Focus 18: Reaction Dynamics

From Collisions to Electron Transfer

Physical Chemistry Course

Mindanao State University – Iligan Institute of Technology
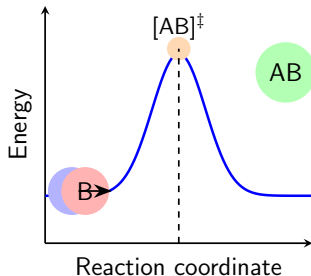
November 25, 2025

Outline

What is Reaction Dynamics?

Reaction Dynamics studies the detailed molecular mechanisms of chemical reactions
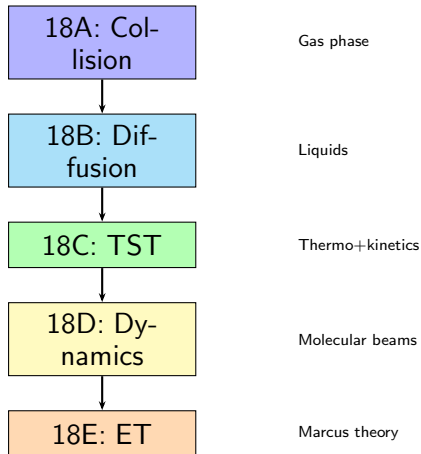
Beyond traditional kinetics:

- 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-μs

The Journey Through Focus 18

18A: Collision	Gas phase
↓	
18B: Diffusion	Liquids
↓	
18C: TST	Thermo+kinetics
↓	
18D: Dynamics	Molecular beams
↓	
18E: ET	Marcus theory

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
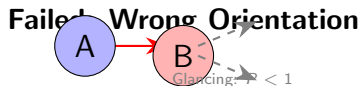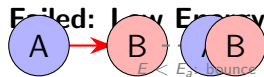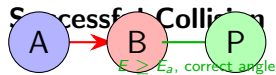
Topic 18A: Collision Theory

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

Successful Collision

A → B — P
$E \geq E_a$, correct angle

Failed: Low Energy

A → B B
$E < E_a$, bounce

Failed: Wrong Orientation

A → B
Glancing: $P < 1$
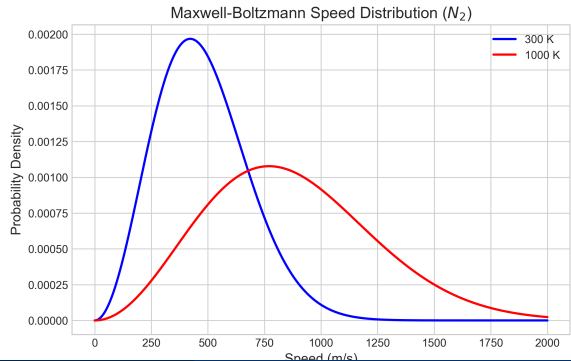
Kinetic Molecular Theory Background

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

Maxwell-Boltzmann Speed Distribution (N_2)

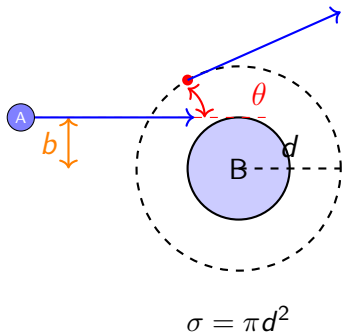# Collision Cross-Section - Hard Sphere Model

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: $\sigma = \pi d^2$

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

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

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: $\bar{v}_{rel} = \left(\frac{8 k_B T}{\pi \mu} \right)^{1/2}$
- 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 m^{-3} s^{-1}

Special Case: Identical Molecules

For collisions between identical molecules $A + A$:

Modified Formula:

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

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

For identical molecules:

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

Worked Example: Collision Rate for N_2 (Part 1)

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

Step 1: Number density from ideal gas law

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

Step 2: Mean relative speed

Mass of N_2: $m = 28$ amu $= 4.65 \times 10^{-26}$ kg

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

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

Step 3: Calculate collision density

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

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

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

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:

- $Z_{AB} \sim 10^{34}$ collisions m^{-3} 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 $\varepsilon + d\varepsilon$:
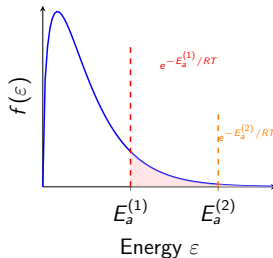
$$f(\varepsilon) = \frac{2\pi}{(\pi k_B T)^{3/2}} \varepsilon^{1/2} e^{-\varepsilon/k_B T}$$

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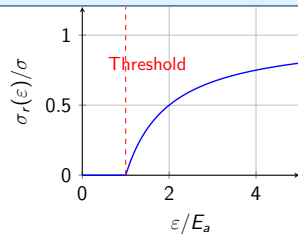
The linear rise from threshold is a simplified model; real reactions may have different energy dependencies.

Derivation of the Collision Theory Rate Constant

Starting Point: Reactive collision rate per unit volume

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

Key Steps:

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

Result after integration:

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

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: $A \sim 10^{10} - 10^{11}$ dm^3 mol^{-1} 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 $H_2 + I_2 \rightarrow 2HI$ at 600 K

Given:
- $\sigma = 0.30$ nm^2 = 3.0×10^{-19} m^2
- $m_{H_2} = 2.016$ amu $= 3.35 \times 10^{-27}$ kg
- $m_{I_2} = 253.8$ amu $= 4.22 \times 10^{-25}$ kg

Step 1: Reduced mass

$$\mu = \frac{m_{H_2} \cdot m_{I_2}}{m_{H_2} + m_{I_2}} = \frac{3.35 \times 10^{-27} \times 4.22 \times 10^{-25}}{4.25 \times 10^{-25}} = 3.32 \times 10^{-27} \text{ kg}$$

Step 2: Mean relative speed

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

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):

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

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} ($dm^3\ mol^{-1}\ s^{-1}$)	A_{theory} ($dm^3\ mol^{-1}\ s^{-1}$)	$P = A_{exp}/A_{theory}$
$2NOCl \rightarrow 2NO + Cl_2$	9.4×10^9	5.9×10^{10}	0.16
$2ClO \rightarrow Cl_2 + O_2$	6.3×10^7	2.5×10^{10}	0.0025
$H_2 + C_2H_4 \rightarrow C_2H_6$	1.2×10^6	7.3×10^{10}	1.7×10^{-5}
$K + Br_2 \rightarrow KBr + Br$	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:

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

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)

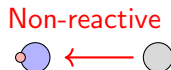# The Steric Factor: Reactive Geometry

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:
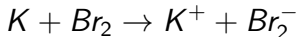

Red dot = reactive site

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

Reaction: $K + Br_2 \rightarrow KBr + Br$ ($P \approx 4.8!$)

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

Mechanism:

1. K has low ionization energy ($I_K = 4.34$ eV)
2. Br_2 has high electron affinity ($E_{ea} = 2.55$ eV)
3. At critical distance R^*, electron transfer becomes favorable:

$$K + Br_2 \rightarrow K^+ + Br_2^-$$

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

Estimate of R^*:

$$I_K - E_{ea} = \frac{e^2}{4\pi\varepsilon_0 R^*}$$

$$R^* \approx 0.8 \text{ nm} \quad (\text{vs. } d \approx 0.3 \text{ nm})$$

The Harpoon Mechanism: Visualization

Three-Step Process:

(1) Approach: K and Br_2 approach as neutrals

(2) Electron Jump: At R^*, electron transfers to Br_2

(3) Harpoon: Coulombic attraction pulls ions together
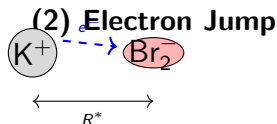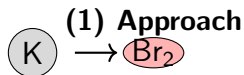
> **Reactive cross-section much larger than geometric!**

(1) Approach

$K \longrightarrow Br_2$

(2) Electron Jump

$K^+ \dashrightarrow Br_2$

$\longleftrightarrow R^*$

(3) "Harpoon"

$K^+ Br_2$

Temperature Dependence of Reaction Rates

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

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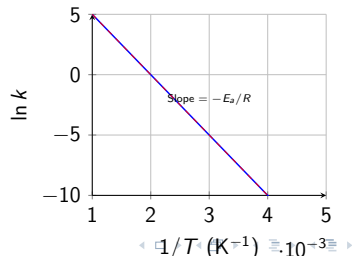
$$\ln k = \ln A + \frac{1}{2}\ln T - \frac{E_a}{RT}$$

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

Slope $= -E_a/R$

$1/T$ (K^{-1}) $\cdot 10^{-3}$

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:

$$A + M \underset{k_a'}{\overset{k_a}{\rightleftharpoons}} A^* + M$$

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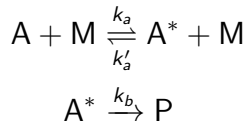
Rate of product formation: $\frac{d[P]}{dt} = k_b[A^*]$

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:

$$\frac{d[P]}{dt} = \frac{k_a k_b [M]}{}$$

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: $A^* \to P$
- 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

Rearrange to Lindemann form:
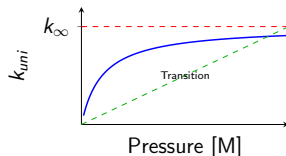
$$\frac{1}{k_{uni}} = \frac{1}{k_\infty} + \frac{k_a'}{k_a k_b [M]} = \frac{1}{k_\infty} + \frac{1}{k_a [M]}$$

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!

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?

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 ($\sim 10^{10} - 10^{11}$ dm^3 mol^{-1} 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 $\sigma = 0.40$ nm^2.

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

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

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

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

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 ($\sim 10^{25}$ m^{-3})
- Long mean free path (~ 100 nm)
- Collision frequency $\sim 10^{10}$ s^{-1}

Liquid Phase:

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

Solvent Cage Effect:
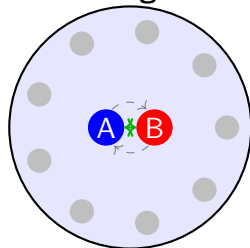
Trapped by solvent
Multiple collisions

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: $\sim 10^{13}$ s^{-1}
- Cage lifetime: $\sim 10^{-11}$ s
- Effective "single" encounter

Encounter Dynamics:
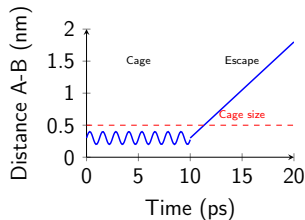
Two Limiting Regimes

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 ($E_a \approx E_{viscosity}$)
- Examples: Radical recombination, H^+ + 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:

$$A + B \underset{k_{-d}}{\overset{k_d}{\rightleftharpoons}} [AB] \xrightarrow{k_a} P$$

Elementary Steps:
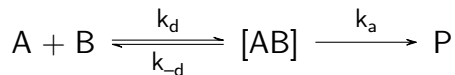
1. **Diffusion together:** $A + B \xrightarrow{k_d} [AB]$
   - k_d: Diffusion rate constant
   - Formation of encounter pair
   - Limited by diffusion coefficient D

2. **Diffusion apart:** $[AB] \xrightarrow{k_{-d}} A + B$
   - k_{-d}: Separation rate constant
   - Breakup of encounter pair
   - Also diffusion-controlled

3. **Reaction:** $[AB] \xrightarrow{k_a} P$
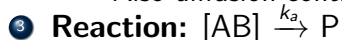
Mechanism: Energy Diagram

Free Energy Profile:

- A + B → [AB]: Diffusion barrier (small)

AB → [AB]‡: Activation barrier

AB ‡ → P: Reaction

The rate-limiting step depends on relative barrier heights!

Energy Diagram:
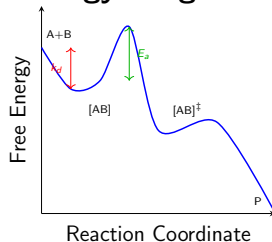
Steady-State Treatment (Part 1)

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

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

Solve for [AB]:

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

Rate of product formation:

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

Steady-State Treatment (Part 2)

Overall rate constant:

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

Rearrange to resistance form:

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

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

Two resistances in series: diffusion and activation

Interpretation: Like electrical resistances, the slower step dominates!

Limiting Cases from the General Expression

General Result:

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

Case 1: Diffusion Control

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

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

- Rate independent of k_a
- Maximum possible rate
- $k_{eff} \sim 10^{10}$ M^{-1} s^{-1}
- Weak temperature dependence
- $E_a \approx E_{viscosity} \approx 10 - 20$ 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 (mol m^{-2} s^{-1}) - flow rate per unit area
- D: Diffusion coefficient (m^2 s^{-1})
- $\frac{\partial c}{\partial x}$: Concentration gradient
- Negative sign: Flow from high to low concentration

Typical Values: $D \sim 10^{-9}$ m^2 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_2O	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 $r \to \infty$: $[B] = [B]_{bulk}$ (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):

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

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:

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

Smoluchowski Result for k_d

From flux calculation:

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

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

$$\boxed{k_d = 4\pi R^* D N_A}$$

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

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

Remarkable Result:

Numerical Estimate of Diffusion Limit

For water at 25°C:

Given:

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

Calculation:

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

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

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

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 (M^{-1} s^{-1})	E_a (kJ/mol)
$H^+ + OH^- \to H_2O$	1.4×10^{11}	13
$H_3O^+ + OH^-$	1.3×10^{11}	12
$\bullet\ CH_3 + \bullet\ CH_3$	$\sim 10^{10}$	8
$Fe^{2+} + Fe^{3+}$ (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
- Fe^{2+}/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
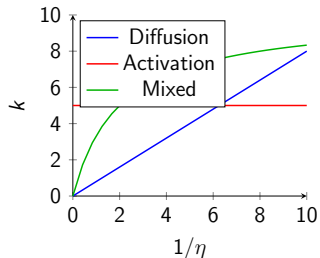
Kramers Theory:
More sophisticated treatment including friction:

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

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

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 ($\partial c/\partial t = 0$):

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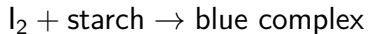
General solution:

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

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:

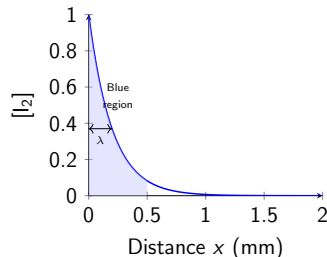$$I_2 + \text{starch} \rightarrow \text{blue complex}$$

Observation:

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

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

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

Concentration Profile:

The Damköhler Number

Dimensionless parameter comparing reaction and diffusion rates:

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

where L is characteristic length scale.
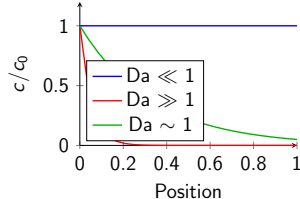
Physical Interpretation:

Da $\ll$ 1: Diffusion-limited

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

Da $\gg$ 1: Mass-transfer limited

Concentration Profiles:

Worked Example 1: Calculate k_d for Specific Molecules

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

Given:
- $r_A = r_B = 0.5$ nm $= 5 \times 10^{-10}$ m
- $T = 298$ K
- $\eta_{water} = 8.9 \times 10^{-4}$ 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 $= 1.0 \times 10^{-9}$ m
2. Diffusion coefficient for each molecule:
$$D = \frac{k_B T}{6\pi\eta r} = \frac{1.381 \times 10^{-23} \times 298}{6\pi \times 8.9 \times 10^{-4} \times 5 \times 10^{-10}} = 4.9 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$$

Worked Example 1 (continued)

3. Combined diffusion coefficient:

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

4. Smoluchowski rate constant:

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

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

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

Convert to M^{-1} s^{-1}:

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

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

Worked Example 2: Determine Reaction Control Regime

Problem: A reaction has $k_{obs} = 5 \times 10^8$ M^{-1} s^{-1} in water at 25°C. The activation energy is $E_a = 25$ 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: $E_a \sim 10 - 20$ kJ/mol
- Observed: $E_a = 25$ 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
   - $k_{eff}^{-1} = k_d^{-1} + (Kk_a)^{-1}$
   - Two resistances in series
3. **Smoluchowski Theory:** $k_d = 4\pi R^* D N_A \approx \frac{8RT}{3\eta}$
   - Diffusion limit: $\sim 10^{10}$ M^{-1} 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 ($\eta = 0.89$ mPa·s).

Problem 2: For a reaction with $k_{obs} = 2 \times 10^9$ M^{-1} s^{-1} at 25°C, estimate what fraction of encounters lead to reaction. Assume $k_d = 7 \times 10^9$ M^{-1} 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 $k = 1.0$ s^{-1} and $D = 10^{-9}$ m^2 s^{-1}.

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

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

Scan to Open:

Or navigate to:
Reaction_Dynamics_Interactive/

Topic 18C: Overview

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

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

Goals:

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

The Reaction Coordinate

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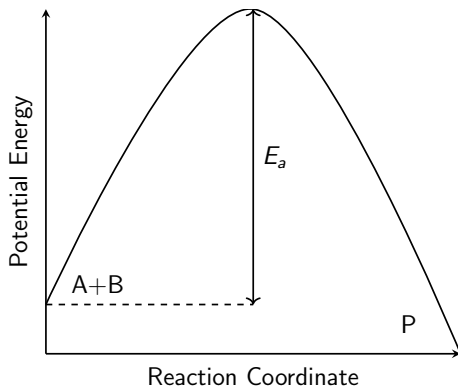
Fundamental Assumptions of TST

Three Key Assumptions:

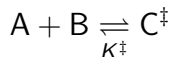1. **Quasi-Equilibrium:** The activated complex $C^{\ddagger}$ is in equilibrium with reactants.

$$A + B \underset{K^{\ddagger}}{\rightleftharpoons} C^{\ddagger}$$

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.

$$A + B \underset{K^\ddagger}{\rightleftharpoons} C^\ddagger \xrightarrow{k^\ddagger} P$$
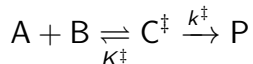
The rate of reaction is:

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

- $[C^\ddagger]$: 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:

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

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

Factorization of Reaction Coordinate

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

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

For this mode:

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

Therefore:

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

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

Rate of Decay

How fast does $C^{\ddagger}$ 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:

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

Rate of reaction:

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

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

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

The frequency $\nu^{\ddagger}$ cancels!

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

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: $\frac{k_B T}{h} \approx 6.2 \times 10^{12}$ 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, $\approx 6 \times 10^{12}$ 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 $k_r \approx 6 \times 10^{12}$ s^{-1} - the diffusion-limited rate.

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:

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

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 $\Delta^{\ddagger} S^{\circ}$.

Physical Meaning:

$$\Delta^{\ddagger}S^{\circ} = S^{\circ}_{C^{\ddagger}} - S^{\circ}_{A} - S^{\circ}_{B}$$

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

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

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

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

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

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

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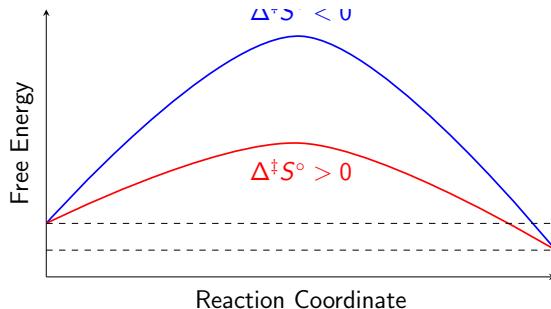- Typically: $\Delta^{\ddagger}S^{\circ} > 0$

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

- Similar structure to reactants
- Minor reorganization at transition state

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

Free Energy Diagrams

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

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

Hammond Postulate

Relating TS structure to thermodynamics:

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

Implications:

Endergonic Reaction:

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

Exergonic Reaction:

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

Application: Helps predict effects of substituents on reaction rates.

The Kinetic Salt Effect

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

Debye-Hückel Theory predicts:

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

- I: Ionic strength of solution $= \frac{1}{2} \sum_i c_i z_i^2$.
- z_A, z_B: Charges of reactants.
- A: Constant $= 0.509$ 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: $S_2O_8^{2-} + I^-$
- $z_A z_B = (-2)(-1) = +2 > 0$: rate increases
- Ionic atmosphere reduces repulsion

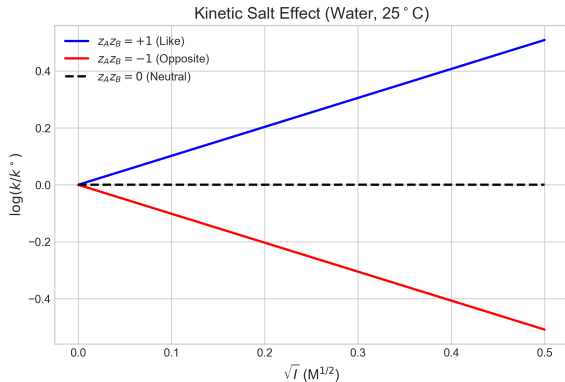**Opposite charges ($z_A z_B < 0$):** Rate decreases with ionic strength.

- Example: $[Co(NH_3)_5Br]^{2+} + OH^-$
- $z_A z_B = (+2)(-1) = -2 < 0$: 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.

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

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

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

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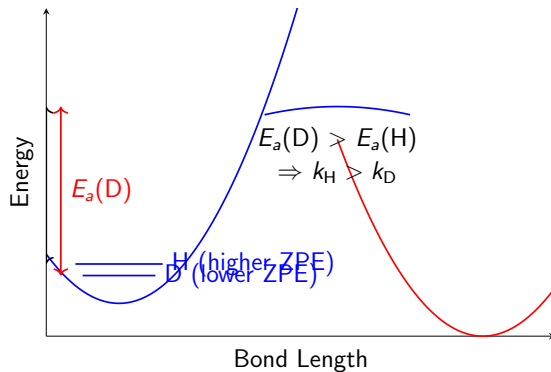
Difference in E_a: $\Delta E_a \approx \frac{1}{2} h(\nu_H - \nu_D) \approx 5$ kJ/mol

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:

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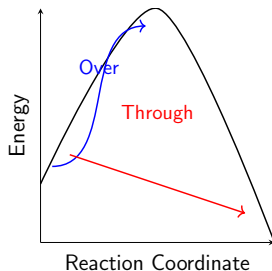- Unusual temperature dependence (rate less sensitive to T)

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:** $E_a = E_0 + \alpha \Delta H_{rxn}$

Worked Example 1: Calculating Rate Constant

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

Solution:

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

$$\Delta^{\ddagger}G^{\circ} = \Delta^{\ddagger}H^{\circ} - T\Delta^{\ddagger}S^{\circ}$$

$$= 85000 - 298 \times (-45) = 85000 + 13410 = 98410 \text{ J/mol}$$

Step 2: Apply Eyring equation

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

$$= \frac{1.381 \times 10^{-23} \times 298}{6.626 \times 10^{-34}} \times e^{-98410/(8.314 \times 298)}$$

$$= 6.21 \times 10^{12} \times e^{-39.7} = 6.21 \times 10^{12} \times 7.84 \times 10^{-18}$$

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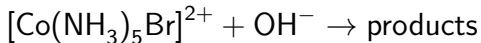
From Eyring plot: $\ln(k/T) = \ln(k_B/h) + \Delta^{\ddagger}S^{\circ}/R - \Delta^{\ddagger}H^{\circ}/(RT)$

Calculate slope:

$$\text{slope} = \frac{\ln(k_2/T_2) - \ln(k_1/T_1)}{1/T_2 - 1/T_1}$$

$$= \frac{\ln(8.2 \times 10^{-3}/320) - \ln(1.5 \times 10^{-3}/300)}{1/320 - 1/300}$$

$$= \frac{-10.05 - (-10.72)}{-2.08 \times 10^{-4}} = \frac{0.67}{-2.08 \times 10^{-4}} = -3221 \text{ K}$$

Worked Example 3: Salt Effect

Problem: For the reaction:

$$[Co(NH_3)_5Br]^{2+} + OH^- \rightarrow \text{products}$$

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

Solution:
Charges: $z_A = +2$, $z_B = -1$, so $z_A z_B = -2$
Apply salt effect equation:

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

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

Practice Problem 1

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

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

Answers:

opsep=0pt,itemsep=1pt[(a)]$\Delta^\ddagger G^\circ = 83.8$
kJ/molopsep=0pt,itemsep=1pt[(b)]$k = 9.8 \times 10^{-3}$
s^{-1}opsep=0pt,itemsep=1pt[(c)]More ordered
($\Delta^\ddagger S^\circ < 0$)opsep=0pt,itemsep=1pt[(d)]$k(350\ \text{K}) = 0.51$ s^{-1} ($50\times$ faster)

Practice Problem 2

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

- a) Calculate the kinetic isotope effect k_H/k_D.
- b) Is this a primary or secondary KIE?
- c) What does this tell you about the mechanism?
- d) Estimate the difference in activation energies.

Answers:

(a) KIE $= 6.0$

(b) Primary KIE

(c) C-H bond breaking occurs in rate-determining step

(d) $\Delta E_a \approx 4.4$ kJ/mol (from $\ln(6.0) = \Delta E_a/(RT)$)

Practice Problem 3

Problem: For an ionic reaction:

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

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

Answers:

opsep=0pt,itemsep=1pt[(a)]Slope $\approx$ 2.0opsep=0pt,itemsep=1pt[(b)]From slope $= 2Az_A z_B$: $z_A z_B = +2$opsep=0pt,itemsep=1pt[(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:

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

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

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

Answer: $\Delta^\ddagger H^\circ = 70.7$ kJ/mol, $\Delta^\ddagger S^\circ = +14.5$ J/(mol·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.

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

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
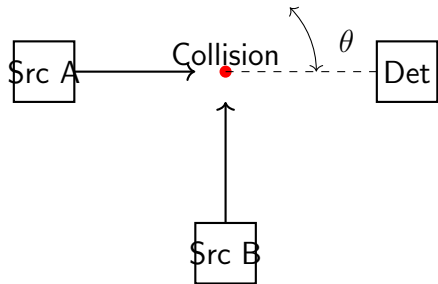
Components:

- **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
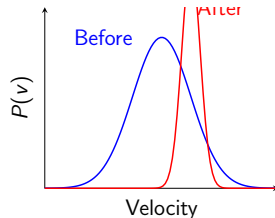
After Expansion:

- Narrow velocity distribution
- Effective $T \sim 1\text{-}10$ K
- All molecules move with $v \approx \bar{v}$

Result: Collision energy is well-defined!

Collision Energy and Impact Parameter

Center-of-Mass Energy:

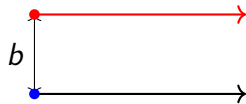For two molecules with velocities $\vec{v}_A$ and $\vec{v}_B$:

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

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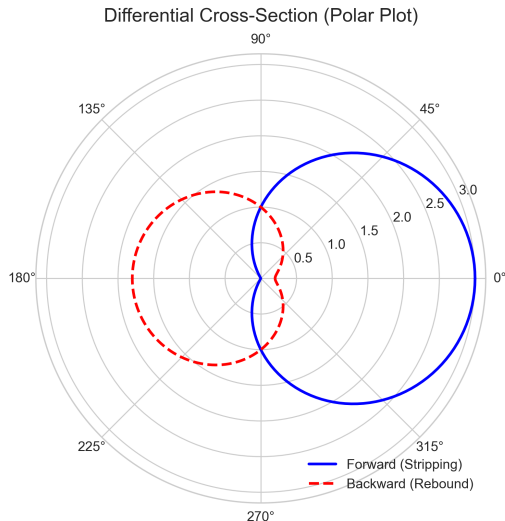
$$dN = \sigma(\theta, \phi) I_{\text{inc}} d\Omega$$

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

Information Content:
- Scattering probability vs angle

Differential Cross-Section (Polar Plot)

— Forward (Stripping)
--- Backward (Rebound)

Types of Scattering Patterns

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

- "Stripping" mechanism
- Grazing collision (large b)
- Fast, direct reaction
- Example: $K + Br_2 \rightarrow KBr + Br$
- 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: $K + CH_3I$
- Products bounce back

Newton Diagram

Relating Lab Frame to Center-of-Mass Frame:

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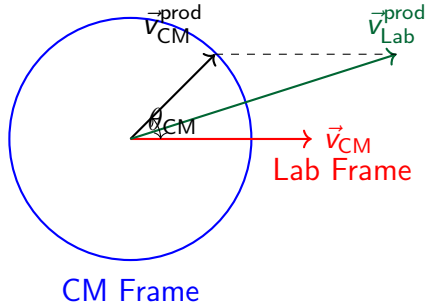
$$\vec{v}_{\text{Lab}} = \vec{v}_{\text{CM}}^{\text{prod}} + \vec{v}_{\text{CM}}$$

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: $H + D_2(v=0, J=0) \rightarrow HD(v', J') + D$

- 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/Zeeman selection
- **State detection:** Laser-induced fluorescence (LIF), REMPI

Ultimate Goal: Complete characterization:

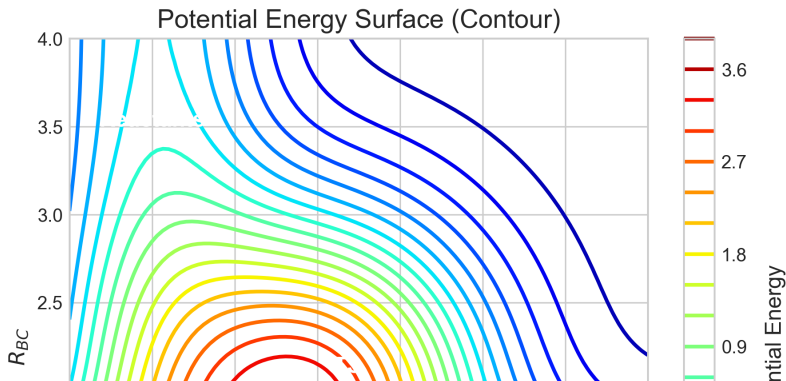$$\sigma(E_{\text{coll}}, v, J, b \to v', J', \theta, \phi)$$

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}.

Potential Energy Surface (Contour)

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, ωB97X-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.
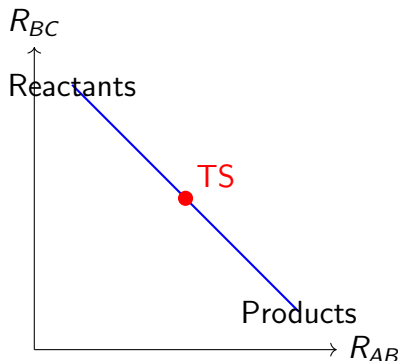
Intrinsic Reaction Coordinate (IRC): Path of steepest descent from TS to reactants and products.

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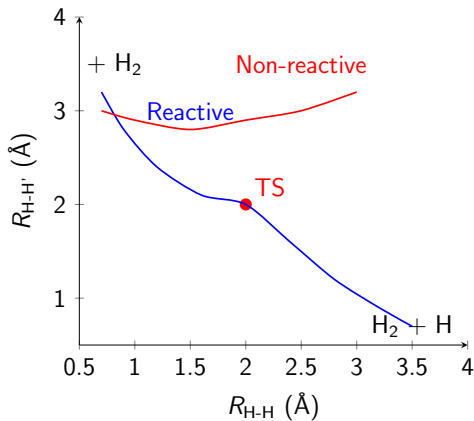
Blue: Passes through TS region $\rightarrow$ reaction. Red: Turns back $\rightarrow$ no reaction.

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: $K + Br_2$ (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: $H + Cl_2$
- 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 $\sigma_r(E_{\text{trans}}, v = 0)$ vs. $\sigma_r(E_{\text{trans}}, v = 1)$
- 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

Classic Example of Attractive Surface

Mechanism:

1. At large distance ($R \sim 6$ Å): Electron jumps from K to Br_2
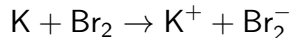
$$K + Br_2 \rightarrow K^+ + Br_2^-$$

2. Coulomb attraction pulls ions together (fast!)
3. K^+ approaches Br_2^-, forming KBr^- complex
4. Br^- leaves with high kinetic energy

Harpoon Mechanism: $K + Br_2 \rightarrow KBr + Br$ (Part 2)

Experimental Observations:

- Very large cross-section: $\sigma \sim 200$ Å^2 (vs. ~ 10 Å^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
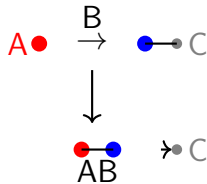
Example: $K + CH_3I \rightarrow KI + CH_3$

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

Quantum Effects in Dynamics (Part 2)

When Classical Trajectories Fail (continued):

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

4. **Quantized Product States:**
   - Classical: continuous energy distribution
   - Quantum: discrete vibrational/rotational levels

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

Worked Example 1: Collision Energy

Problem: In a crossed molecular beam experiment, H atoms (mass = 1 amu) with velocity 2000 m/s collide with D_2 molecules (mass = 4 amu) at rest. Calculate the collision energy.

Solution:
Step 1: Calculate reduced mass

$$\mu = \frac{m_H \cdot m_{D_2}}{m_H + m_{D_2}} = \frac{1 \times 4}{1 + 4} = 0.8 \text{ amu}$$

Convert to kg: $\mu = 0.8 \times 1.66 \times 10^{-27} = 1.33 \times 10^{-27}$ kg
Step 2: Relative velocity

$$v_{rel} = v_H - v_{D_2} = 2000 - 0 = 2000 \text{ m/s}$$

Step 3: Collision energy

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

Worked Example 2: Reactive Cross-Section

Problem: For the reaction $H + D_2 \rightarrow HD + D$, the maximum impact parameter for reaction at $E_{coll} = 0.5$ eV is $b_{max} = 1.8$ Å. Calculate:

a) The reactive cross-section σ_r

b) The reaction probability if geometric cross-section is $\sigma_{geom} = 10$ Å^2

Solution:

(a) Reactive cross-section:

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

(b) Reaction probability (opacity function):

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

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 $E_{coll} = 0.1$ eV:

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

Calculate the average translational and rotational energy of products.

Solution:

Total available energy:

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

Energy remaining for translation + rotation:

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

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

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

Practice Problem 1

Problem: In a crossed beam experiment, Ar atoms (40 amu) with $v = 1500$ m/s collide with O_2 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) $v_{rel} = \sqrt{1500^2 + 800^2} = 1700$ m/s

(b) $E_{coll} = 0.17$ eV

(c) $v_{CM} = 1056$ m/s (along Ar beam direction)

Practice Problem 2

Problem: For the reaction $Cl + HBr \rightarrow HCl + Br$:

- Barrier is "late" (in product valley)
- $E_a = 8$ 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) $E_a^{eff} \approx 8 - 0.3(25) \approx 0.5$ 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 $\sigma_0 = 15 \ \text{Å}^2/\text{sr}$.

- (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) $\sigma_{\text{total}} = 20\pi \ \text{Å}^2 \approx 63 \ \text{Å}^2$

Practice Problem 4

Problem: For $H + H_2 \rightarrow H_2 + H$ reaction:

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

(a) What causes the difference?

(b) Estimate the effective tunneling distance if the barrier width is 0.5 Å

(c) Would the isotopic reaction $D + D_2 \rightarrow D_2 + D$ show a larger or smaller difference?

Answers:

(a) Quantum tunneling through the barrier

(b) Tunneling reduces effective barrier by ~ 8 kJ/mol (20%)

(c) Smaller difference - heavier mass reduces tunneling probability:

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

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

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 $\rightarrow$ vibrationally hot products
   - Repulsive surface $\rightarrow$ 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

Scan to Open:

Or navigate to:

`Reaction Dynamics Interactive/`

Topic 18E: Overview

Electron Transfer (ET) Reactions

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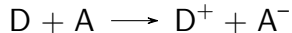
- **Simplest** class of reactions: just electron movement
- No bonds broken or formed in elementary step
- Ubiquitous in chemistry, biology, materials science
- **Marcus Theory:** Rudolph Marcus, Nobel Prize 1992

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:

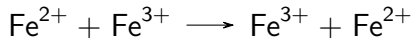$$Fe^{2+} + Fe^{3+} \longrightarrow Fe^{3+} + Fe^{2+}$$

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

2. Cross Reactions:

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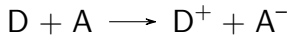
- $\Delta_r G^\circ \neq 0$
- Thermodynamically driven
- Rate depends on driving force AND reorganization

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

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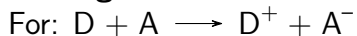
$$\Delta_r G^\circ = -F(E_{D^+/D} - E_{A/A^-})$$

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

Example:

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

Marcus Theory Parabolas
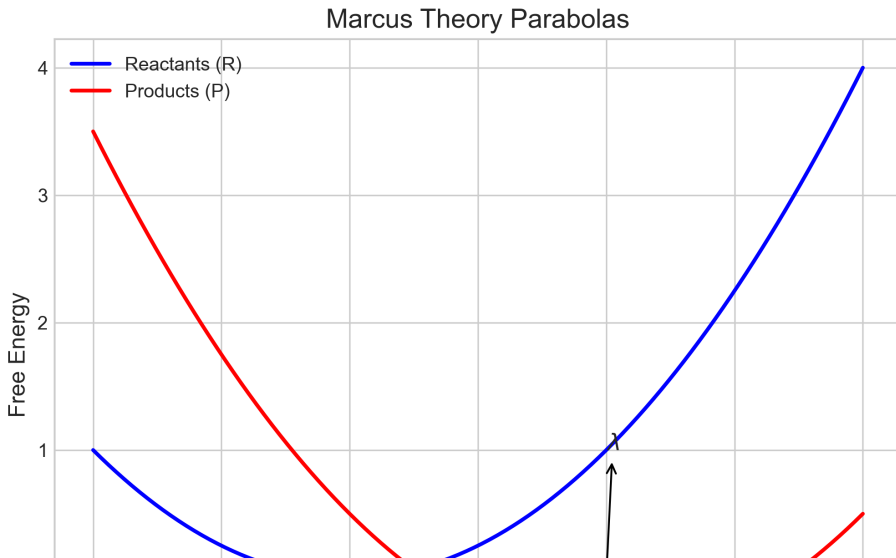
Reorganization Energy (λ)

Total reorganization energy:

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

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

Dielectric Continuum Model:

$$\lambda_{\text{out}} = \frac{e^2}{4\pi\varepsilon_0} \left(\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{d} \right) \left(\frac{1}{\varepsilon_{\text{op}}} - \frac{1}{\varepsilon_s} \right)$$

- 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

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

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

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 ($\sim 10^{13}$ 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)

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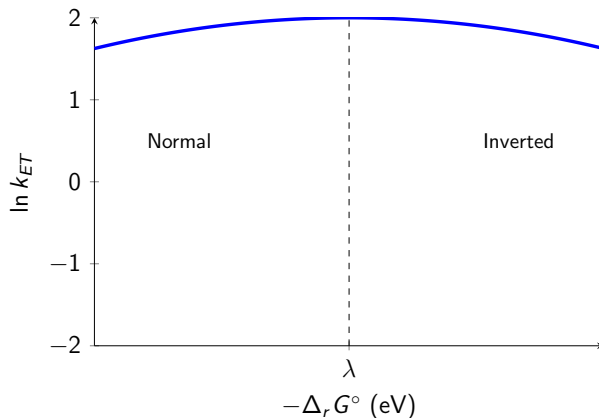
Key Prediction: After reaching maximum at $-\Delta_r G^\circ = \lambda$, rate decreases!

Why does rate decrease with more driving force?
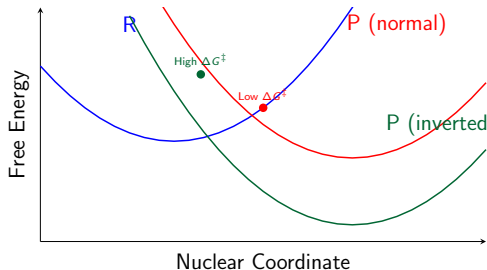
In inverted region: Surfaces intersect at high energy because product well is too far down.

Challenge: Hard to observe - requires large $|\Delta_r G°|$ while keeping λ small.

Early Evidence (Close & 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: $\beta \approx$ 16-20 nm^{-1} (fast decay)
- Through π-conjugated bridge: $\beta \approx$ 2-5 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.

For: $D_1 + A_2 \longrightarrow D_1^+ + A_2^-$
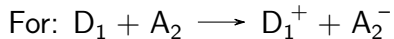
$$k_{12} = \sqrt{k_{11} k_{22} K_{12} f_{12}}$$

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:** P680 $\rightarrow$ Pheophytin $\rightarrow$ Q_A $\rightarrow$ Q_B
- **Respiration:** NADH $\rightarrow$ Complex I $\rightarrow$ Q $\rightarrow$ Complex III $\rightarrow$ Cyt c $\rightarrow$ Complex IV $\rightarrow$ 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 ($\varepsilon_s = 80$, $n = 1.33$).

Solution:

$$\lambda_{\text{out}} = \frac{e^2}{4\pi\varepsilon_0}\left(\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{d}\right)\left(\frac{1}{n^2} - \frac{1}{\varepsilon_s}\right)$$

Constants: $\frac{e^2}{4\pi\varepsilon_0} = 1.44$ eV·nm

$$\lambda_{\text{out}} = 1.44\left(\frac{1}{2(0.3)} + \frac{1}{2(0.3)} - \frac{1}{0.8}\right)\left(\frac{1}{1.77} - \frac{1}{80}\right)$$

$$= 1.44(1.67 + 1.67 - 1.25)(0.565 - 0.0125)$$

$$= 1.44(2.09)(0.553) = 1.66 \text{ eV}$$

Worked Example 2: Marcus Activation Energy

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

a) The activation energy $\Delta G^\ddagger$
b) The rate constant at 298 K (assume $\nu_n = 10^{13}$ 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:

$$k_{ET} = 10^{13} \exp\left(-\frac{0.09 \times 96.5}{8.314 \times 0.298}\right) = 10^{13} \exp(-3.50)$$

$$= 10^{13} \times 0.030 = 3.0 \times 10^{11} \text{ s}^{-1}$$

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

Worked Example 3: Inverted Region

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

a) $\Delta_r G^{\circ} = -1.0$ eV (barrierless)
b) $\Delta_r G^{\circ} = -2.0$ eV (inverted)

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

Solution:

(a) Barrierless:

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

(b) Inverted:

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

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

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

Practice Problem 1

Problem: An ET reaction has the following parameters:

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

(a) Calculate $\Delta G^\ddagger$

(b) Is this in normal, barrierless, or inverted region?

(c) If distance increases to 1.5 nm, by what factor does rate decrease?

Answers:

(a) $\Delta G^\ddagger = 0.01$ eV

(b) Normal region $(-\Delta_r G^\circ < \lambda)$

(c) 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:

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

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

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

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

Solution:

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

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

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 $\Delta G^\ddagger$ for each step

b) Which step is fastest?

c) Why is the back-reaction slow despite being exergonic overall?

Answers:

(a) $\Delta G^\ddagger(1 \rightarrow 2) = 0.078$ eV; $\Delta G^\ddagger(2 \rightarrow 3) = 0.028$ eV; $\Delta G^\ddagger(\text{back}) = 0.2$ eV

(b) Step $2 \rightarrow 3$ (lowest barrier)

(c) Back-reaction has endergonic $\Delta_r G^\circ$, creating large barrier

Practice Problem 4

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

A photosynthetic reaction center has:

- Forward ET: $\lambda = 0.5$ eV
- Back ET: $\lambda = 0.5$ eV

(a) What driving force gives fastest forward ET?

(b) If actual $\Delta_r G^\circ = -0.3$ eV, what is $\Delta G^\ddagger$?

(c) For back ET with $\Delta_r G^\circ = +0.3$ eV, what is the barrier?

(d) How does this design prevent energy loss?

Answers:

(a) $\Delta_r G^\circ = -0.5$ eV $(= -\lambda)$

(b) $\Delta G^\ddagger = 0.02$ eV (fast)

(c) $\Delta G^\ddagger = 0.32$ eV (slow!)

(d) Endergonic back-reaction has huge barrier $\rightarrow$ prevents wasteful back-transfer

Summary: Topic 18E

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

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

2. **Reorganization Energy:** $\lambda = \lambda_{\text{in}} + \lambda_{\text{out}}$
   - Cost to rearrange nuclei before ET

3. **Marcus Equation:**

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

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

4. **Distance Dependence:** $k_{ET} \propto \exp(-\beta r)$
   - Electron tunneling through barrier

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

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:

Or navigate to:

`Reaction_Dynamics_Interactive/`

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