.

### Goals:

- Calculate rates from thermodynamic properties ( $\Delta G^\ddagger$ ,  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$ ).
- Explain kinetic salt effects.
- Explain kinetic isotope effects.

# The Reaction Coordinate

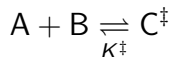
- **Reactants (A+B)**
- **Transition State ( $\ddagger$ ):** Point of maximum energy.
- **Activated Complex ( $C^\ddagger$ ):** The molecular species at the transition state.
- **Products (P)**



# Fundamental Assumptions of TST

## Three Key Assumptions:

- ① **Quasi-Equilibrium:** The activated complex  $C^\ddagger$  is in equilibrium with reactants.



- ② **Factorization:** The reaction coordinate motion can be separated from other degrees of freedom.
- ③ **One-Way Crossing:** Once formed,  $C^\ddagger$  always proceeds to products (transmission coefficient  $\kappa \approx 1$ ).

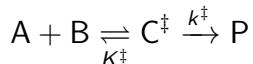
**Validity:** These assumptions work well when:

- Barrier is high compared to  $k_B T$
- No significant recrossing of barrier
- No quantum tunneling (for classical TST)



# The Big Idea

**Fundamental Approach:** The activated complex  $C^\ddagger$  is in **quasi-equilibrium** with the reactants.



The rate of reaction is:

$$\text{Rate} = k^\ddagger [C^\ddagger]$$

- $[C^\ddagger]$ : Concentration of activated complex (from equilibrium).
- $k^\ddagger$ : Frequency of crossing the barrier.

## Strategy:

- 1 Calculate  $[C^\ddagger]$  from equilibrium thermodynamics
- 2 Calculate  $k^\ddagger$  from the reaction coordinate vibration frequency
- 3 Combine to get the rate constant

# Statistical Mechanics Foundation

## Partition Functions:

For a molecular species  $i$ , the molecular partition function is:

$$q_i = \sum_j g_j e^{-\epsilon_j/k_B T}$$

The equilibrium constant relates to partition functions:

$$K^\ddagger = \frac{[C^\ddagger]}{[A][B]} = \frac{q_{C^\ddagger}}{q_A q_B} \frac{N_A}{V} e^{-E_0/RT}$$

where  $E_0$  is the zero-point energy difference.

**Key Insight:** The partition function includes contributions from:

- Translation:  $q_{\text{trans}} \propto VT^{3/2}m^{3/2}$
- Rotation:  $q_{\text{rot}} \propto T^{3/2}$  (nonlinear)
- Vibration:  $q_{\text{vib}} = \prod_i \frac{1}{1 - e^{-h\nu_i/k_B T}}$

# Factorization of Reaction Coordinate

**Critical Step:** Separate the reaction coordinate from  $q_{C^\ddagger}$

The transition state has one "loose" vibration along the reaction coordinate with frequency  $\nu^\ddagger$ .

For this mode:

$$q_{RC} = \frac{1}{1 - e^{-h\nu^\ddagger/k_B T}} \approx \frac{k_B T}{h\nu^\ddagger} \quad (\text{classical limit})$$

Therefore:

$$q_{C^\ddagger} = \left( \frac{k_B T}{h\nu^\ddagger} \right) \bar{q}_{C^\ddagger}$$

where  $\bar{q}_{C^\ddagger}$  is the partition function with the reaction coordinate removed.

# Rate of Decay

## How fast does $\mathbf{C}^\ddagger$ fall apart into products?

- The motion along the reaction coordinate is a "loose vibration".
- Frequency of this vibration =  $\nu^\ddagger$ .
- Rate constant for crossing:  $k^\ddagger = \kappa \nu^\ddagger$ .
- $\kappa$ : Transmission coefficient (usually  $\approx 1$ ).

## Physical Picture:

- At the transition state, the molecule "vibrates" along the reaction path
- Each vibration has a chance to proceed to products
- For classical barrier crossing: every forward crossing leads to products ( $\kappa = 1$ )
- For tunneling or recrossing:  $\kappa \neq 1$

# Derivation of Eyring Equation - Step 1

## Concentration of activated complex:

From equilibrium:

$$[C^\ddagger] = K^\ddagger [A][B]$$

Substituting partition functions:

$$[C^\ddagger] = \frac{q_{C^\ddagger}}{q_A q_B} \frac{N_A}{V} e^{-E_0/RT} [A][B]$$

Factor out reaction coordinate:

$$[C^\ddagger] = \frac{k_B T}{h \nu^\ddagger} \frac{\bar{q}_{C^\ddagger}}{q_A q_B} \frac{N_A}{V} e^{-E_0/RT} [A][B]$$

# Derivation of Eyring Equation - Step 2

Rate of reaction:

$$\text{Rate} = \kappa \nu^\ddagger [\text{C}^\ddagger]$$

Substitute expression for  $[\text{C}^\ddagger]$ :

$$\text{Rate} = \kappa \nu^\ddagger \times \frac{k_B T}{h \nu^\ddagger} \frac{\bar{q}_{\text{C}^\ddagger}}{q_A q_B} \frac{N_A}{V} e^{-E_0/RT} [\text{A}][\text{B}]$$

The frequency  $\nu^\ddagger$  cancels!

$$\text{Rate} = \kappa \frac{k_B T}{h} \frac{\bar{q}_{\text{C}^\ddagger}}{q_A q_B} \frac{N_A}{V} e^{-E_0/RT} [\text{A}][\text{B}]$$

# The Eyring Equation - Final Form

## Rate constant:

$$k_r = \kappa \frac{k_B T}{h} \bar{K}^\ddagger$$

Or in thermodynamic terms:

$$k_r = \kappa \frac{k_B T}{h} e^{-\Delta^\ddagger G^\circ / RT}$$

where  $\Delta^\ddagger G^\circ$  is the standard Gibbs energy of activation.

## Key Features:

- Universal pre-factor:  $\frac{k_B T}{h} \approx 6.2 \times 10^{12} \text{ s}^{-1}$  at 298 K
- Temperature dependence:  $T e^{-\Delta^\ddagger H^\circ / RT}$  (not just exponential!)
- Connection to thermodynamics through  $\Delta^\ddagger G^\circ$

# Eyring Equation - Interpretation

$$k_r = \frac{k_B T}{h} e^{-\Delta^\ddagger G^\circ / RT}$$

- $\frac{k_B T}{h}$ : **Universal Frequency Factor.**
  - At 300 K,  $\approx 6 \times 10^{12} \text{ s}^{-1}$ .
  - Sets the fundamental timescale of chemical reactions.
  - Origin: Typical vibrational frequency at TS.
- $\Delta^\ddagger G^\circ$ : **Gibbs Energy of Activation.**
  - Determines the barrier height.
  - Includes both enthalpy and entropy contributions.
  - Can be measured experimentally.

**Maximum Rate:** If  $\Delta^\ddagger G^\circ = 0$ , then  $k_r \approx 6 \times 10^{12} \text{ s}^{-1}$  - the **diffusion-limited rate**.



# Common Mistakes with TST

## Watch Out For:

### 1 Confusing $E_a$ and $\Delta^\ddagger H^\circ$

- They differ by  $RT$  (solution) or  $2RT$  (gas, bimolecular)
- Relationship:  $E_a = \Delta^\ddagger H^\circ + nRT$  where  $n = 1$  or  $2$

### 2 Forgetting transmission coefficient $\kappa$

- Usually  $\approx 1$  but not always!
- Tunneling:  $\kappa > 1$  (quantum effects)
- Recrossing:  $\kappa < 1$  (barrier recrossing)

### 3 Using $\ln k$ instead of $\ln(k/T)$ for Eyring plot

- Arrhenius: plot  $\ln k$  vs  $1/T \rightarrow \text{slope} = -E_a/R$
- Eyring: plot  $\ln(k/T)$  vs  $1/T \rightarrow \text{slope} = -\Delta^\ddagger H^\circ/R$

# Thermodynamic Formulation

Expand  $\Delta^\ddagger G^\circ = \Delta^\ddagger H^\circ - T\Delta^\ddagger S^\circ$ :

$$k_r = \frac{k_B T}{h} e^{\Delta^\ddagger S^\circ / R} e^{-\Delta^\ddagger H^\circ / RT}$$

**Comparison with Arrhenius ( $k = Ae^{-E_a/RT}$ ):**

- **Enthalpy** ( $\Delta^\ddagger H^\circ$ )  $\leftrightarrow$  Activation Energy ( $E_a$ ).
- **Entropy** ( $\Delta^\ddagger S^\circ$ )  $\leftrightarrow$  Pre-exponential Factor ( $A$ ).

**Key Advantage:** TST separates:

- Energetic barrier ( $\Delta^\ddagger H^\circ$ )
- Structural/entropic effects ( $\Delta^\ddagger S^\circ$ )

# Relating TST to Arrhenius Parameters

## Enthalpy vs. Activation Energy:

Starting from definitions:

$$E_a = RT^2 \frac{d \ln k}{dT}$$

For Eyring equation  $k = \frac{k_B T}{h} e^{-\Delta^\ddagger G^\circ / RT}$ :

- **Solution:**  $E_a = \Delta^\ddagger H^\circ + RT$
- **Gas Phase (bimolecular):**  $E_a = \Delta^\ddagger H^\circ + 2RT$
- **Gas Phase (unimolecular):**  $E_a = \Delta^\ddagger H^\circ + RT$

## Entropy vs. A-Factor:

$$A = \frac{ek_B T}{h} e^{\Delta^\ddagger S^\circ / R}$$

where  $e = 2.718$  (Euler's number).

# Eyring Plot

## Linearization for experimental analysis:

Take logarithm of  $k = \frac{k_B T}{h} e^{\Delta^\ddagger S^\circ / R} e^{-\Delta^\ddagger H^\circ / RT}$ :

$$\ln \left( \frac{k}{T} \right) = \ln \left( \frac{k_B}{h} \right) + \frac{\Delta^\ddagger S^\circ}{R} - \frac{\Delta^\ddagger H^\circ}{RT}$$

**Plot:**  $\ln(k/T)$  vs.  $1/T$  gives straight line

- **Slope:**  $-\Delta^\ddagger H^\circ / R$
- **Intercept:**  $\ln(k_B/h) + \Delta^\ddagger S^\circ / R$

**Advantage over Arrhenius:** Direct determination of  $\Delta^\ddagger H^\circ$  and  $\Delta^\ddagger S^\circ$ .

# Activation Entropy ( $\Delta^\ddagger S^\circ$ ) - Part 1

## Physical Meaning:

$$\Delta^\ddagger S^\circ = S_{C^\ddagger}^\circ - S_A^\circ - S_B^\circ$$

## Negative $\Delta^\ddagger S^\circ$ (Associative):

Transition state is **more ordered** than reactants.

- Example: Dimerization ( $A + A \rightarrow A_2^\ddagger$ )
- Two molecules coming together lose translational freedom
- Typically:  $\Delta^\ddagger S^\circ \approx -100$  to  $-150$  J/(mol·K)

# Activation Entropy ( $\Delta^\ddagger S^\circ$ ) - Part 2

## Positive $\Delta^\ddagger S^\circ$ (Dissociative):

Transition state is **more disordered** than reactants.

- Example: Bond breaking in unimolecular decomposition
- Increased vibrational freedom
- Typically:  $\Delta^\ddagger S^\circ > 0$

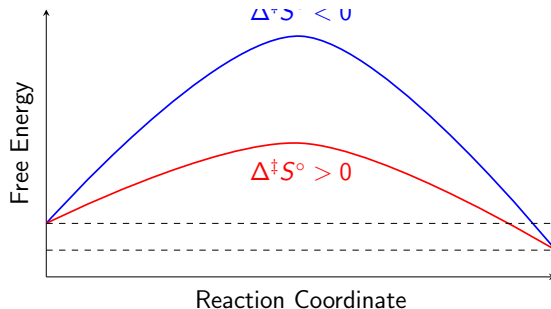
## Near-Zero $\Delta^\ddagger S^\circ$ :

- Similar structure to reactants
- Minor reorganization at transition state

**The sign of  $\Delta^\ddagger S^\circ$  reveals the geometry of the transition state**

# Free Energy Diagrams

Effect of  $\Delta^\ddagger S^\circ$  on reaction profile:



At higher  $T$ : Negative  $\Delta^\ddagger S^\circ$  becomes more unfavorable ( $-T\Delta^\ddagger S^\circ$  increases).

# Hammond Postulate

## Relating TS structure to thermodynamics:

**Hammond Postulate:** The structure of the transition state resembles the structure of the nearest stable species (reactant, product, or intermediate).

### Implications:

#### Endergonic Reaction:

- TS resembles products
- "Late" transition state
- Product-like structure

#### Exergonic Reaction:

- TS resembles reactants
- "Early" transition state
- Reactant-like structure

**Application:** Helps predict effects of substituents on reaction rates.



# The Kinetic Salt Effect

For reactions between ions in solution:  $A^{z_A} + B^{z_B} \rightarrow C^\ddagger \rightarrow P$

Debye-Hückel Theory predicts:

$$\log(k_r) = \log(k_r^\circ) + 2A z_A z_B \sqrt{I}$$

- $I$ : Ionic strength of solution  $= \frac{1}{2} \sum_i c_i z_i^2$ .
- $z_A, z_B$ : Charges of reactants.
- $A$ : Constant  $= 0.509 \text{ M}^{-1/2}$  for water at  $25^\circ\text{C}$ .
- $k_r^\circ$ : Rate constant at zero ionic strength.

**Physical Origin:**

- Ionic atmosphere screens charge interactions
- Affects activation energy for charged reactants
- Charge on TS:  $z_\ddagger = z_A + z_B$

# Kinetic Salt Effect - Predictions (Part 1)

## Effect of Ionic Strength on Rate:

**Like charges ( $z_A z_B > 0$ ):** Rate **increases** with ionic strength.

- Example:  $\text{S}_2\text{O}_8^{2-} + \text{I}^-$
- $z_A z_B = (-2)(-1) = +2 > 0$ : rate increases
- Ionic atmosphere reduces repulsion

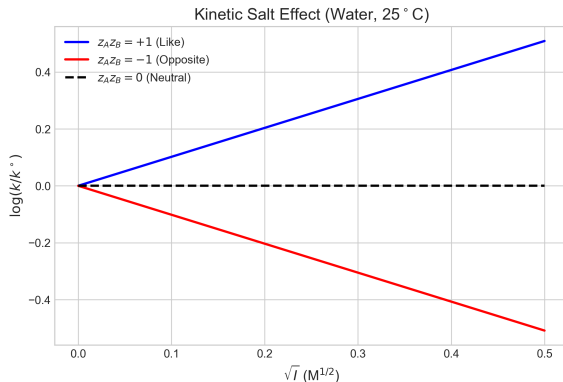
**Opposite charges ( $z_A z_B < 0$ ):** Rate **decreases** with ionic strength.

- Example:  $[\text{Co}(\text{NH}_3)_5\text{Br}]^{2+} + \text{OH}^-$
- $z_A z_B = (+2)(-1) = -2 < 0$ : rate decreases
- Ionic atmosphere screens attraction

# Kinetic Salt Effect - Predictions (Part 2)

## Summary:

- $z_A z_B > 0$ : rate increases with  $I$
- $z_A z_B < 0$ : rate decreases with  $I$
- $z_A z_B = 0$ : no primary salt effect



Interactive calculator: See notebook at end

**Slope of plot gives information about charges in the transition state**

# Kinetic Isotope Effects (KIE) - Part 1

**What happens if we replace H with D (or  $^{12}\text{C}$  with  $^{13}\text{C}$ )?**

**Origin:** Zero-point energy (ZPE) difference.

$$\text{ZPE} = \frac{1}{2}h\nu = \frac{1}{2}h\frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

**Physical Effect:**

- Heavier isotope has lower ZPE (smaller  $\nu$ )
- C-D bond is stronger than C-H bond by  $\sim 5$  kJ/mol
- Requires more energy to break
- Reaction becomes slower

$$\frac{k_H}{k_D} \approx 7 \text{ (at } 25^\circ\text{C)}$$

# Kinetic Isotope Effects (KIE) - Part 2

## Types of KIE:

**Primary KIE:** Bond to H/D breaks in rate-determining step

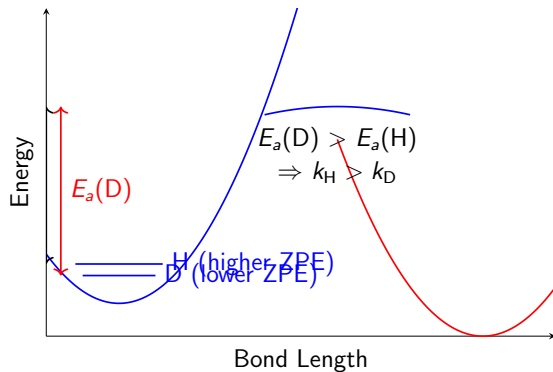
- $k_H/k_D = 2-10$  (typical range)
- Large effect indicates bond breaking at TS
- Example: C-H bond cleavage in radical abstraction

**Secondary KIE:** Bond to H/D does not break

- $k_H/k_D = 1.1-1.5$  (small effect)
- Due to hybridization changes at TS
- Example: Adjacent to reaction center

**KIE is a powerful tool for identifying mechanisms and rate-determining steps**

# Zero-Point Energy and KIE



Difference in  $E_a$ :  $\Delta E_a \approx \frac{1}{2}h(\nu_H - \nu_D) \approx 5 \text{ kJ/mol}$

# Quantum Tunneling (Part 1)

**Classical TST assumes:** Over-the-barrier crossing.

**Quantum Reality:** Particles can pass *through* the barrier!

**When is tunneling important?**

- Significant for light particles ( $\text{H}^+$ ,  $\text{e}^-$ )
- More important at low temperatures
- Pronounced for narrow, high barriers

**Experimental Evidence:**

- $k_{\text{H}}/k_{\text{D}} \gg 7$  (e.g., 10-100, much larger than classical KIE)
- Curved Arrhenius plots (concave upward)
- Unusual temperature dependence (rate less sensitive to  $T$ )

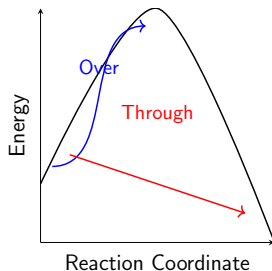
# Quantum Tunneling (Part 2)

## Two Pathways:

**Over:** Classical barrier crossing

**Through:** Quantum tunneling

Tunneling bypasses the activation barrier!



## Bell's Correction:

$$\kappa = \frac{Q_{\text{tunnel}}}{Q_{\text{classical}}} = \frac{u/2}{\sin(u/2)}, \quad u = \frac{h\nu_{\text{barrier}}}{k_B T}$$



# Linear Free Energy Relationships

## Brønsted Catalysis Law:

For acid-catalyzed reactions:

$$\log k = \log G + \alpha \log K_a$$

where  $K_a$  is the acidity constant.

- $\alpha$ : Brønsted coefficient ( $0 \leq \alpha \leq 1$ )
- Measures how much charge is transferred in TS
- $\alpha \approx 0$ : TS resembles reactants (early TS)
- $\alpha \approx 1$ : TS resembles products (late TS)

## Related Relationships:

- **Hammett equation:** For substituted benzene derivatives
- **Marcus relationship:** For electron transfer
- **Polanyi relationship:**  $E_a = E_0 + \alpha \Delta H_{\text{rxn}}$

# Worked Example 1: Calculating Rate Constant

**Problem:** A reaction has  $\Delta^\ddagger H^\circ = 85 \text{ kJ/mol}$  and  $\Delta^\ddagger S^\circ = -45 \text{ J/(mol}\cdot\text{K)}$ . Calculate the rate constant at 298 K.

**Solution:**

Step 1: Calculate  $\Delta^\ddagger G^\circ$

$$\begin{aligned}\Delta^\ddagger G^\circ &= \Delta^\ddagger H^\circ - T\Delta^\ddagger S^\circ \\ &= 85000 - 298 \times (-45) = 85000 + 13410 = 98410 \text{ J/mol}\end{aligned}$$

Step 2: Apply Eyring equation

$$\begin{aligned}k &= \frac{k_B T}{h} e^{-\Delta^\ddagger G^\circ / RT} \\ &= \frac{1.381 \times 10^{-23} \times 298}{6.626 \times 10^{-34}} \times e^{-98410 / (8.314 \times 298)} \\ &= 6.21 \times 10^{12} \times e^{-39.7} = 6.21 \times 10^{12} \times 7.84 \times 10^{-18}\end{aligned}$$

## Worked Example 2: Activation Parameters from Data

**Problem:** Rate constants measured at two temperatures:

- $k(300\text{ K}) = 1.5 \times 10^{-3}\text{ s}^{-1}$
- $k(320\text{ K}) = 8.2 \times 10^{-3}\text{ s}^{-1}$

Calculate  $\Delta^\ddagger H^\circ$  and  $\Delta^\ddagger S^\circ$  (assume  $\kappa = 1$ ).

**Solution:**

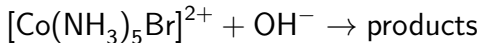
From Eyring plot:  $\ln(k/T) = \ln(k_B/h) + \Delta^\ddagger S^\circ/R - \Delta^\ddagger H^\circ/(RT)$

Calculate slope:

$$\begin{aligned}\text{slope} &= \frac{\ln(k_2/T_2) - \ln(k_1/T_1)}{1/T_2 - 1/T_1} \\ &= \frac{\ln(8.2 \times 10^{-3}/320) - \ln(1.5 \times 10^{-3}/300)}{1/320 - 1/300} \\ &= \frac{-10.05 - (-10.72)}{-2.08 \times 10^{-4}} = \frac{0.67}{-2.08 \times 10^{-4}} = -3221\text{ K}\end{aligned}$$

## Worked Example 3: Salt Effect

**Problem:** For the reaction:



The rate constant at zero ionic strength is  $k_0 = 1.2 \times 10^{-4} \text{ M}^{-1}\text{s}^{-1}$ . Predict the rate constant at  $I = 0.05 \text{ M}$ .

**Solution:**

Charges:  $z_A = +2$ ,  $z_B = -1$ , so  $z_A z_B = -2$

Apply salt effect equation:

$$\begin{aligned}\log(k) &= \log(k_0) + 2A z_A z_B \sqrt{I} \\ &= \log(1.2 \times 10^{-4}) + 2(0.509)(-2)\sqrt{0.05} \\ &= -3.92 + 2(0.509)(-2)(0.224) = -3.92 - 0.456 = -4.38\end{aligned}$$

$$k = 10^{-4.38} = 4.2 \times 10^{-5} \text{ M}^{-1}\text{s}^{-1}$$

# Practice Problem 1

**Problem:** At 298 K:  $\Delta^\ddagger H^\circ = 60 \text{ kJ/mol}$ ,  $\Delta^\ddagger S^\circ = -80 \text{ J/(mol}\cdot\text{K)}$

1. Calculate  $\Delta^\ddagger G^\circ$  at 298 K.
2. Calculate the rate constant ( $\kappa = 1$ ).
3. Is TS more or less ordered?
4. How does  $k$  change at 350 K?

## Answers:

$\Delta^\ddagger G^\circ = 83.8$

$\text{kJ/mol}$   
 $k = 9.8 \times 10^{-3}$

$\text{s}^{-1}$   
More ordered

$(\Delta^\ddagger S^\circ < 0)$   
 $k(350 \text{ K}) = 0.51 \text{ s}^{-1}$  (50× faster)

# Practice Problem 2

**Problem:** The rate constant for H-abstraction by a radical is  $k_H = 5.0 \times 10^6 \text{ M}^{-1}\text{s}^{-1}$  at 298 K. The same reaction with deuterium has  $k_D = 8.3 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$ .

- t1t Calculate the kinetic isotope effect  $k_H/k_D$ .
- t2t Is this a primary or secondary KIE?
- t3t What does this tell you about the mechanism?
- t4t Estimate the difference in activation energies.

## Answers:

opsep=0pt,itemsep=1.5pt[(a)] KIE = 6.0opsep=0pt,itemsep=1.5pt[(b)] Primary  
KIEopsep=0pt,itemsep=1.5pt[(c)] C-H bond breaking occurs in rate-determining  
stepopsep=0pt,itemsep=1.5pt[(d)]  $\Delta E_a \approx 4.4 \text{ kJ/mol}$  (from  $\ln(6.0) = \Delta E_a/(RT)$ )

# Practice Problem 3

**Problem:** For an ionic reaction:

$\sqrt{I} \text{ (M}^{1/2}\text{)}$	$k \text{ (M}^{-1}\text{s}^{-1}\text{)}$
0	$2.0 \times 10^{-3}$
0.1	$3.2 \times 10^{-3}$
0.2	$5.1 \times 10^{-3}$

- 1 Plot  $\log k$  vs  $\sqrt{I}$  and find slope.
- 2 Determine  $z_A z_B$ .
- 3 Like or opposite charge?

**Answers:**

opsep=0pt,itemsep=1.5pt[(a)] Slope  $\approx 2.0$  opsep=0pt,itemsep=1.5pt[(b)] From slope  
=  $2Az_A z_B$ :  $z_A z_B = +2$  opsep=0pt,itemsep=1.5pt[(c)] Like charges

# Practice Problem 4

**Problem:** An Eyring plot gives:

- Slope =  $-8500\text{ K}$
- Intercept =  $25.5$

Calculate  $\Delta^\ddagger H^\circ$  and  $\Delta^\ddagger S^\circ$ .

**Solution:**

From slope:

$$\Delta^\ddagger H^\circ = -R \times \text{slope} = 8.314 \times 8500 = 70.7\text{ kJ/mol}$$

From intercept:

$$\text{intercept} = \ln(k_B/h) + \Delta^\ddagger S^\circ/R$$

$$25.5 = 23.76 + \Delta^\ddagger S^\circ/8.314$$

$$\Delta^\ddagger S^\circ = (25.5 - 23.76) \times 8.314 = 14.5\text{ J/(mol}\cdot\text{K)}$$

**Answer:**  $\Delta^\ddagger H^\circ = 70.7\text{ kJ/mol}$ ,  $\Delta^\ddagger S^\circ = +14.5\text{ J/(mol}\cdot\text{K)}$

Positive entropy suggests a dissociative transition state



# Summary: Topic 18C

- ① **Eyring Equation:** Links rates to thermodynamics through  $\Delta^\ddagger G^\circ$ .

$$k = \frac{k_B T}{h} e^{-\Delta^\ddagger G^\circ / RT}$$

- ② **Activation Parameters:**

- $\Delta^\ddagger H^\circ \approx E_a - RT$  (solution)
- $\Delta^\ddagger S^\circ$  reflects structure of transition state

- ③ **Salt Effects:** Ionic strength affects rates between ions.

$$\log(k) = \log(k_0) + 2A z_A z_B \sqrt{I}$$

- ④ **Isotope Effects:** Probe bond breaking and tunneling.

- ⑤ **LFER:** Connect structure to reactivity (Brønsted, Hammett).

# Topic 18C: Key Takeaways

## Essential Equations:

- **Eyring equation:**  $k_r = \frac{k_B T}{h} e^{-\Delta^\ddagger G^\circ / RT}$
- **Thermodynamic form:**  $k_r = \frac{k_B T}{h} e^{\Delta^\ddagger S^\circ / R} e^{-\Delta^\ddagger H^\circ / RT}$
- **Eyring plot:**  $\ln(k/T)$  vs  $1/T \rightarrow \text{slope} = -\Delta^\ddagger H^\circ / R$
- **KIE:**  $\frac{k_H}{k_D} = e^{\Delta E_a / RT}$  (measures bond breaking)

## When to use TST:

Precise rate predictions

Understanding entropy effects ( $\Delta^\ddagger S^\circ$ )

Isotope effects & tunneling

Temperature dependence beyond Arrhenius

**NOT** when barrier recrossing is significant ( $\kappa \ll 1$ )

**Key Insight:** TST connects thermodynamics to kinetics through the transition state!

# Interactive Learning: Topic 18C

## Explore Transition-State Theory Interactively!

### Interactive Jupyter Notebook Features:

- **Eyring Plot Generator:** Calculate  $\Delta^\ddagger H^\circ$  and  $\Delta^\ddagger S^\circ$
- **KIE Calculator:** Explore kinetic isotope effects
- **Tunneling Correction:** Quantum effects visualization
- **Salt Effect Explorer:** Ionic strength impacts
- **Entropy of Activation:** Interpret TS structure
- **Practice Problems:** Interactive TST calculations

**Notebook:** 03\_Transition\_State\_Theory.ipynb

Scan to Open:



Or navigate to:

Reaction\_Dynamics\_Interactive/

# Topic 18D: Overview

## Zooming in to the Molecular Level

- **Goal:** Understand exactly what happens during a single collision.
- **Experiment:** Molecular Beams.
- **Theory:** Potential Energy Surfaces (PES) and Trajectories.

## Key Questions:

- How does energy distribution affect reactivity?
- In what direction do products fly away?
- What is the detailed reaction path?
- How does energy partition between products?

**Pioneers:** Herschbach, Lee, Polanyi (Nobel Prize 1986)

# Why Molecular Beams?

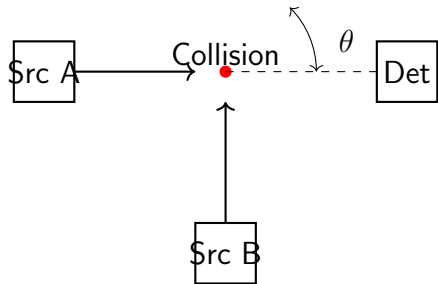
## Problem with Bulk Gas Experiments:

- Multiple collisions
- Maxwell-Boltzmann distribution of velocities
- Difficult to isolate single reactive event
- Cannot control initial conditions precisely

## Molecular Beam Advantages:

- **Single collision** conditions (high vacuum,  $\sim 10^{-6}$  torr)
- **Control** of velocity, quantum states, collision angle
- **Measure** angular distribution of products
- **Detect** product quantum states (vibrational, rotational)
- **State-to-state** chemistry:  $A(v,J) + B \rightarrow C(v',J') + D$

# Molecular Beams - Experimental Setup



## Components:

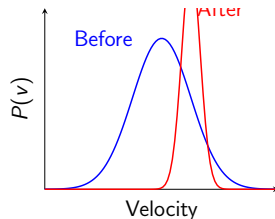
- **Sources:** Supersonic expansion (velocity selection)
- **Collision Zone:** Crossed beams at controlled angle
- **Detector:** Mass spectrometer + time-of-flight (TOF) analysis
- **Vacuum:**  $10^{-6}$  to  $10^{-8}$  torr to prevent multiple collisions

# Velocity Selection: Supersonic Expansion

**Technique:** Gas expands through small nozzle into vacuum

## Before Expansion:

- Maxwell-Boltzmann distribution
- $T \sim 300$  K
- Wide velocity spread



## After Expansion:

- Narrow velocity distribution
  - Effective  $T \sim 1$ -10 K
  - All molecules move with  $v \approx \bar{v}$
- Result:** Collision energy is well-defined!

# Collision Energy and Impact Parameter

## Center-of-Mass Energy:

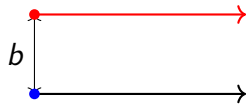
For two molecules with velocities  $\vec{v}_A$  and  $\vec{v}_B$ :

$$E_{\text{coll}} = \frac{1}{2} \mu v_{\text{rel}}^2$$

where  $\mu = \frac{m_A m_B}{m_A + m_B}$  is reduced mass.

## Impact Parameter $b$ :

- Distance of closest approach if no interaction
- Small  $b$ : Head-on collision
- Large  $b$ : Grazing collision
- Maximum  $b$  for reaction:  $b_{\text{max}}$
- Reactive cross-section:  $\sigma_r = \pi b_{\text{max}}^2$





# Differential Cross-Section

## Definition:

We measure the **Differential Cross-Section**

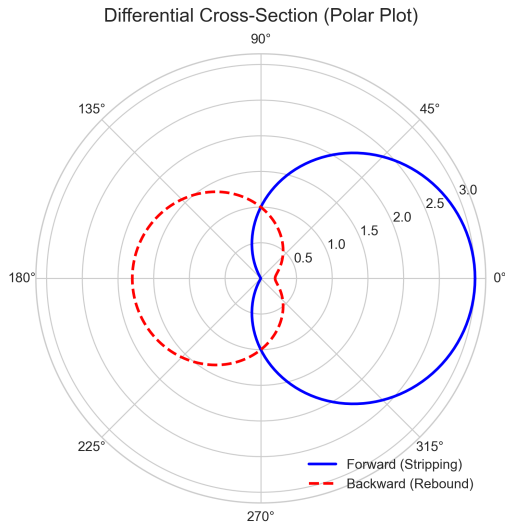
$\sigma(\theta, \phi)$ :

$$dN = \sigma(\theta, \phi) I_{\text{inc}} d\Omega$$

- $dN$ : Particles scattered into  $d\Omega$
- $I_{\text{inc}}$ : Incident flux
- $\sigma(\theta)$ : Angular cross-section
- Units: area/steradian ( $\text{\AA}^2/\text{sr}$ )

## Information Content:

- Scattering probability vs angle



# Types of Scattering Patterns

## Forward Scattering ( $\theta \approx 0$ ):

- "Stripping" mechanism
- Grazing collision (large  $b$ )
- Fast, direct reaction
- Example:  $\text{K} + \text{Br}_2 \rightarrow \text{KBr} + \text{Br}$
- Products fly forward

## Sideways Scattering ( $\theta \approx 90$ ):

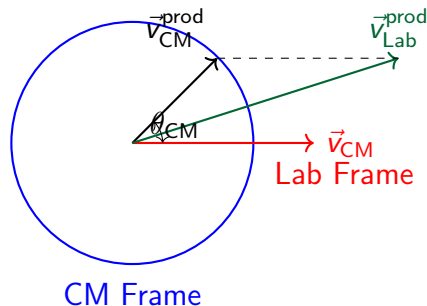
- Complex formation
- Long-lived intermediate
- Symmetric angular distribution

## Backward Scattering ( $\theta \approx 180$ ):

- "Rebound" mechanism
- Head-on collision (small  $b$ )
- Strong repulsive interaction
- Example:  $\text{K} + \text{CH}_3$
- Products bounce back

# Newton Diagram

## Relating Lab Frame to Center-of-Mass Frame:



$$\vec{v}_{Lab} = \vec{v}_{CM}^{\text{prod}} + \vec{v}_{CM}$$

Detector measures lab angles; theory predicts CM angles.

# State-to-State Chemistry (Part 1)

**Modern Achievement:** Prepare reactants in specific quantum states and measure product states.

**Example:**  $\text{H} + \text{D}_2(v=0, J=0) \rightarrow \text{HD}(v', J') + \text{D}$

- Prepare  $\text{D}_2$  in ground vibrational and rotational state
- Measure HD product distribution over  $v'$  and  $J'$
- Map out complete energy disposal

**Advantages:**

- Most detailed information possible
- Direct test of theory
- Reveals quantum effects

# State-to-State Chemistry (Part 2)

## Experimental Techniques:

- **State preparation:** Laser excitation, Stark/Zeman selection
- **State detection:** Laser-induced fluorescence (LIF), REMPI

**Ultimate Goal:** Complete characterization:

$$\sigma(E_{\text{coll}}, v, J, b \rightarrow v', J', \theta, \phi)$$

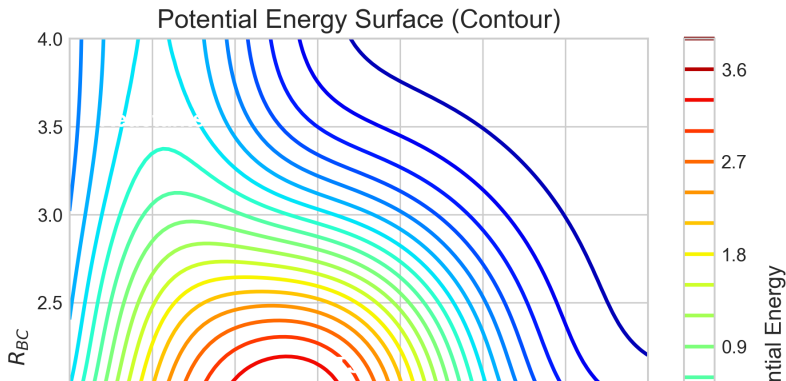
This is the **full quantum scattering matrix**!

**Challenge:** Enormous amount of data, but worth it for fundamental understanding

# Potential Energy Surfaces (PES)

## The Landscape of Reaction

- Plot Potential Energy  $V$  vs. atomic coordinates.
- For  $A + BC \rightarrow AB + C$  (collinear):
- Axes:  $R_{AB}$  and  $R_{BC}$ .



# How to Calculate PES (Part 1)

## Theoretical Methods:

### ① Ab Initio Quantum Chemistry:

- Solve Schrödinger equation for electrons
- Born-Oppenheimer approximation (nuclei fixed)
- Methods: HF, MP2, CCSD(T), CASSCF
- Very accurate but computationally expensive

### ② Density Functional Theory (DFT):

- Faster than ab initio
- Good accuracy for many systems
- Functionals: B3LYP, M06-2X,  $\omega$ B97X-D

# How to Calculate PES (Part 2)

## Theoretical Methods (continued):

### ③ Semi-Empirical/Fitted:

- LEPS (London-Eyring-Polanyi-Sato)
- Fit to experimental data
- Fast but less accurate

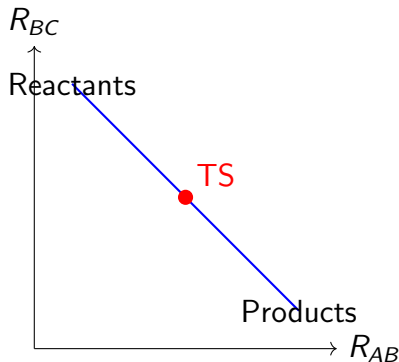
## Trade-offs:

- Accuracy vs. computational cost
- Ab initio: Most accurate, most expensive
- DFT: Good balance for most systems
- Semi-empirical: Fast screening, less reliable



# Features of PES

- **Reactant Valley:** A far from BC.
- **Product Valley:** AB far from C.
- **Saddle Point:** The Transition State.
- Maximum along reaction path.
- Minimum perpendicular to path.
- **Reaction Path:** Minimum energy route (MEP).
- **Barrier Height:** Energy at saddle point.



**Intrinsic Reaction Coordinate (IRC):** Path of steepest descent from TS to reactants and products.

# Classical Trajectory Calculations (Part 1)

**Method:** Solve Newton's equations on the PES

- 1 Start with initial conditions: positions, velocities,  $E_{\text{coll}}$ ,  $b$
- 2 Calculate forces:  $\vec{F}_i = -\nabla_i V(\vec{R})$
- 3 Integrate equations of motion:  $m_i \ddot{\vec{R}}_i = \vec{F}_i$
- 4 Follow trajectory until products separate
- 5 Record: reaction outcome, scattering angle, product energies

# Classical Trajectory Calculations (Part 2)

## Statistical Analysis:

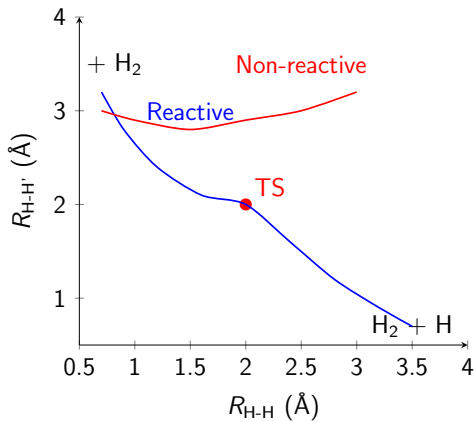
- Run thousands of trajectories
- Sample different  $b$  and initial conditions
- Calculate average cross-sections, energy distributions

## Limitations:

- Classical mechanics (no tunneling)
- Can violate zero-point energy (ZPE)
- No quantum interference effects
- Need ZPE constraints for realistic simulations

**When to use:** Heavy atoms, high energies, statistical averaging

# Trajectory Example: $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$



Blue: Passes through TS region  $\rightarrow$  reaction. Red: Turns back  $\rightarrow$  no reaction.

# Product Energy Distribution

## Where does the energy go?

Total available energy:  $E_{\text{avail}} = E_{\text{coll}} + \Delta H_{\text{rxn}}$

## Partitioning:

- **Translation:**  $E_{\text{trans}}$  (kinetic energy of products flying apart)
- **Vibration:**  $E_{\text{vib}}$  (internal vibration of product molecules)
- **Rotation:**  $E_{\text{rot}}$  (molecular rotation)

$$E_{\text{avail}} = E_{\text{trans}} + E_{\text{vib}} + E_{\text{rot}}$$

## Distribution depends on PES topology:

- Attractive surface  $\rightarrow$  vibrationally "hot" products
- Repulsive surface  $\rightarrow$  translationally "hot" products

# Attractive vs. Repulsive Surfaces

## Where is the barrier located?

### Attractive (Early Barrier):

- Barrier in reactant valley
- TS resembles reactants
- **Translational energy** helps cross barrier
- Products are **vibrationally excited**
- Example:  $\text{K} + \text{Br}_2$  (Harpoon reaction)
- Energy flows: Translation  $\rightarrow$  Vibration

### Repulsive (Late Barrier):

- Barrier in product valley
- TS resembles products
- **Vibrational energy** helps cross barrier
- Products are **translationally excited**
- Example:  $\text{H} + \text{Cl}_2$
- Energy flows: Vibration  $\rightarrow$  Translation

# Polanyi's Rules (Part 1)

**Polanyi's Rule 1:** For reactions with early barriers, translational energy is more effective than vibrational energy in promoting reaction.

**Polanyi's Rule 2:** For reactions with late barriers, vibrational energy is more effective than translational energy in promoting reaction.

**Key Insight:** The location of the barrier determines which type of energy is most effective.

# Polanyi's Rules (Part 2)

## Intuitive Explanation:

- **Early Barrier:** Need speed to "run up" the entrance valley before bonds rearrange.
- **Late Barrier:** Need stretched bonds (vibration) to help make the turn into the product valley.

## Experimental Verification:

- Compare  $\sigma_r(E_{\text{trans}}, \nu = 0)$  vs.  $\sigma_r(E_{\text{trans}}, \nu = 1)$
- Prepare reactants with vibrational excitation
- Measure which form of energy enhances reactivity more

**Impact:** Guide for controlling chemical reactions with laser excitation



# Energy Disposal: Surprisal Analysis

**Question:** How does actual product energy distribution compare to statistical expectation?

## Statistical (Phase Space) Prediction:

- Assume all product states equally accessible
- Predict:  $P_{\text{stat}}(v') \propto \rho(E_{\text{avail}} - E_{v'})$
- Density of states  $\rho$  increases with energy

## Surprisal:

$$I(v') = -\ln \left( \frac{P_{\text{obs}}(v')}{P_{\text{stat}}(v')} \right)$$

- $I(v') > 0$ : Less than statistical (vibration "starved")
- $I(v') < 0$ : More than statistical (vibration "enhanced")

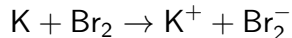
**Reveals:** Direct vs. complex mechanism

# Harpoon Mechanism: $\text{K} + \text{Br}_2 \rightarrow \text{KBr} + \text{Br}$ (Part 1)

## Classic Example of Attractive Surface

### Mechanism:

- 1 At large distance ( $R \sim 6 \text{ \AA}$ ): Electron jumps from K to  $\text{Br}_2$



- 2 Coulomb attraction pulls ions together (fast!)
- 3  $\text{K}^+$  approaches  $\text{Br}_2^-$ , forming  $\text{KBr}^-$  complex
- 4  $\text{Br}^-$  leaves with high kinetic energy

# Harpoon Mechanism: $\text{K} + \text{Br}_2 \rightarrow \text{KBr} + \text{Br}$ (Part 2)

## Experimental Observations:

- Very large cross-section:  $\sigma \sim 200 \text{ \AA}^2$  (vs.  $\sim 10 \text{ \AA}^2$  typical)
- Forward scattering (stripping mechanism)
- KBr product highly vibrationally excited
- Low activation energy

## Why "Harpoon"?

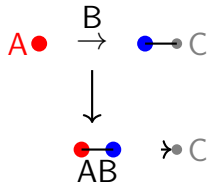
- Electron "thrown" from K at long range
- Like harpooning a whale from distance
- Ionic attraction then "reels in" the reactants
- Fast, efficient reaction

# Spectator Stripping

**Mechanism:** In  $A + BC \rightarrow AB + C$ , atom C is a "spectator"

## Characteristics:

- Fast, direct reaction
- C atom barely affected
- AB bond forms while BC bond breaks
- High impact parameter (grazing collision)
- Forward scattering
- C "stripped off" from BC



**Example:**  $K + CH_3I \rightarrow KI + CH_3$

- $CH_3$  group acts as spectator
- $KI$  formed in collision zone
- $CH_3$  continues forward with little deflection

# Quantum Effects in Dynamics (Part 1)

## When Classical Trajectories Fail:

### ① Tunneling:

- Light atoms (H, D) can tunnel through barriers
- Important for H-transfer reactions
- Classical:  $k = 0$  below barrier; Quantum:  $k > 0$

### ② Zero-Point Energy (ZPE):

- Molecules have  $\text{ZPE} = \frac{1}{2}h\nu$  even at  $\nu = 0$
- Classical trajectories can violate ZPE
- Need ZPE constraints in classical simulations

# Quantum Effects in Dynamics (Part 2)

## When Classical Trajectories Fail (continued):

### ③ Resonances:

- Quasi-bound states in complex region
- Show up as oscillations in  $\sigma_r(E)$
- Pure quantum effect (interference)

### ④ Quantized Product States:

- Classical: continuous energy distribution
- Quantum: discrete vibrational/rotational levels

**Bottom Line:** Quantum dynamics needed for light atoms, low energies, or detailed state-to-state studies.

# Worked Example 1: Collision Energy

**Problem:** In a crossed molecular beam experiment, H atoms (mass = 1 amu) with velocity 2000 m/s collide with D<sub>2</sub> molecules (mass = 4 amu) at rest. Calculate the collision energy.

## Solution:

Step 1: Calculate reduced mass

$$\mu = \frac{m_{\text{H}} \cdot m_{\text{D}_2}}{m_{\text{H}} + m_{\text{D}_2}} = \frac{1 \times 4}{1 + 4} = 0.8 \text{ amu}$$

Convert to kg:  $\mu = 0.8 \times 1.66 \times 10^{-27} = 1.33 \times 10^{-27} \text{ kg}$

Step 2: Relative velocity

$$v_{\text{rel}} = v_{\text{H}} - v_{\text{D}_2} = 2000 - 0 = 2000 \text{ m/s}$$

Step 3: Collision energy

$$E_{\text{coll}} = \frac{1}{2} \mu v_{\text{rel}}^2 = \frac{1}{2} (1.33 \times 10^{-27}) (2000)^2 = 2.66 \times 10^{-21} \text{ J}$$

## Worked Example 2: Reactive Cross-Section

**Problem:** For the reaction  $\text{H} + \text{D}_2 \rightarrow \text{HD} + \text{D}$ , the maximum impact parameter for reaction at  $E_{\text{coll}} = 0.5 \text{ eV}$  is  $b_{\text{max}} = 1.8 \text{ \AA}$ . Calculate:

- a) The reactive cross-section  $\sigma_r$
- b) The reaction probability if geometric cross-section is  $\sigma_{\text{geom}} = 10 \text{ \AA}^2$

**Solution:**

(a) Reactive cross-section:

$$\sigma_r = \pi b_{\text{max}}^2 = \pi (1.8)^2 = 10.2 \text{ \AA}^2$$

(b) Reaction probability (opacity function):

$$P = \frac{\sigma_r}{\sigma_{\text{geom}}} = \frac{10.2}{10} = 1.02 \approx 1.0$$

**Interpretation:** At this energy, essentially all collisions within the geometric cross-section lead to reaction (high reactivity).



## Worked Example 3: Energy Partitioning

**Problem:** For the reaction  $F + H_2 \rightarrow HF + H$  at  $E_{\text{coll}} = 0.1 \text{ eV}$ :

- $\Delta H_{\text{rxn}} = -1.4 \text{ eV}$  (exothermic)
- Measured: HF products have  $\langle E_{\text{vib}} \rangle = 1.0 \text{ eV}$

Calculate the average translational and rotational energy of products.

**Solution:**

Total available energy:

$$E_{\text{avail}} = E_{\text{coll}} + |\Delta H_{\text{rxn}}| = 0.1 + 1.4 = 1.5 \text{ eV}$$

Energy remaining for translation + rotation:

$$E_{\text{trans}} + E_{\text{rot}} = E_{\text{avail}} - E_{\text{vib}} = 1.5 - 1.0 = 0.5 \text{ eV}$$

Typical ratio:  $E_{\text{rot}} : E_{\text{trans}} \approx 1 : 2$  (rule of thumb)

$$E_{\text{rot}} \approx 0.17 \text{ eV}, \quad E_{\text{trans}} \approx 0.33 \text{ eV}$$

# Practice Problem 1

**Problem:** In a crossed beam experiment, Ar atoms (40 amu) with  $v = 1500$  m/s collide with O<sub>2</sub> molecules (32 amu) with  $v = 800$  m/s at 90°. Calculate:

- a) The magnitude of the relative velocity
- b) The collision energy in eV
- c) The center-of-mass velocity

**Answers:**

- (a)  $v_{\text{rel}} = \sqrt{1500^2 + 800^2} = 1700$  m/s
- (b)  $E_{\text{coll}} = 0.17$  eV
- (c)  $v_{\text{CM}} = 1056$  m/s (along Ar beam direction)

# Practice Problem 2

**Problem:** For the reaction  $\text{Cl} + \text{HBr} \rightarrow \text{HCl} + \text{Br}$ :

- Barrier is "late" (in product valley)
- $E_a = 8 \text{ kJ/mol}$
- a) According to Polanyi's rules, would vibrational or translational energy be more effective?
- b) If HBr has vibrational energy  $25 \text{ kJ/mol}$ , estimate the effective activation energy.
- c) Predict whether products will be vibrationally or translationally "hot".

**Answers:**

- (a) Vibrational energy (late barrier)
- (b)  $E_a^{\text{eff}} \approx 8 - 0.3(25) \approx 0.5 \text{ kJ/mol}$  (much lower!)
- (c) Products will be translationally hot (repulsive surface)

# Practice Problem 3

**Problem:** A reaction has measured differential cross-section:

$$\sigma(\theta) = \sigma_0 \cos^2(\theta)$$

where  $\sigma_0 = 15 \text{ \AA}^2/\text{sr}$ .

- a) Sketch the angular distribution
- b) Is this forward or backward scattering?
- c) What mechanism does this suggest?
- d) Calculate the total cross-section:  $\sigma_{\text{total}} = \int \sigma(\theta) d\Omega$

**Answers:**

- (a) Maximum at  $\theta = 0$  and  $180$ , zero at  $90$
- (b) Both forward and backward (symmetric)
- (c) Head-on collision with rebound
- (d)  $\sigma_{\text{total}} = 20\pi \text{ \AA}^2 \approx 63 \text{ \AA}^2$

# Practice Problem 4

**Problem:** For  $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$  reaction:

- Classical barrier:  $E_a^{\text{classical}} = 40 \text{ kJ/mol}$
- Measured barrier:  $E_a^{\text{obs}} = 32 \text{ kJ/mol}$

- a) What causes the difference?
- b) Estimate the effective tunneling distance if barrier width is  $0.5 \text{ \AA}$
- c) Would  $\text{D} + \text{D}_2 \rightarrow \text{D}_2 + \text{D}$  show larger or smaller difference?

**Answers:**

- (a) Quantum tunneling through the barrier
- (b) Reduces effective barrier by  $\sim 8 \text{ kJ/mol}$  (20%)
- (c) Smaller - heavier mass reduces tunneling

# Practice Problem 4 - Tunneling Equation

## Tunneling probability:

$$P_{\text{tunnel}} \propto \exp \left( -\frac{\sqrt{2m\Delta E} \cdot d}{\hbar} \right)$$

where:

- $m$  = particle mass
- $\Delta E$  = barrier height above particle energy
- $d$  = barrier width

## Isotope effect:

For D vs H:  $m_D = 2m_H$ , so:

$$\frac{P_{\text{tunnel,D}}}{P_{\text{tunnel,H}}} \propto \exp(-d\sqrt{m_D}/\hbar) / \exp(-d\sqrt{m_H}/\hbar) = e^{-(\sqrt{2}-1)d\sqrt{m_H}/\hbar} \approx 0.24$$

Tunneling probability decreases by factor of  $\sim 4$  for deuterium.

# Modern Developments in Reaction Dynamics (Part 1)

## Cutting Edge Techniques:

### ① Femtochemistry (A. Zewail, Nobel 1999):

- Femtosecond laser pulses ( $10^{-15}$  s)
- Watch bonds break and form in real time
- "Molecular movies" of reactions

### ② Coulomb Explosion Imaging:

- Remove all electrons instantly
- Nuclei fly apart by Coulomb repulsion
- Measure 3D structure at instant of explosion

# Modern Developments in Reaction Dynamics (Part 2)

## Cutting Edge Techniques (continued):

### ③ Cold Molecule Chemistry:

- Molecules cooled to  $\mu\text{K}$  with lasers
- Study reactions at ultralow energies
- Quantum effects dominate

### ④ High-Dimensional Quantum Dynamics:

- Beyond 3-atom systems
- Full quantum treatment of 4-, 5-, 6-atom reactions
- Enables prediction without experiments

**Impact:** From "what happens" to "why and how" at atomic resolution



# Summary: Topic 18D

- ① **Molecular Beams:** Enable study of single collisions with controlled conditions
  - State selection, velocity control, angular resolution
- ② **Differential Cross-Sections:** Reveal reaction mechanisms
  - Forward: stripping; Backward: rebound; Sideways: complex
- ③ **Potential Energy Surfaces:** Map of reaction landscape
  - Calculated from quantum chemistry
  - Used for trajectory calculations
- ④ **Energy Distribution:** Not statistical!
  - Attractive surface → vibrationally hot products
  - Repulsive surface → translationally hot products
- ⑤ **Polanyi's Rules:** Connect barrier location to energy requirements
  - Early barrier: translation promotes; Late barrier: vibration promotes

# Topic 18D: Key Takeaways

## Essential Concepts:

- **Molecular beams:** Single-collision conditions reveal reaction dynamics
- **Differential cross-section:**  $\sigma(\theta) \rightarrow$  angular distribution of products
- **PES:** Multi-dimensional energy landscape guides reactive trajectories
- **Polanyi's Rules:**  $E_{\text{trans}}$  vs  $E_{\text{vib}}$  effectiveness depends on barrier type

## Key Techniques:

Molecular beam experiments (state-to-state chemistry)

Classical trajectory calculations (Newton's equations on PES)

Quantum scattering (for light atoms, tunneling)

Newton diagrams (velocity vector analysis)

**Key Insight:** *Where* energy is placed matters as much as *how much*!

# Interactive Learning: Topic 18D

## Explore Molecular Collision Dynamics Interactively!

### Interactive Jupyter Notebook Features:

- **3D PES Visualizer:** Rotate and explore potential surfaces
- **Trajectory Simulator:** Watch reactive vs non-reactive paths
- **Molecular Beam Setup:** Understand crossed-beam experiments
- **Differential Cross-Section:** Analyze angular distributions
- **Newton Diagrams:** Product velocity vectors
- **State-to-State Dynamics:** Quantum state resolution

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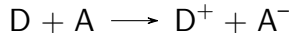


Or navigate to:

[Reaction Dynamics Interactive/](#)

# Topic 18E: Overview

## Electron Transfer (ET) Reactions



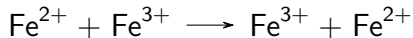
- **Simplest** class of reactions: just electron movement
- No bonds broken or formed in elementary step
- Ubiquitous in chemistry, biology, materials science
- **Marcus Theory:** Rudolph Marcus, Nobel Prize 1992

### Examples:

- **Biology:** Photosynthesis, respiration (cytochrome chains)
- **Chemistry:** Redox reactions, fuel cells, batteries
- **Materials:** Organic electronics, solar cells

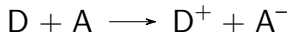
# Types of Electron Transfer Reactions (Part 1)

## 1. Self-Exchange Reactions:



- $\Delta_r G^\circ = 0$  (no driving force)
- Rate depends only on reorganization energy
- Used to measure intrinsic barrier

## 2. Cross Reactions:



- $\Delta_r G^\circ \neq 0$
- Thermodynamically driven
- Rate depends on driving force AND reorganization

# Types of Electron Transfer Reactions (Part 2)

## 3. Inner vs. Outer Sphere:

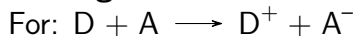
- **Outer Sphere:** Electron tunnels, no ligand exchange
- **Inner Sphere:** Bridge ligand shared, chemical bond formation

## Comparison:

- Outer sphere: Simple, predictable by Marcus theory
- Inner sphere: More complex, involves bond making/breaking
- Most biological ET is outer sphere
- Transition metal chemistry has both types

# Thermodynamics of Electron Transfer

**Driving Force:** Determined by reduction potentials



$$\Delta_r G^\circ = -F(E_{D^+/D} - E_{A/A^-})$$

where  $F$  is Faraday constant (96485 C/mol).

**Example:**

- $\text{Ru}(\text{bpy})_3^{2+}$  (D):  $E^\circ = -1.3 \text{ V}$  vs. NHE
- $\text{MV}^{2+}$  (A):  $E^\circ = -0.45 \text{ V}$  vs. NHE
- $\Delta_r G^\circ = -F(-1.3 - (-0.45)) = -F(-0.85) = +82 \text{ kJ/mol}$

Positive  $\Delta_r G^\circ \rightarrow$  endergonic, need excitation.

# The Franck-Condon Principle

**Key Concept:** Electrons move **much faster** than nuclei.

- Electron transfer time:  $\sim 10^{-15}$  s (femtoseconds)
- Nuclear motion time:  $\sim 10^{-13}$  s (100 fs)

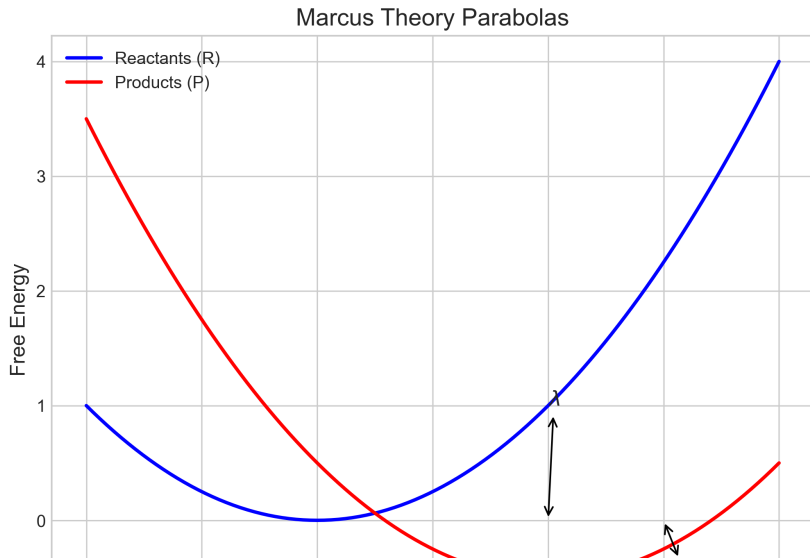
**Franck-Condon Principle:** Electron transfer occurs at **fixed nuclear geometry** - a "vertical" transition on energy diagram.

## Consequences:

- Energy must be conserved at the instant of transfer
- Reactant and product energy surfaces must intersect
- Nuclei must reorganize *before* electron jumps
- Reorganization creates activation barrier



# Potential Energy Surfaces for ET



# Reorganization Energy ( $\lambda$ )

**Total reorganization energy:**

$$\lambda = \lambda_{\text{in}} + \lambda_{\text{out}}$$

## 1. Inner Sphere ( $\lambda_{\text{in}}$ ):

- Changes in bond lengths and angles of D and A
- Example:  $\text{Fe}^{2+}$  has longer bonds than  $\text{Fe}^{3+}$
- Typical: 0.2-1.0 eV for transition metal complexes
- Small for organic molecules with delocalized  $\pi$  systems

## 2. Outer Sphere ( $\lambda_{\text{out}}$ ):

- Reorientation of solvent molecules
- Ions polarize solvent differently
- Depends on: solvent dielectric constant, ion size
- Typical: 0.5-1.5 eV in polar solvents

# Marcus Formula for $\lambda_{\text{out}}$

## Dielectric Continuum Model:

$$\lambda_{\text{out}} = \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{d} \right) \left( \frac{1}{\epsilon_{\text{op}}} - \frac{1}{\epsilon_s} \right)$$

- $r_D, r_A$ : radii of donor and acceptor
- $d$ : distance between donor and acceptor
- $\epsilon_{\text{op}}$ : optical dielectric constant  $= n^2$
- $\epsilon_s$ : static dielectric constant

## Physical Meaning:

- Electronic polarization (fast) follows electron instantly:  $\epsilon_{\text{op}}$
- Nuclear/orientational polarization (slow) lags behind:  $\epsilon_s$
- Difference creates reorganization barrier

# Deriving Marcus Equation - Step 1

**Harmonic Approximation:** Model surfaces as parabolas

Reactant:  $G_R(q) = \frac{1}{2}k(q - q_R)^2$

Product:  $G_P(q) = \frac{1}{2}k(q - q_P)^2 + \Delta_r G^\circ$

**Assumptions:**

- Same force constant  $k$  for both surfaces
- Shift in equilibrium position:  $\Delta q = q_P - q_R$
- Reorganization energy:  $\lambda = \frac{1}{2}k(\Delta q)^2$

Find intersection point (TS) where  $G_R(q^\ddagger) = G_P(q^\ddagger)$ .

# Deriving Marcus Equation - Step 2

**At intersection:**

$$\frac{1}{2}k(q^\ddagger - q_R)^2 = \frac{1}{2}k(q^\ddagger - q_P)^2 + \Delta_r G^\circ$$

Solve for  $q^\ddagger$ :

$$q^\ddagger = q_R + \frac{\Delta q}{2} + \frac{\Delta_r G^\circ}{k\Delta q}$$

Activation energy:

$$\Delta G^\ddagger = G_R(q^\ddagger) - G_R(q_R) = \frac{1}{2}k(q^\ddagger - q_R)^2$$

Substitute and simplify using  $\lambda = \frac{1}{2}k(\Delta q)^2$ :

$$\Delta G^\ddagger = \frac{(\Delta_r G^\circ + \lambda)^2}{4\lambda}$$

This is the **Marcus Equation** for activation energy!

# The Marcus Equation

## Rate constant for electron transfer:

$$k_{ET} = \kappa \nu_n \exp \left( -\frac{\Delta G^\ddagger}{RT} \right)$$

where  $\nu_n$  is nuclear frequency factor ( $\sim 10^{13} \text{ s}^{-1}$ ).

Substituting Marcus activation energy:

$$k_{ET} = \kappa \nu_n \exp \left( -\frac{(\Delta_r G^\circ + \lambda)^2}{4\lambda RT} \right)$$

## Key Parameters:

- $\Delta_r G^\circ$ : Driving force (thermodynamics)
- $\lambda$ : Reorganization energy (barrier height)
- $\kappa$ : Electronic transmission coefficient (tunneling)

# Three Regimes of ET (Part 1)

**Analyze  $\Delta G^\ddagger = \frac{(\Delta_r G^\circ + \lambda)^2}{4\lambda}$ :**

**1. Normal Region ( $-\Delta_r G^\circ < \lambda$ ):**

$$\Delta G^\ddagger = \frac{\lambda}{4} \left( 1 + \frac{\Delta_r G^\circ}{\lambda} \right)^2$$

- Barrier decreases as reaction becomes more exergonic
- Rate increases with driving force (normal behavior)

**2. Barrierless ( $-\Delta_r G^\circ = \lambda$ ):**

$$\Delta G^\ddagger = 0$$

- **Maximum rate:** surfaces intersect at reactant minimum
- Diffusion-controlled limit

# Three Regimes of ET (Part 2)

## 3. Inverted Region ( $-\Delta_r G^\circ > \lambda$ ):

- Barrier *increases* as reaction becomes more exergonic
- Rate *decreases* with driving force (counter-intuitive!)

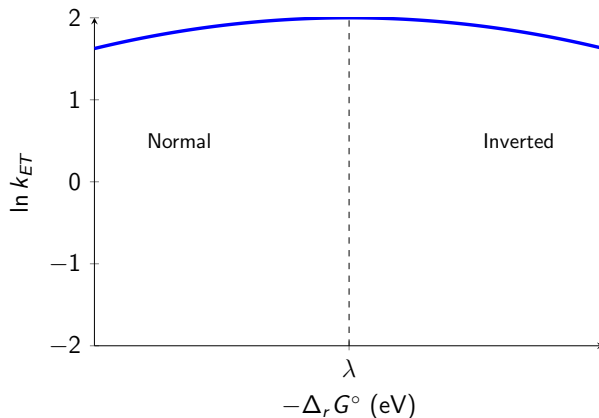
**Marcus' most famous prediction: Making a reaction more exergonic can slow it down!**

## Summary:

- Normal: Faster with more driving force
- Barrierless: Maximum at  $-\Delta_r G^\circ = \lambda$
- Inverted: Slower with more driving force



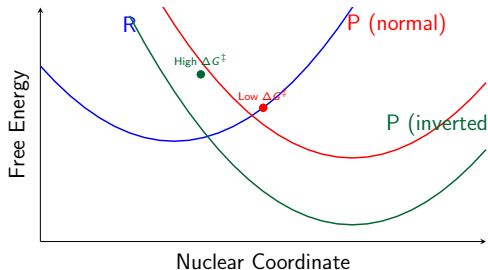
# Marcus Parabola: Rate vs. Driving Force



**Key Prediction:** After reaching maximum at  $-\Delta_r G^\circ = \lambda$ , rate decreases!

# The Inverted Region - Explanation

Why does rate decrease with more driving force?



In inverted region: Surfaces intersect at **high energy** because product well is too far down.

# Experimental Evidence for Inverted Region (Part 1)

**Challenge:** Hard to observe - requires large  $|\Delta_r G^\circ|$  while keeping  $\lambda$  small.

## Early Evidence (Closs & Miller, 1984):

- Intramolecular ET in rigid molecules
- Donor-Bridge-Acceptor systems
- Fixed distance, variable driving force
- Observed rate maximum and subsequent decrease

**Breakthrough:** First direct confirmation of Marcus inverted region

# Experimental Evidence for Inverted Region (Part 2)

## Modern Examples:

- Photoinduced back-electron transfer in donor-acceptor dyads
- Observed in porphyrin-quinone systems
- Common in photosynthetic reaction centers
- Used to slow down unproductive back-reactions

## Biological Significance:

- Nature uses inverted region to prevent energy-wasting back-transfer
- Essential for efficient energy conversion
- Protects high-energy charge-separated states

# Distance Dependence of ET

**Electronic Coupling:** Electron must **tunnel** between D and A.

$$H_{DA} \propto \exp(-\beta r/2)$$

where:

- $H_{DA}$ : Electronic coupling matrix element
- $r$ : edge-to-edge distance
- $\beta$ : decay parameter (depends on medium)

**Rate Dependence:**

$$k_{ET} \propto H_{DA}^2 \propto \exp(-\beta r)$$

**Typical  $\beta$  values:**

- Vacuum/protein:  $\beta \approx 16\text{-}20 \text{ nm}^{-1}$  (fast decay)
- Through  $\pi$ -conjugated bridge:  $\beta \approx 2.5 \text{ nm}^{-1}$  (slow decay)

# Semiclassical Marcus-Hush Theory (Part 1)

## Full Expression:

$$k_{ET} = \frac{2\pi}{\hbar} H_{DA}^2 \frac{1}{\sqrt{4\pi\lambda k_B T}} \exp\left(-\frac{(\Delta_r G^\circ + \lambda)^2}{4\lambda k_B T}\right)$$

## This combines:

- Quantum mechanics (electron tunneling)
- Classical mechanics (nuclear reorganization)
- Statistical mechanics (thermal activation)

# Semiclassical Marcus-Hush Theory (Part 2)

## Three Factors:

### ① **Electronic Factor:** $H_{DA}^2$

- Tunneling probability
- Decreases exponentially with distance

### ② **Nuclear Factor:** $\frac{1}{\sqrt{4\pi\lambda k_B T}}$

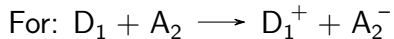
- Franck-Condon weighted density of states
- Pre-exponential factor

### ③ **Activation Factor:** $\exp\left(-\frac{(\Delta_r G^\circ + \lambda)^2}{4\lambda k_B T}\right)$

- Marcus activation energy
- Temperature dependent

# Marcus Cross Relation

**Goal:** Predict rate of cross reaction from self-exchange rates.



$$k_{12} = \sqrt{k_{11}k_{22}K_{12}f_{12}}$$

where:

- $k_{11}$ : self-exchange rate of  $D_1/D_1^+$
- $k_{22}$ : self-exchange rate of  $A_2/A_2^-$
- $K_{12}$ : equilibrium constant =  $\exp(-\Delta_r G^\circ/RT)$
- $f_{12}$ : correction factor (usually  $\approx 1$  for small  $\Delta_r G^\circ$ )

**Utility:**

- Self-exchange rates are easier to measure
- Predict rates for many cross reactions
- Test consistency of Marcus theory



# Biological Electron Transfer (Part 1)

## Electron Transport Chains:

- **Photosynthesis:**  $\text{P680} \rightarrow \text{Pheophytin} \rightarrow \text{Q}_A \rightarrow \text{Q}_B$
- **Respiration:**  $\text{NADH} \rightarrow \text{Complex I} \rightarrow \text{Q} \rightarrow \text{Complex III} \rightarrow \text{Cyt c} \rightarrow \text{Complex IV} \rightarrow \text{O}_2$

## Design Principles:

### ① Forward ET in Normal Region:

- $-\Delta_r G^\circ < \lambda \rightarrow$  fast forward transfer

### ② Back ET in Inverted Region:

- $-\Delta_r G^\circ > \lambda \rightarrow$  slow wasteful back-transfer
- Prevents energy loss

# Biological Electron Transfer (Part 2)

## Design Principles (continued):

### ③ Optimal Distances:

- Typically 10-15 Å edge-to-edge
- Fast enough but selective
- Prevents short-circuits

### ④ Protein Bridges:

- Lower  $\beta$  through aromatic residues
- Facilitate long-range transfer
- Guide electron path

**Result:** Efficient directional ET with minimal energy loss!

## Worked Example 1: Calculating $\lambda_{\text{out}}$

**Problem:** Calculate  $\lambda_{\text{out}}$  for ET between two spherical ions with  $r_D = r_A = 0.3$  nm separated by  $d = 0.8$  nm in water ( $\epsilon_s = 80$ ,  $n = 1.33$ ).

**Solution:**

$$\lambda_{\text{out}} = \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{d} \right) \left( \frac{1}{n^2} - \frac{1}{\epsilon_s} \right)$$

Constants:  $\frac{e^2}{4\pi\epsilon_0} = 1.44 \text{ eV}\cdot\text{nm}$

$$\begin{aligned}\lambda_{\text{out}} &= 1.44 \left( \frac{1}{2(0.3)} + \frac{1}{2(0.3)} - \frac{1}{0.8} \right) \left( \frac{1}{1.77} - \frac{1}{80} \right) \\ &= 1.44(1.67 + 1.67 - 1.25)(0.565 - 0.0125) \\ &= 1.44(2.09)(0.553) = 1.66 \text{ eV}\end{aligned}$$

## Worked Example 2: Marcus Activation Energy

**Problem:** For an ET reaction with  $\lambda = 1.0$  eV and  $\Delta_r G^\circ = -0.4$  eV, calculate:

- a) The activation energy  $\Delta G^\ddagger$
- b) The rate constant at 298 K (assume  $\nu_n = 10^{13} \text{ s}^{-1}$ ,  $\kappa = 1$ )

**Solution:**

(a) Marcus equation:

$$\Delta G^\ddagger = \frac{(\Delta_r G^\circ + \lambda)^2}{4\lambda} = \frac{(-0.4 + 1.0)^2}{4(1.0)} = \frac{(0.6)^2}{4} = 0.09 \text{ eV}$$

(b) Rate constant:

$$\begin{aligned} k_{ET} &= 10^{13} \exp\left(-\frac{0.09 \times 96.5}{8.314 \times 0.298}\right) = 10^{13} \exp(-3.50) \\ &= 10^{13} \times 0.030 = 3.0 \times 10^{11} \text{ s}^{-1} \end{aligned}$$

$$k_{ET} = 3.0 \times 10^{11} \text{ s}^{-1}$$

## Worked Example 3: Inverted Region

**Problem:** For the same system ( $\lambda = 1.0$  eV), calculate  $\Delta G^\ddagger$  for:

a)  $\Delta_r G^\circ = -1.0$  eV (barrierless)

b)  $\Delta_r G^\circ = -2.0$  eV (inverted)

Compare with normal region ( $\Delta_r G^\circ = -0.4$  eV,  $\Delta G^\ddagger = 0.09$  eV).

**Solution:**

(a) Barrierless:

$$\Delta G^\ddagger = \frac{(-1.0 + 1.0)^2}{4(1.0)} = 0 \text{ eV}$$

(b) Inverted:

$$\Delta G^\ddagger = \frac{(-2.0 + 1.0)^2}{4(1.0)} = \frac{1.0}{4} = 0.25 \text{ eV}$$

**Trend:**  $\Delta G^\ddagger = 0.09 \rightarrow 0 \rightarrow 0.25$  eV

Rate **increases** then **decreases** as  $-\Delta_r G^\circ$  increases!

# Practice Problem 1

**Problem:** An ET reaction has the following parameters:

- $\lambda = 0.8 \text{ eV}$
- $\Delta_r G^\circ = -0.6 \text{ eV}$
- Distance:  $r = 1.0 \text{ nm}$
- $\beta = 10 \text{ nm}^{-1}$

- Calculate  $\Delta G^\ddagger$
- Is this in normal, barrierless, or inverted region?
- If distance increases to  $1.5 \text{ nm}$ , by what factor does rate decrease?

**Answers:**

- $\Delta G^\ddagger = 0.01 \text{ eV}$
- Normal region ( $-\Delta_r G^\circ < \lambda$ )
- Rate decreases by factor  $\exp(\beta\Delta r) = \exp(10 \times 0.5) \approx 150$

# Practice Problem 2

**Problem:** The self-exchange rate constants are:

- $\text{Fe}^{2+}/\text{Fe}^{3+}$ :  $k_{11} = 4.0 \text{ M}^{-1}\text{s}^{-1}$
- $\text{Ru}^{2+}/\text{Ru}^{3+}$ :  $k_{22} = 4.0 \times 10^2 \text{ M}^{-1}\text{s}^{-1}$

For cross reaction  $\text{Fe}^{2+} + \text{Ru}^{3+} \longrightarrow \text{Fe}^{3+} + \text{Ru}^{2+}$ :

- $\Delta_r G^\circ = -15 \text{ kJ/mol}$
- $K_{12} = \exp(15000/(8.314 \times 298)) = 403$

Estimate  $k_{12}$  using Marcus cross relation ( $f_{12} \approx 1$ ).

**Solution:**

$$k_{12} = \sqrt{k_{11}k_{22}K_{12}} = \sqrt{4.0 \times 400 \times 403} = \sqrt{6.4 \times 10^5}$$

$$k_{12} \approx 800 \text{ M}^{-1}\text{s}^{-1}$$

# Practice Problem 3

**Problem:** A biological ET chain has three steps:

Step	$\Delta_r G^\circ$ (eV)	$\lambda$ (eV)
$1 \rightarrow 2$	-0.3	0.8
$2 \rightarrow 3$	-0.5	0.8
$3 \rightarrow 1$ (back)	+0.8	0.8

- a) Calculate  $\Delta G^\ddagger$  for each step
- b) Which step is fastest?
- c) Why is the back-reaction slow despite being exergonic overall?

**Answers:**

- (a)  $\Delta G^\ddagger(1 \rightarrow 2) = 0.078$  eV;  $\Delta G^\ddagger(2 \rightarrow 3) = 0.028$  eV;  $\Delta G^\ddagger(\text{back}) = 0.2$  eV
- (b) Step  $2 \rightarrow 3$  (lowest barrier)
- (c) Back-reaction has endergonic  $\Delta_r G^\circ$ , creating large barrier



# Practice Problem 4

**Problem:** For optimal ET rate (barrierless), we need  $-\Delta_r G^\circ = \lambda$ .

A photosynthetic reaction center has:

- Forward ET:  $\lambda = 0.5$  eV
- Back ET:  $\lambda = 0.5$  eV
- a) What driving force gives fastest forward ET?
- b) If actual  $\Delta_r G^\circ = -0.3$  eV, what is  $\Delta G^\ddagger$ ?
- c) For back ET with  $\Delta_r G^\circ = +0.3$  eV, what is the barrier?
- d) How does this design prevent energy loss?

**Answers:**

- (a)  $\Delta_r G^\circ = -0.5$  eV ( $= -\lambda$ )
- (b)  $\Delta G^\ddagger = 0.02$  eV (fast)
- (c)  $\Delta G^\ddagger = 0.32$  eV (slow!)
- (d) Endergonic back-reaction has huge barrier  $\rightarrow$  prevents wasteful back-transfer

# Summary: Topic 18E

- ① **Franck-Condon Principle:** ET is vertical transition at fixed nuclear geometry

$$\text{Time}_{\text{electron}} \ll \text{Time}_{\text{nuclear}}$$

- ② **Reorganization Energy:**  $\lambda = \lambda_{\text{in}} + \lambda_{\text{out}}$

- Cost to rearrange nuclei before ET

- ③ **Marcus Equation:**

$$\Delta G^\ddagger = \frac{(\Delta_r G^\circ + \lambda)^2}{4\lambda}$$

- Normal region: rate increases with  $-\Delta_r G^\circ$
- Barrierless:  $-\Delta_r G^\circ = \lambda$  (maximum rate)
- Inverted region: rate decreases with  $-\Delta_r G^\circ$

- ④ **Distance Dependence:**  $k_{ET} \propto \exp(-\beta r)$

- Electron tunneling through barrier

- ⑤ **Biological Applications:** Optimized ET chains use normal + inverted regions

# Topic 18E: Key Takeaways

## Essential Equations:

- **Marcus equation:**  $k_{ET} = Ae^{-\Delta G^\ddagger/RT}$  where  $\Delta G^\ddagger = \frac{(\lambda + \Delta G^\circ)^2}{4\lambda}$
- **Reorganization energy:**  $\lambda = \lambda_{in} + \lambda_{out}$  (inner + outer sphere)
- **Distance dependence:**  $k_{ET} \propto e^{-\beta r}$  (tunneling decay)
- **Three regimes:** Normal, activationless ( $-\Delta G^\circ = \lambda$ ), inverted

## Key Applications:

Photosynthesis & respiration (biological ET chains)

Solar cells & molecular electronics

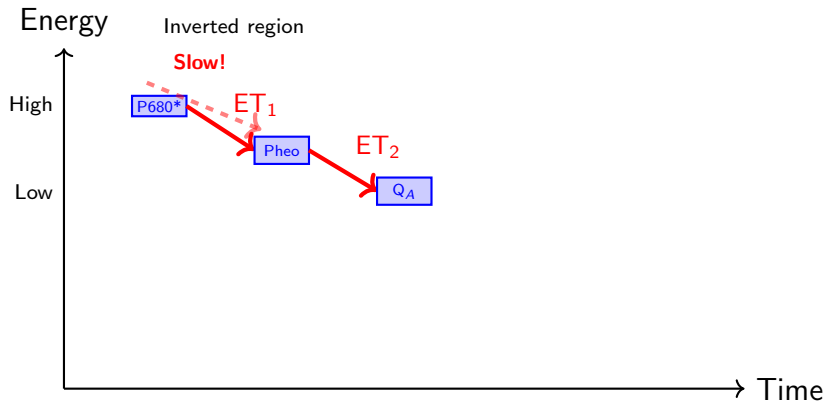
Self-exchange reactions ( $\Delta G^\circ = 0$ )

Understanding why some reactions slow down as they become more exergonic!

**Key Insight:** Marcus inverted region explains nature's optimization of ET efficiency!

# Real-World ET: Photosynthesis

Photosystem II uses Marcus theory principles for high efficiency!



- **Forward ET:** Normal region ( $-\Delta G < \lambda$ )  $\Rightarrow$  **Fast!** (ps-ns)

# Interactive Learning: Topic 18E

## Explore Electron Transfer Theory Interactively!

### Interactive Jupyter Notebook Features:

- **Marcus Parabola Explorer:** Visualize normal, barrierless, inverted
- **Reorganization Energy Calculator:** Inner + outer sphere
- **Driving Force vs Rate:** Interactive  $k$  vs  $-\Delta_r G^\circ$  plots
- **Tunneling Distance Decay:** Exponential  $\beta$  dependence
- **Biological ET Chains:** Photosynthesis, respiration
- **Real Systems:** Ru complexes, cytochrome c

Scan to Open:



Or navigate to:

[Reaction\\_Dynamics\\_Interactive/](#)

# Comparison of Theories

Theory	Collision	Diffusion	TST	Marcus
Phase	Gas	Liquid	All	All
Key parameter	$\sigma, E_a$	$D, \eta$	$\Delta^\ddagger G^\circ$	$\lambda$
Rate equation	$\sigma v e^{-E_a/RT}$	$4\pi RD$	$\frac{kT}{h} e^{-\Delta G^\ddagger/RT}$	$ H_{AB} ^2 e^{-\Delta G^\ddagger/RT}$
Entropy?	No	No	<b>Yes</b>	<b>Yes</b>
Quantum?	No	No	Limited	<b>Yes</b>
Best for	Simple gas rxns	Fast rxns	General	ET

**Each theory has its domain of applicability**

# Common Themes

## Throughout Focus 18:

### 1 Energy matters

- Activation barriers control rates
- Energy distribution among modes
- Quantum vs. classical regimes

### 2 Geometry matters

- Molecular orientation (steric factors)
- Potential energy surfaces
- Reaction paths

### 3 Potential energy surfaces

- Central concept in all theories
- Saddle points = transition states
- Guide reaction dynamics



# Applications

**Reaction dynamics principles apply to:**

## **Atmospheric Chemistry:**

- Ozone formation/depletion
- Radical reactions
- Aerosol chemistry

## **Combustion:**

- Flame chemistry
- Explosions
- Engine efficiency

## **Materials Science:**

- Surface reactions

## **Biochemistry:**

- Enzyme mechanisms
- Electron transport chains
- Photosynthesis

## **Energy Conversion:**

- Solar cells
- Batteries
- Fuel cells

## **Pharmaceuticals:**

- Drug design



# Further Resources

## Recommended Reading:

- Atkins & de Paula: *Physical Chemistry*, Chapter 18
- Steinfeld, Francisco & Hase: *Chemical Kinetics and Dynamics*
- Levine: *Molecular Reaction Dynamics*
- Marcus: Nobel Lecture (1992) on electron transfer

## Interactive Resources:

- Jupyter notebooks for each topic (see QR codes throughout)
- PhET simulations: Collision theory, reaction dynamics
- Computational chemistry software: Gaussian, ORCA, Q-Chem

## Advanced Topics:

- Femtochemistry (Nobel Prize 1999 - Ahmed Zewail)
- Attosecond science
- Machine learning potentials

# Questions?

Thank you for your attention!

*From simple collisions to complex electron transfer,  
reaction dynamics reveals the beauty of chemistry at the molecular level*