

Focus 18: Reaction Dynamics

From Collisions to Electron Transfer

Physical Chemistry Course

Mindanao State University – Iligan Institute of Technology

November 30, 2025

Outline

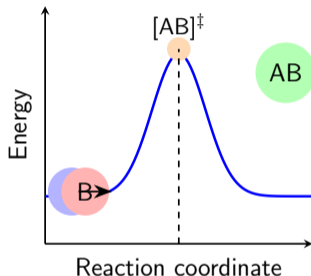
- 1 Introduction
- 2 Topic 18A: Collision Theory
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What is Reaction Dynamics?

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

Beyond traditional kinetics:

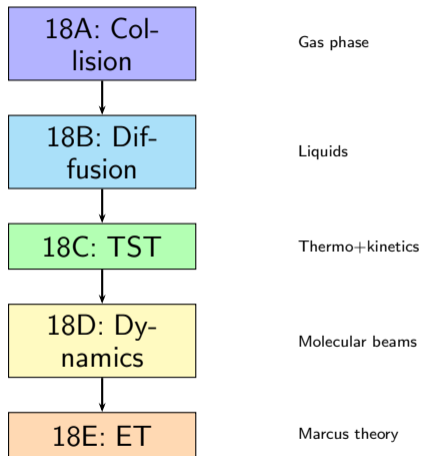
- How do molecules collide?
- What happens during collision?
- Where does energy go?
- What is the reaction path?
- How fast can reactions be?



Time scales:

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

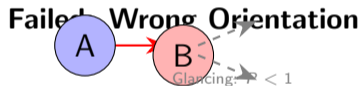
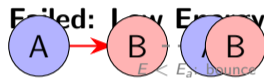
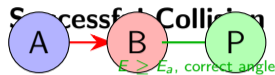
The Simplest Model:

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

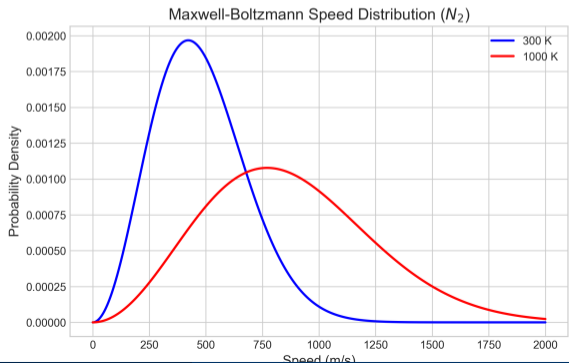
Maxwell-Boltzmann Distribution of Speeds:

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: $v_p = \left(\frac{2k_B T}{m} \right)^{1/2}$

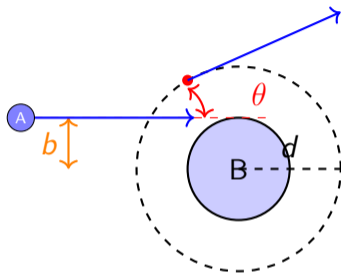


Collision Cross-Section - Hard Sphere Model

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: $\sigma = \pi d^2$

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



$$\sigma = \pi d^2$$

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 Δt , 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:

- σ = 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 N₂ (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 N₂: $m = 28 \text{ amu} = 4.65 \times 10^{-26} \text{ kg}$

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 N₂ (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 ε and $\varepsilon + d\varepsilon$:

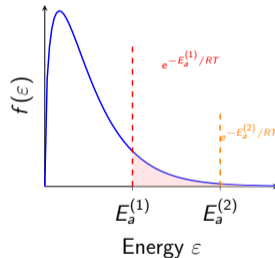
$$f(\varepsilon) = \frac{2\pi}{(\pi k_B T)^{3/2}} \varepsilon^{1/2} e^{-\varepsilon/k_B T}$$

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



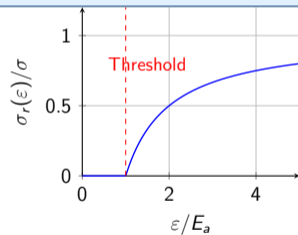
Reactive Cross-Section: Energy Dependence

The collision cross-section depends on collision energy ε :

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

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 σ
- 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 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_{exp} match A_{theory} ?

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

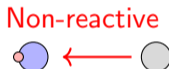
Orientation Matters:

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

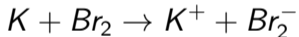
Case Study: The Harpoon Mechanism ($P > 1$)

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 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^* :

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

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

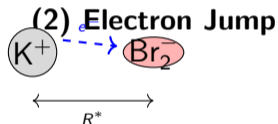
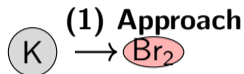
The Harpoon Mechanism: Visualization

Three-Step Process:

(1) Approach: K and Br₂ approach as neutrals

(2) Electron Jump: At R^* , electron transfers to Br₂

(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:

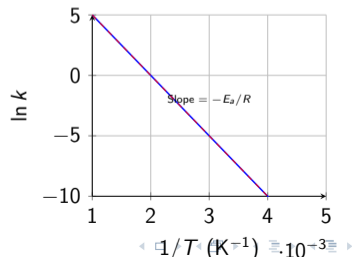
$$\ln k = \ln A + \frac{1}{2} \ln T - \frac{E_a}{RT}$$

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:** $A^* \xrightarrow{k_b} P$

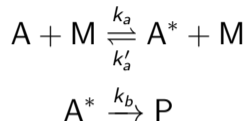
Key Idea:

- 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: $\frac{d[P]}{dt} = k_b[A^*]$

Steady-state approximation for A^* :

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

Solve for $[A^*]$:

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

Overall rate:

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

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:

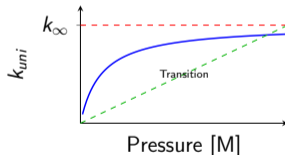
$$\frac{1}{k_{uni}} = \frac{1}{k_{\infty}} + \frac{k'_a}{k_a k_b [M]} = \frac{1}{k_{\infty}} + \frac{1}{k_a [M]}$$

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 , σ 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

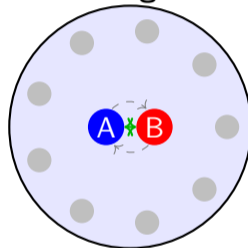
Gas Phase:

- 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

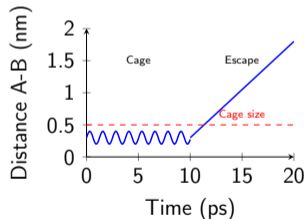
Encounter Pair

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

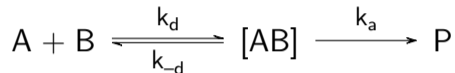
Slow Reaction

- $k_a \ll k_{-d}$ (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:



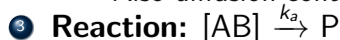
Elementary Steps:



- 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:

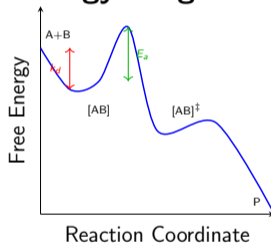
- $A + B \rightarrow [AB]$: Diffusion barrier (small)

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

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

Rearrange to resistance form:

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

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 η :

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

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 ² /s)
H ₂ 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:

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

Experimental Verification

Examples of Diffusion-Controlled Reactions:

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

Observations:

- H^+/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

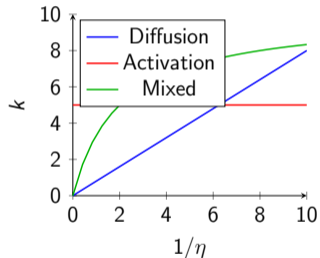
Kramers Theory:

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:

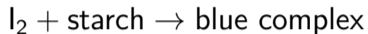
$$c(x) = Ae^{-x/\lambda} + Be^{x/\lambda}$$

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

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

Example: Iodine Diffusion in Starch Solution

Experiment: I_2 vapor diffuses into aqueous starch solution where it reacts:



Observation:

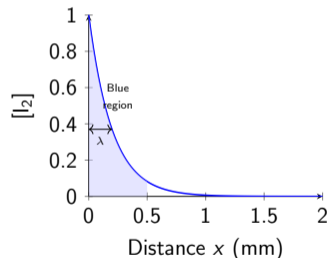
- Sharp blue front moves down column
- Front position: $x_f \propto \sqrt{t}$
- Width of colored region $\sim \lambda$

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.

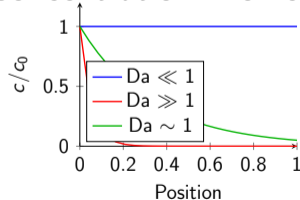
Physical Interpretation:

$Da \ll 1$: 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 = 5×10^{-10} m
- $T = 298$ K
- $\eta_{\text{water}} = 8.9 \times 10^{-4}$ Pa·s
- $k_B = 1.381 \times 10^{-23}$ J K⁻¹
- $N_A = 6.022 \times 10^{23}$ mol⁻¹

Solution:

1. **Contact distance:** $R^* = r_A + r_B = 1.0$ nm = 1.0×10^{-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/η , 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 λ 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

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 η 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)

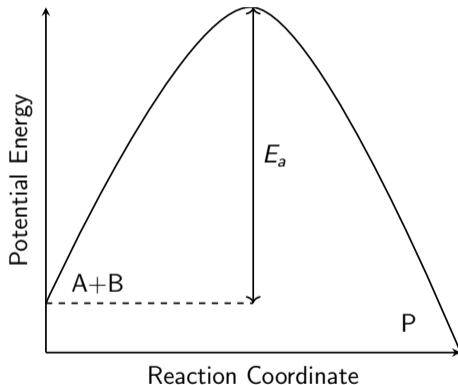
- The most sophisticated "classical" theory of reaction rates.
- Developed by Eyring, Evans, and Polanyi (1930s).
- **Key Concept:** Focus on the species at the top of the energy barrier.

Goals:

- Calculate rates from thermodynamic properties (ΔG^\ddagger , ΔH^\ddagger , ΔS^\ddagger).
- Explain kinetic salt effects.
- Explain kinetic isotope effects.

The Reaction Coordinate

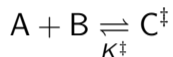
- **Reactants (A+B)**
- **Transition State (\ddagger):** Point of maximum energy.
- **Activated Complex (C^\ddagger):** The molecular species at the transition state.
- **Products (P)**



Fundamental Assumptions of TST

Three Key Assumptions:

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



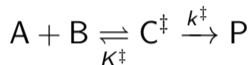
- ② **Factorization:** The reaction coordinate motion can be separated from other degrees of freedom.
- ③ **One-Way Crossing:** Once formed, C^\ddagger always proceeds to products (transmission coefficient $\kappa \approx 1$).

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 ν^\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: $k^\ddagger = \kappa \nu^\ddagger$.
- κ : Transmission coefficient (usually ≈ 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 ν^\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 κ

- Usually ≈ 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: $\Delta^\ddagger S^\circ > 0$

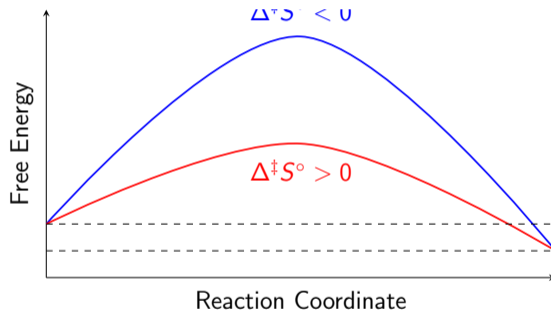
Near-Zero $\Delta^\ddagger S^\circ$:

- 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:

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

- 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°C .
- k_r° : 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

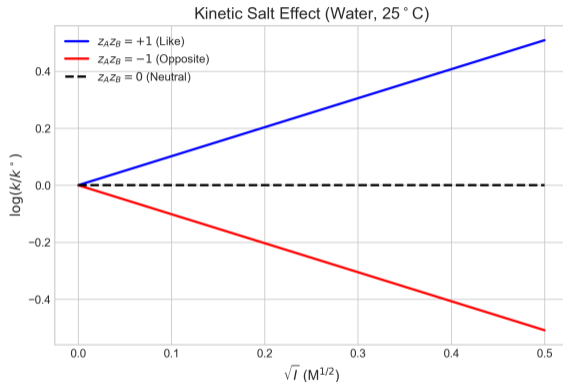
Opposite charges ($z_A z_B < 0$): Rate **decreases** with ionic strength.

- 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}C with ^{13}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 ν)
- C-D bond is stronger than C-H bond by ~ 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

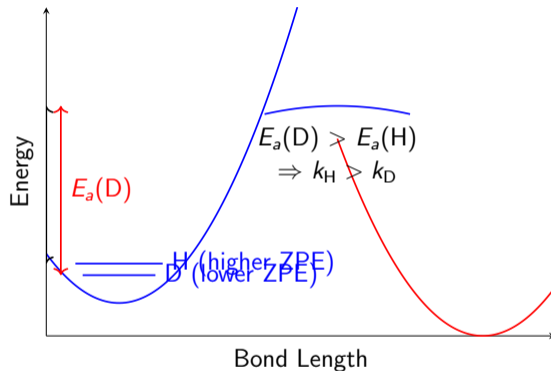
- $k_H/k_D = 2-10$ (typical range)
- Large effect indicates bond breaking at TS
- Example: C-H bond cleavage in radical abstraction

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 (H^+ , 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)

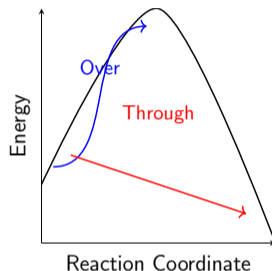
Quantum Tunneling (Part 2)

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.

- α : 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:

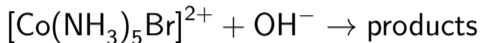
From Eyring plot: $\ln(k/T) = \ln(k_B/h) + \Delta^\ddagger S^\circ/R - \Delta^\ddagger H^\circ/(RT)$

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:

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

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

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 $k_D = 8.3 \times 10^5 \text{ M}^{-1}\text{s}^{-1}$.

- 1. Calculate the kinetic isotope effect k_H/k_D .
- 2. Is this a primary or secondary KIE?
- 3. What does this tell you about the mechanism?
- 4. Estimate the difference in activation energies.

Answers:

opsep=0pt,itemsep=1.5pt[(a)] KIE = 6.0 opsep=0pt,itemsep=1.5pt[(b)] Primary
KIE opsep=0pt,itemsep=1.5pt[(c)] C-H bond breaking occurs in rate-determining
step opsep=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	2.0×10^{-3}
0.1	3.2×10^{-3}
0.2	5.1×10^{-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 ≈ 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 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).

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?

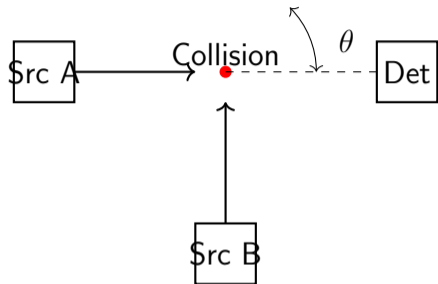
Problem with Bulk Gas Experiments:

- 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:

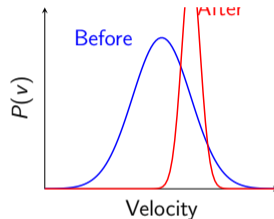
- **Sources:** Supersonic expansion (velocity selection)
- **Collision Zone:** Crossed beams at controlled angle
- **Detector:** Mass spectrometer + time-of-flight (TOF) analysis
- **Vacuum:** 10^{-6} to 10^{-8} torr to prevent multiple collisions

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:

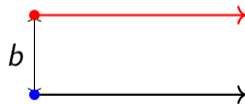
For two molecules with velocities \vec{v}_A and \vec{v}_B :

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

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_{max}
- Reactive cross-section: $\sigma_r = \pi b_{\text{max}}^2$



Differential Cross-Section

Definition:

We measure the **Differential Cross-Section**

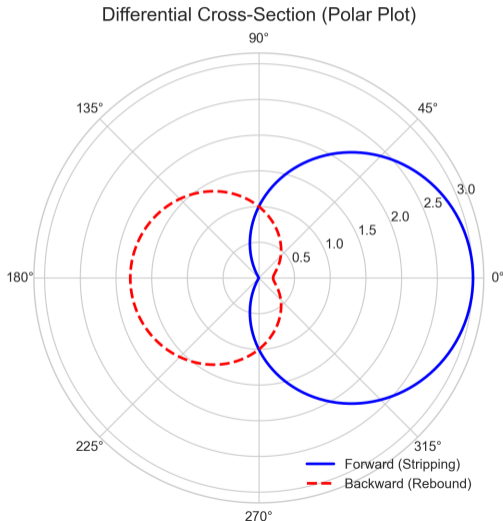
$\sigma(\theta, \phi)$:

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

- dN : Particles scattered into $d\Omega$
- I_{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 ($\theta \approx 90$):

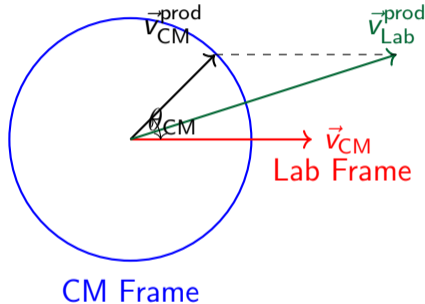
- Complex formation
- Long-lived intermediate
- Symmetric angular distribution

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 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:

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

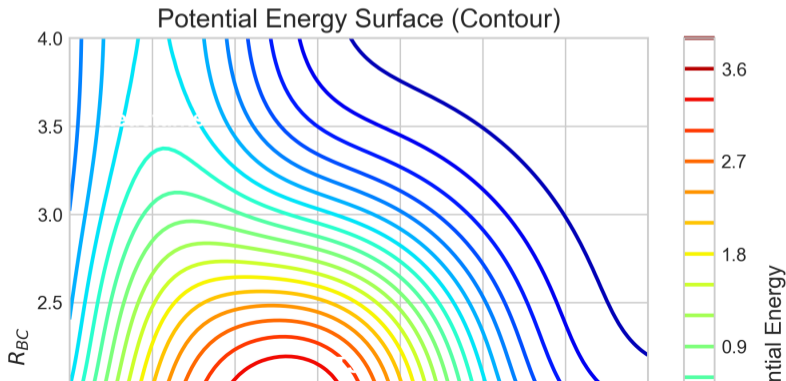
This is the **full quantum scattering matrix**!

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, ω B97X-D

How to Calculate PES (Part 2)

Theoretical Methods (continued):

③ Semi-Empirical/Fitted:

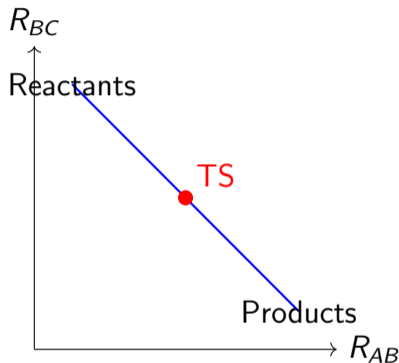
- LEPS (London-Eyring-Polanyi-Sato)
- Fit to experimental data
- Fast but less accurate

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_{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:

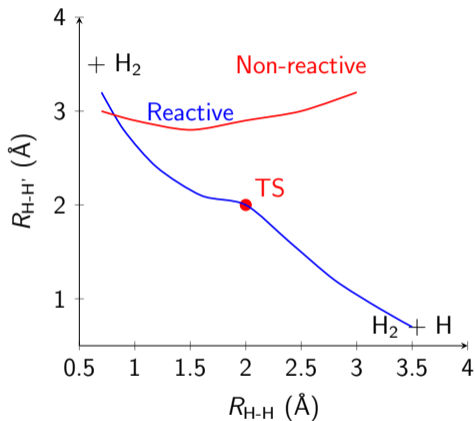
- Run thousands of trajectories
- Sample different b and initial conditions
- Calculate average cross-sections, energy distributions

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_{trans} (kinetic energy of products flying apart)
- **Vibration:** E_{vib} (internal vibration of product molecules)
- **Rotation:** E_{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 ρ 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")

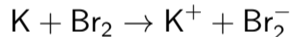
Reveals: Direct vs. complex mechanism

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 Br_2



- 2 Coulomb attraction pulls ions together (fast!)
- 3 K^+ approaches Br_2^- , forming KBr^- complex
- 4 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"?

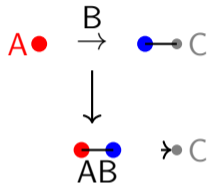
- Electron "thrown" from K at long range
- Like harpooning a whale from distance
- Ionic attraction then "reels in" the reactants
- Fast, efficient reaction

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 D₂ 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 σ_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 O₂ 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 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 \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
- ΔE = 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 ~ 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 μK 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

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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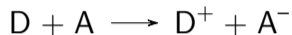


Or navigate to:

[Reaction Dynamics Interactive/](#)

Topic 18E: Overview

Electron Transfer (ET) Reactions



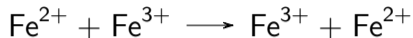
- **Simplest** class of reactions: just electron movement
- No bonds broken or formed in elementary step
- Ubiquitous in chemistry, biology, materials science
- **Marcus Theory:** Rudolph Marcus, Nobel Prize 1992

Examples:

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

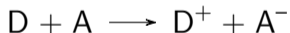
Types of Electron Transfer Reactions (Part 1)

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
- 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.

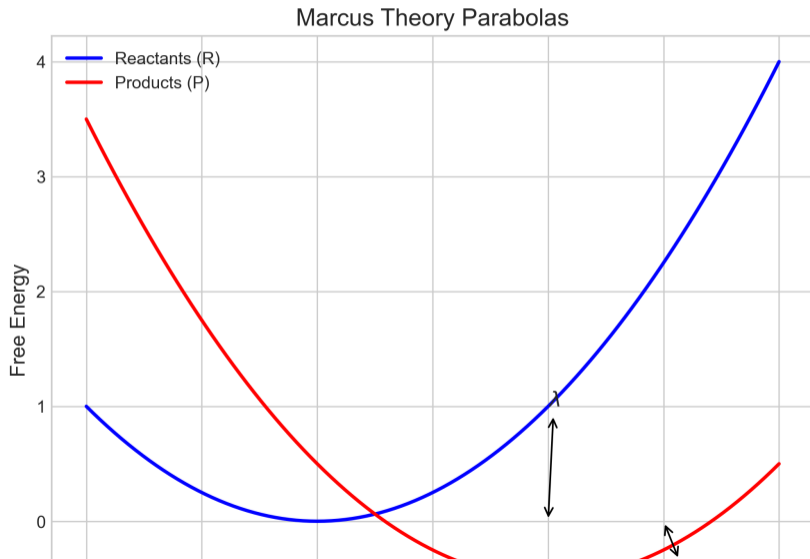
- Electron transfer time: $\sim 10^{-15}$ s (femtoseconds)
- Nuclear motion time: $\sim 10^{-13}$ s (100 fs)

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 (λ)

Total reorganization energy:

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

1. Inner Sphere (λ_{in}):

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

2. Outer Sphere (λ_{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 λ_{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
- ϵ_{op} : optical dielectric constant $= n^2$
- ϵ_s : static dielectric constant

Physical Meaning:

- Electronic polarization (fast) follows electron instantly: ϵ_{op}
- Nuclear/orientational polarization (slow) lags behind: ϵ_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 ν_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)
- λ : Reorganization energy (barrier height)
- κ : 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 ($-\Delta_r G^\circ > \lambda$):

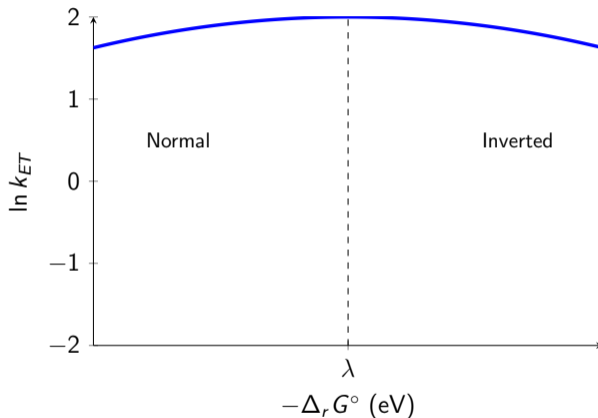
- Barrier *increases* as reaction becomes more exergonic
- Rate *decreases* with driving force (counter-intuitive!)

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

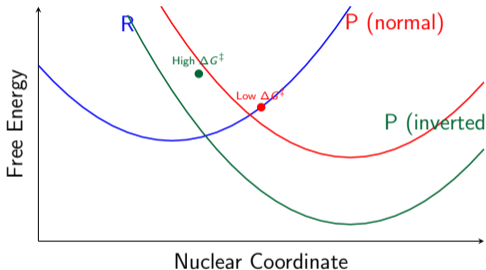
Marcus Parabola: Rate vs. Driving Force



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 λ 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
- β : decay parameter (depends on medium)

Rate Dependence:

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

Typical β values:

- Vacuum/protein: $\beta \approx 16\text{-}20 \text{ nm}^{-1}$ (fast decay)
- Through π -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:** $\frac{1}{\sqrt{4\pi\lambda k_B T}}$

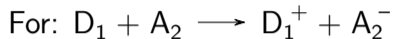
- Franck-Condon weighted density of states
- Pre-exponential factor

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 ≈ 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 β through aromatic residues
- Facilitate long-range transfer
- Guide electron path

Result: Efficient directional ET with minimal energy loss!

Worked Example 1: Calculating λ_{out}

Problem: Calculate λ_{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 ΔG^\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 ΔG^\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 ΔG^\ddagger
- Is this in normal, barrierless, or inverted region?
- If distance increases to 1.5 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)	λ (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 ΔG^\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 ΔG^\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 $-\Delta_r G^{\circ}$

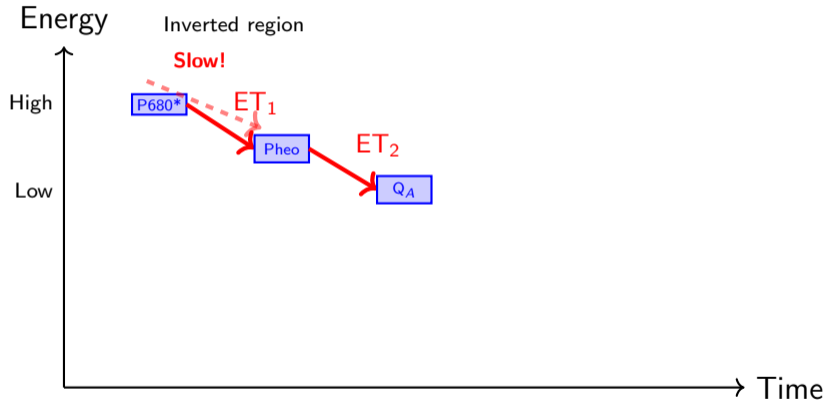
- ④ **Distance Dependence:** $k_{ET} \propto \exp(-\beta r)$

- Electron tunneling through barrier

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

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 β dependence
- **Biological ET Chains:** Photosynthesis, respiration
- **Real Systems:** Ru complexes, cytochrome c

Scan to Open:



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Comparison of Theories

Theory	Collision	Diffusion	TST	Marcus
Phase	Gas	Liquid	All	All
Key parameter	σ, E_a	D, η	$\Delta^\ddagger G^\circ$	λ
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	Yes	Yes
Quantum?	No	No	Limited	Yes
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

4 Quantum effects

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*