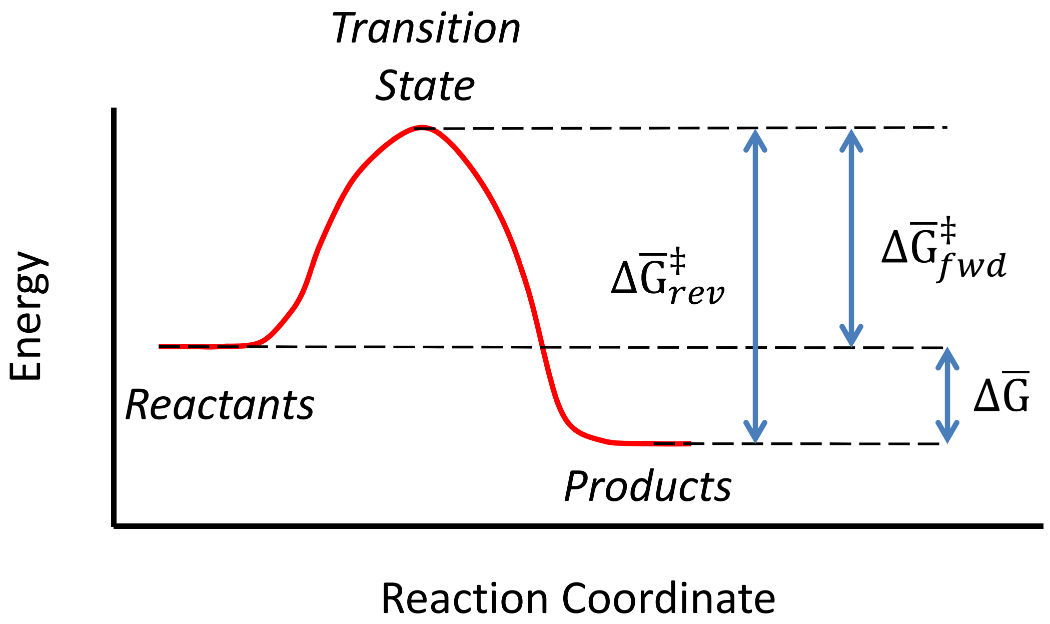
Today: Miscellaneous Topics

- Electron Transfer Reactions
- Electrostatic effects
- Diffusion-limited reactions

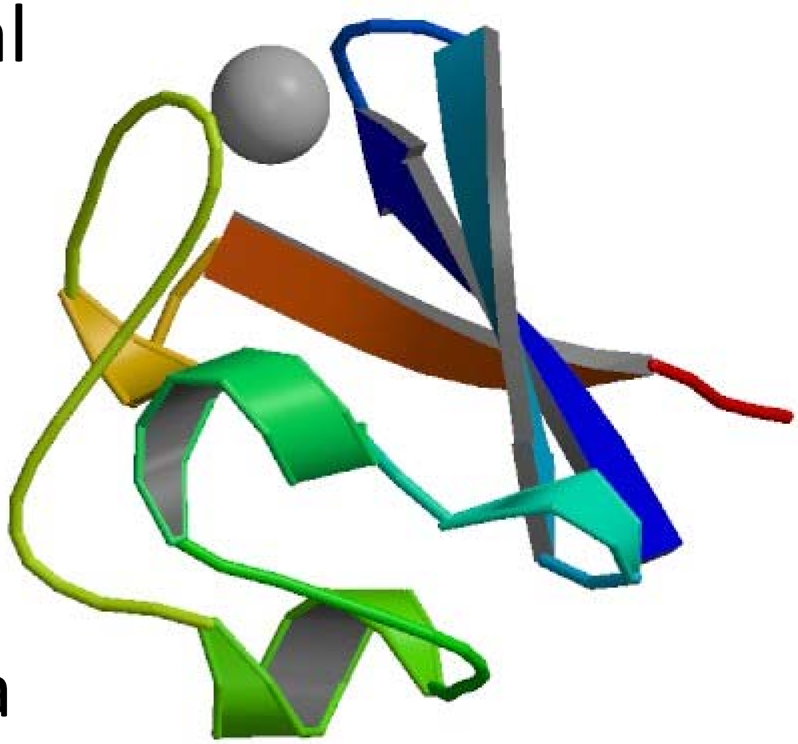
Review: Transition States



- Fundamental relationship: $k = \frac{k_B T}{h} e^{-\frac{\Delta\bar{G}^{\ddagger}}{RT}}$
- Can we predict $\Delta\bar{G}^{\ddagger}$ for *<u>any</u>* system?

Electron Transfer

- Electron transfer essential for metabolic processes: cytochromes in eukaryotes
- **Rubredoxin:** electron carrier protein in bacteria and archaea



RCSB, PDB 1CAD

Simple Model

- Simplest model for electron transfer:

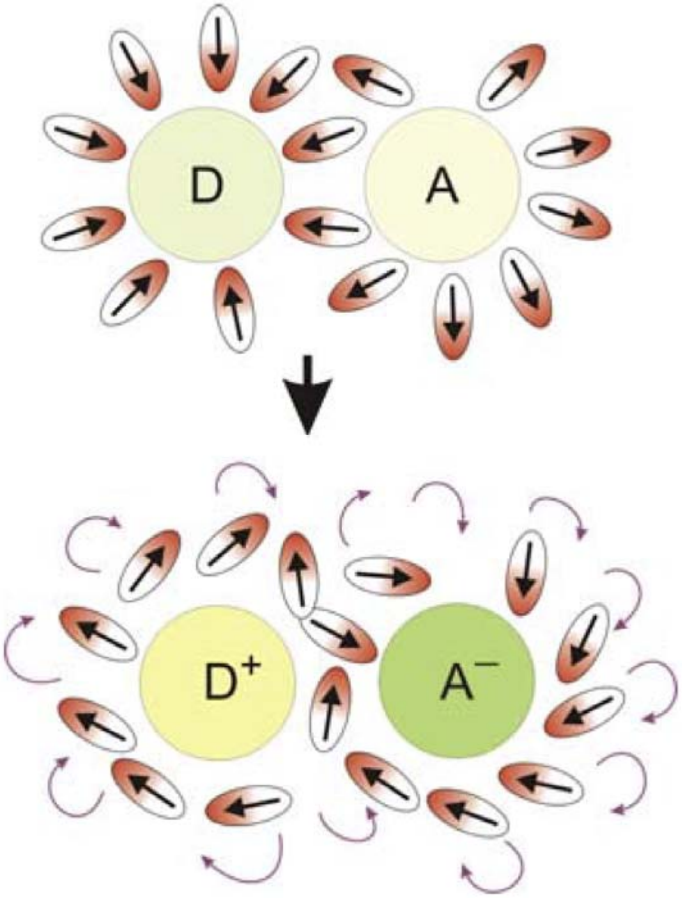
$$^{56}\mathrm{Fe}^{2+} + {}^{54}\mathrm{Fe}^{3+} \rightleftarrows {}^{56}\mathrm{Fe}^{3+} + {}^{54}\mathrm{Fe}^{2+}$$

- No free energy difference (no change)
- Two iron ions must collide to form electron transfer complex
  - Can we devise a mechanism?

Simple Model

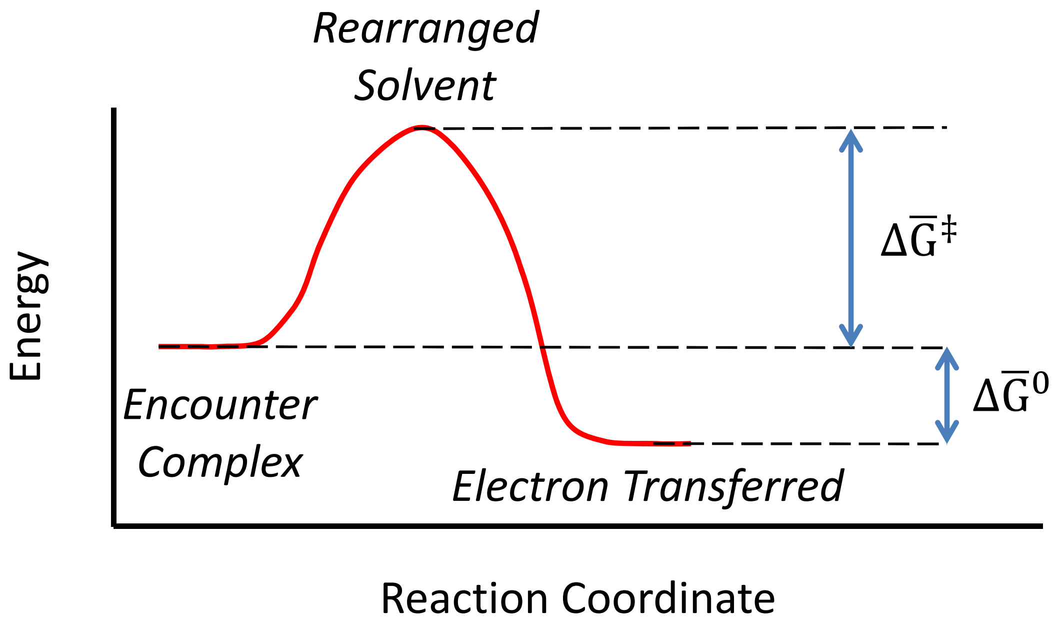
- Encounter complex forms

- Solvent dipoles (water) must reorient to accommodate new charges



Andrei Tomakoff,
http://www.mit.edu/~tokmakof/TDQMS/Notes/12.2.%20Marcus.pdf

Marcus Theory



- Rudolph Marcus (Nobel, 1992):

$$\Delta\bar{G}^{\ddagger} = \frac{\lambda}{4}\left(1+\frac{\Delta\bar{G}^{0}}{\lambda}\right)^{2} \text{ where } \lambda = (\Delta e)^{2}\left(\frac{1}{2a_1}+\frac{1}{2a_2}-\frac{1}{r_{a_1 a_2}}\right)\left(\frac{1}{n^2}-\frac{1}{\epsilon}\right)$$

Marcus Theory

- Transition State Energy:

$$\Delta\bar{G}^{\ddagger} = \frac{\lambda}{4}\left(1 + \frac{\Delta\bar{G}^{0}}{\lambda}\right)^{2}$$

- Solvent Reorientation Energy:

Index of
Refraction

$$\lambda = (\Delta e)^{2}\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r_{a_1 a_2}}\right)\left(\frac{1}{n^{2}} - \frac{1}{\epsilon}\right)$$

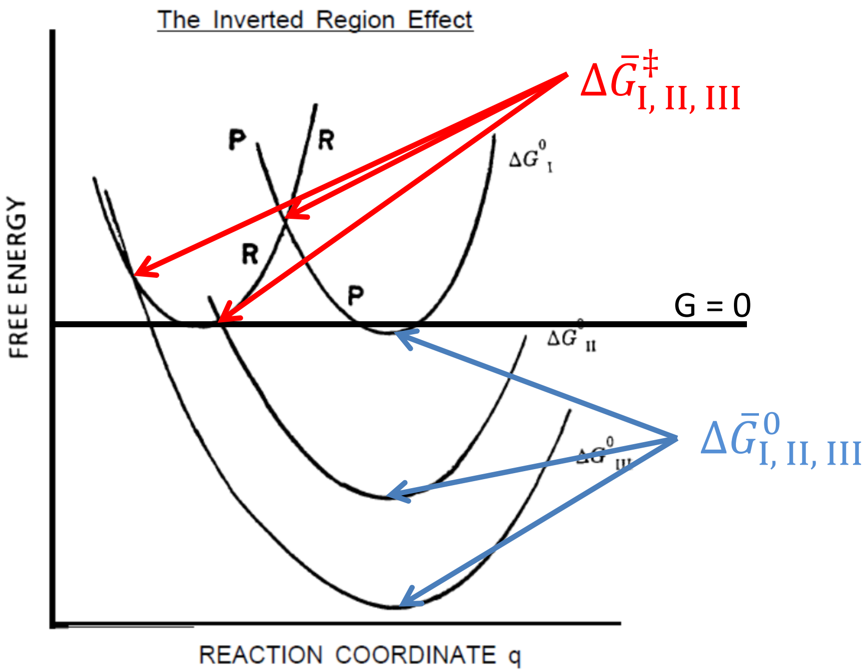
Charge
Transferred (e.g. +1)

Ionic
Radii

Center-to-center
Distance

Relative
Dielectric Constant

Marcus Theory - Significance



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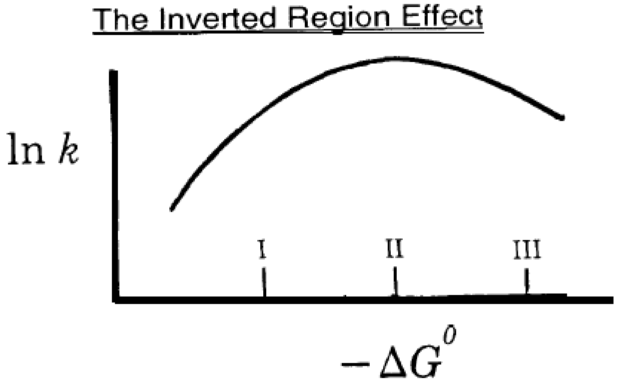


- Parabolic dependence of $\Delta\bar{G}^{\ddagger}$ vs $\Delta\bar{\text{G}}^{0}$

Marcus, R. A. Nobel Prize Lecture (www.nobelprize.org)

Marcus Theory - Significance

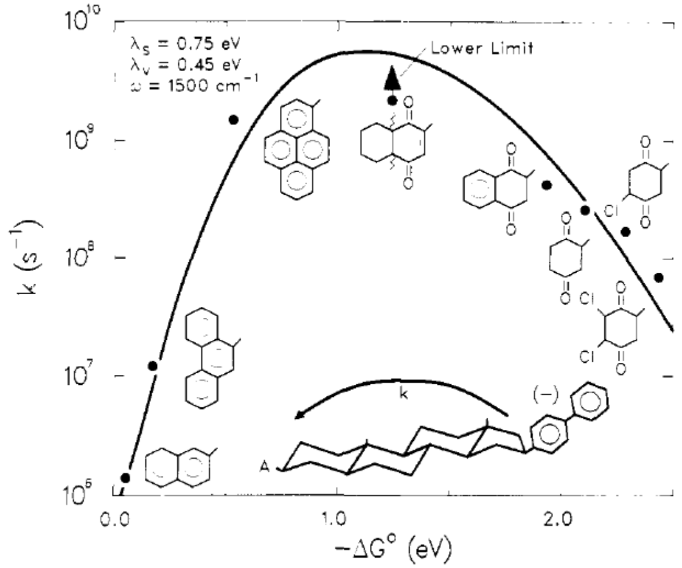
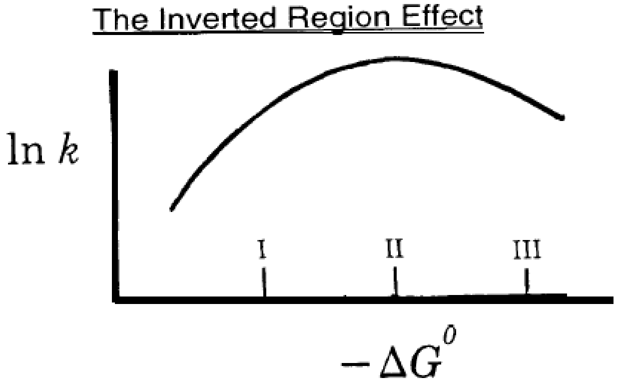


Figure 1. Intramolecular electron-transfer rate constants as a function of free energy change in MTHF solution at 296 K. Electrons transferred from biphenyl ions to the eight different acceptor groups, A (shown labeling the points), in eight bifunctional molecules having the general structure shown in the center of the figure.

$$\Delta\bar{G}^{\ddagger} = \frac{\lambda}{4}\left(1+\frac{\Delta\bar{G}^{0}}{\lambda}\right)^{2}$$



- Parabolic dependence of $\Delta\bar{G}^{\ddagger}$ vs $\Delta\overline{\mathrm{G}}^{0}$

Miller, J. R., *et al*. (1984) *JACS*. **106**: 3047.

Kinetics and Salt Effects

- Transition state theory with activities

$$M + N \overset{K^\ddagger}{\rightleftarrows} [MN]^\ddagger \xrightarrow{k^\ddagger} P$$

- Equilibrium constant (with activity coefficients):

$$K = \frac{\gamma_\ddagger [MN]^\ddagger}{\gamma_M [M] \gamma_N [N]}$$

Rate constant with
unit activity coefficients

- Rate law is then:

$$v = k^\ddagger K^\ddagger \frac{\gamma_M \gamma_N}{\gamma_\ddagger}[M][N] = k_0 \frac{\gamma_M \gamma_N}{\gamma_\ddagger}[M][N]$$

Ionic Strength and Activities

- Recall Debye-Hückel activities (chapter 4):

$$\log \gamma_i = -0.51 Z_i^2 \sqrt{I}$$

$$I = \frac{1}{2} \sum_i c_i Z_i^2$$

- Use these activities to derive an ionic-strength dependence of $\log k$:

$$\log k = \log k_0 + 2(0.51) Z_M Z_N \sqrt{I}$$

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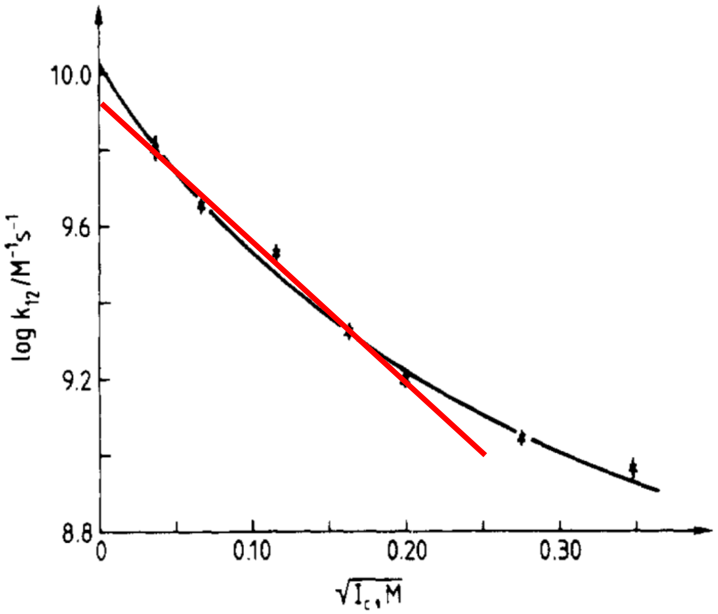
Ionic Strength and Activities

- Applies for low ionic strengths
  - Remember assumptions!
- Must prove that effect is truly “ionic” and not salt-specific
  - Test with multiple salts



Nolte, H., *et al*. (1980) *Biochemistry.* **19**: 3705.

Diffusion Limited Reactions

- Is there a “speed limit” for reactions in solution?

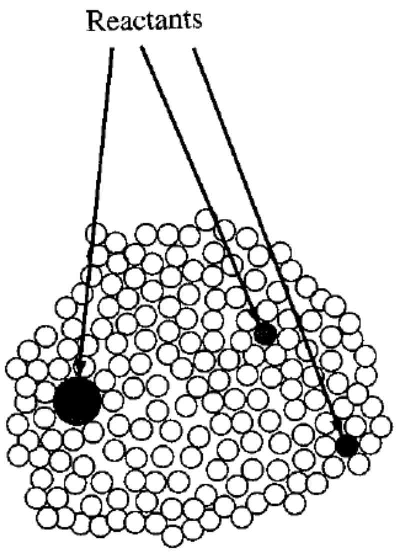
- **Diffusion coefficient:** Relates distance traveled to time in “crowded” environment

$$\langle x^2 \rangle = Dt$$

  - Small molecules ~ 1 x 10^{-5} cm^2 s^{-1}
  - Higher D means more distance covered per unit time

Collision Theory

- More collisions with solvent → harder for molecules to interact
- Rate of collisions should be:
  - Proportional to diffusion constant
  - Proportional to size



Tinoco, p. 372.

Collision Theory

- Arrhenius equation exponent (A):

$$A_{diff} = \frac{4\pi r_{MN}(D_M + D_N)N_A}{1000}$$

- For small molecules A ~ 10^{10}
- Termed “diffusion limited reactions”
  - Low activation energy (not necessarily zero)
  - Fast A coefficient

Collision Theory – Fast Rates

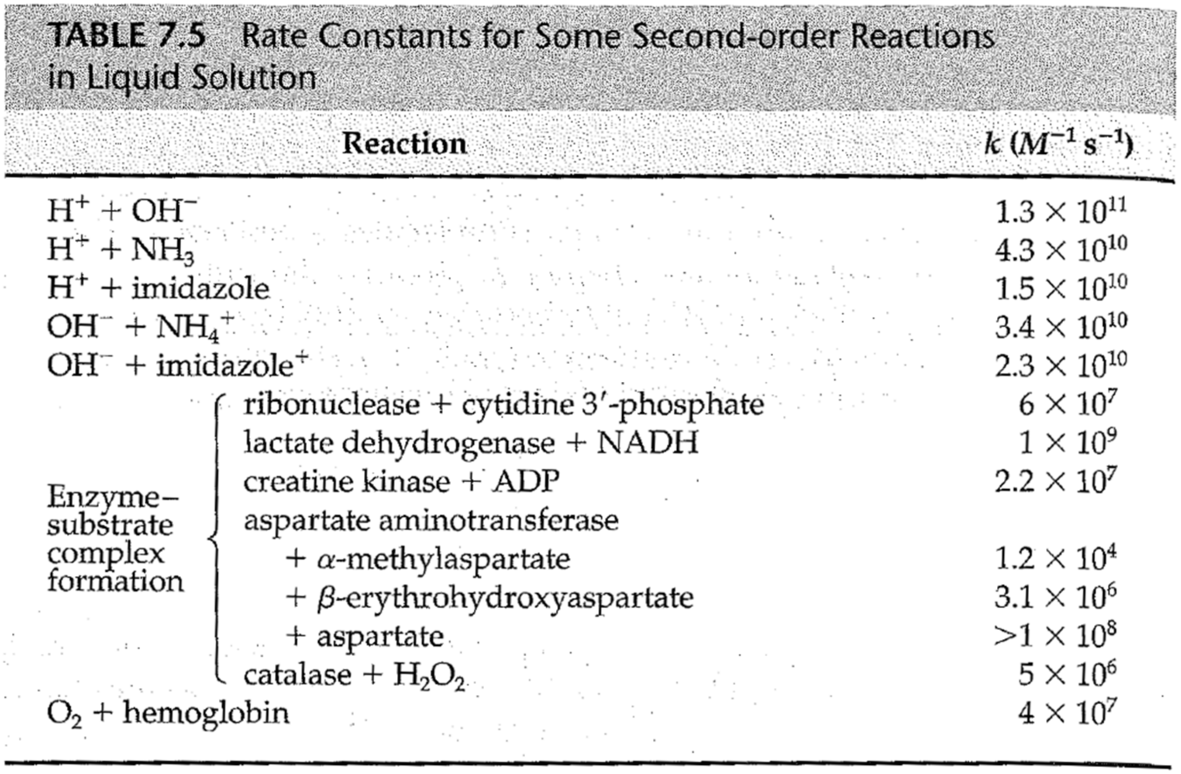


TABLE 7.5 Rate Constants for Some Second-order Reactions in Liquid Solution

	Reaction	**k (M^{-1} s^{-1})**
	$H^+ + OH^-$	1.3×10^{11}
	$H^+ + NH_3$	4.3×10^{10}
	H^+ + imidazole	1.5×10^{10}
	$OH^- + NH_4^+$	3.4×10^{10}
	OH^- + imidazole$^+$	2.3×10^{10}
Enzyme–substrate complex formation	ribonuclease + cytidine 3′-phosphate	6×10^7
	lactate dehydrogenase + NADH	1×10^9
	creatine kinase + ADP	2.2×10^7
	aspartate aminotransferase	
	+ α-methylaspartate	1.2×10^4
	+ β-erythrohydroxyaspartate	3.1×10^6
	+ aspartate	$>1 \times 10^8$
	catalase + H_2O_2	5×10^6
	O_2 + hemoglobin	4×10^7

See a rate of $10^9 - 10^{10}$? → Think diffusion controlled!

Tinoco, p. 374.