



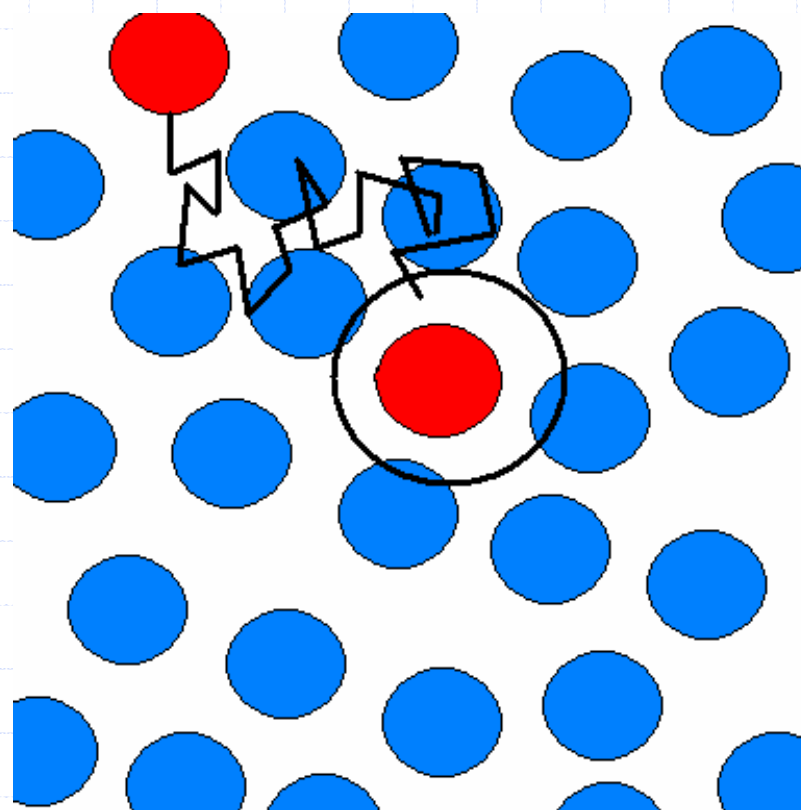
Physical Chemistry

Lecture 8

Reactions in solution and
relaxation methods in fast kinetics

The cage effect

- ◆ In solution, solvent is a major factor in kinetics
- ◆ Limited proximity of reactants
- ◆ Molecules must diffuse into reaction zone



Diffusion control

- ◆ Limiting behavior
 - EVERY molecule entering the cage reacts
- ◆ Diffusive motions control the time it takes to enter the cage
- ◆ Simple bimolecular reaction with diffusion control
- ◆ Typical size of diffusion-controlled rate constant



$$v = 4\pi L(D_A + D_B)d_{AB}[A][B]$$

$$k_{eff} = 4\pi L(D_A + D_B)d_{AB}$$

$$k_{eff} \approx 4 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Rate constants for bimolecular reactions in solution

Reaction	k (298 K)/(dm ³ mol ⁻¹ s ⁻¹)
$\text{H}^+ + \text{HS}^- \rightarrow \text{H}_2\text{S}$	7.5×10^{10}
$\text{H}^+ + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{OH}_2^+$	1×10^8
$\text{OH}^- + \text{HCO}_3^- \rightarrow \text{CO}_3^{2-} + \text{H}_2\text{O}$	6×10^9
$\text{OH}^- + \text{CH}_3\text{OH} \rightarrow \text{CH}_3\text{O}^- + \text{H}_2\text{O}$	3×10^6
$\text{OH}^- + \text{p-C}_6\text{H}_4(\text{COOC}_2\text{H}_5)_2 \rightarrow \text{p-C}_2\text{H}_5\text{OOC}_6\text{H}_4\text{COO}^- + \text{H}_2\text{O}$	5.4×10^{-2}
$\text{hemoglobin} \cdot 3 \text{O}_2 + \text{O}_2 \rightarrow \text{hemoglobin} \cdot 4 \text{O}_2$	2×10^7

From W. C. Gardiner, Jr., *Rates and Mechanisms of Chemical Reactions*, Benjamin, New York, 1969.

Ionic reactions in solution

◆ The charge on an ion affects the reaction rate

◆ Can be understood with activated-complex theory and Debye-Hueckel theory



$$k(T) = \frac{k_B T}{h C^\theta} \left(\frac{\gamma_A \gamma_B}{\gamma_{AB}^{\ddagger}} \right) e^{\Delta S^\ddagger} e^{-\Delta H^\ddagger / RT}$$

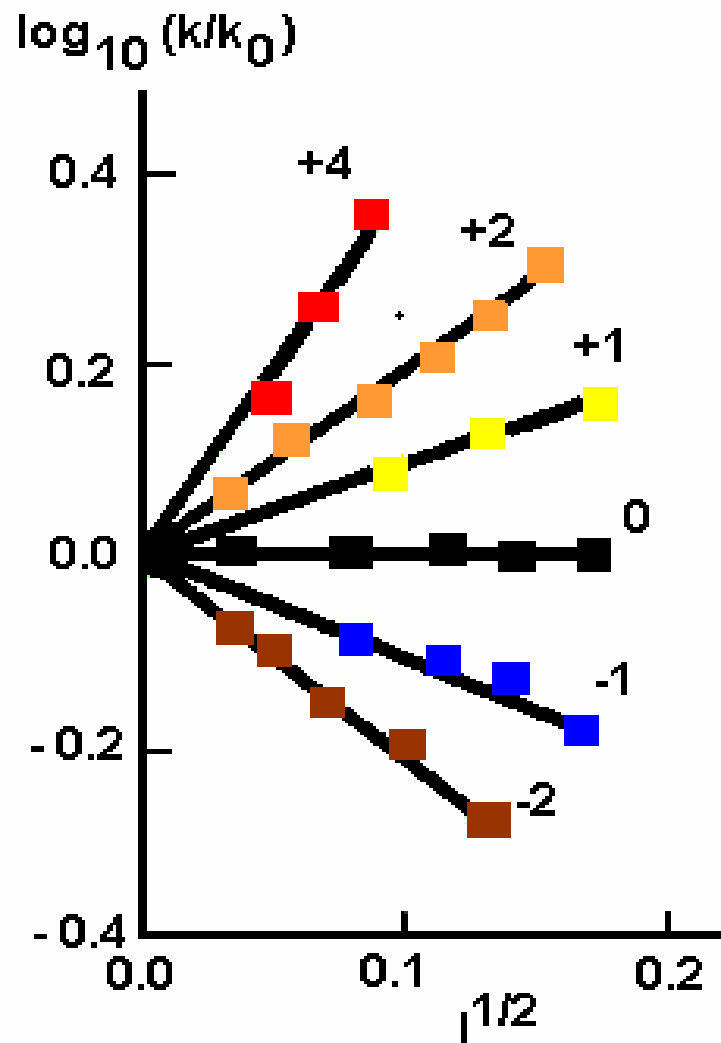
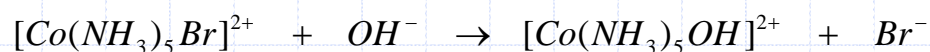
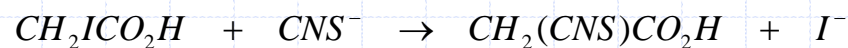
$$\ln k(T) = \ln k_0(T) + 2\alpha |z_A z_B| \sqrt{I}$$

Ionic reactions in solution

◆ Dependence of rate constant on

- Ionic strength
- Product of charges

◆ Example reactions

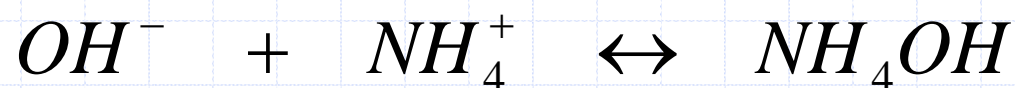


Relaxation methods

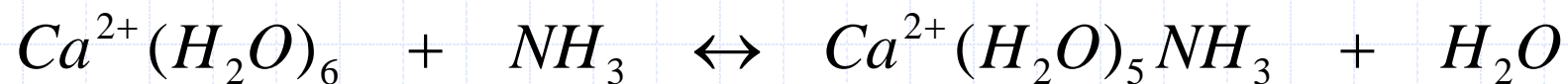
- ◆ For reactions that happens so fast it is not possible to mix reactants uniformly before the reaction is substantially done, one cannot use typical methods of kinetics
- ◆ Alternative is **relaxation method** to determine rate constants
 - Perturb the system from equilibrium
 - Observe the return to equilibrium
- ◆ Types of relaxation methods
 - T-jump
 - P-jump
 - E-jump
 - Laser-pump

Examples of fast reactions

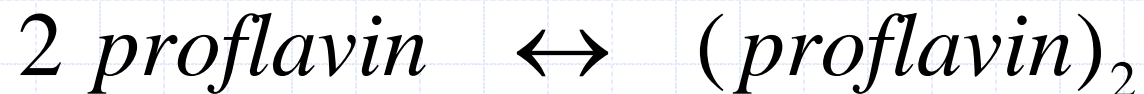
◆ Recombinations



◆ Substitution reactions

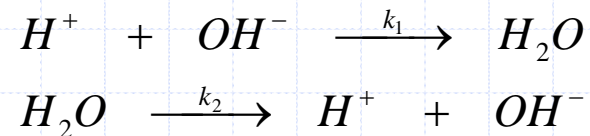


◆ Dimerizations



Relaxation methods

- ◆ Perturbation changes concentrations from equilibrium values
- ◆ Concentrations return to equilibrium values with time constant τ
- ◆ That plus the equilibrium constant gives k_1 and k_2



$$\frac{d[H_2O]}{dt} = k_1[H^+][OH^-] - k_2[H_2O]$$

$$[H_2O] = \overline{[H_2O]} + x$$

$$[H^+] = \overline{[H^+]} - x$$

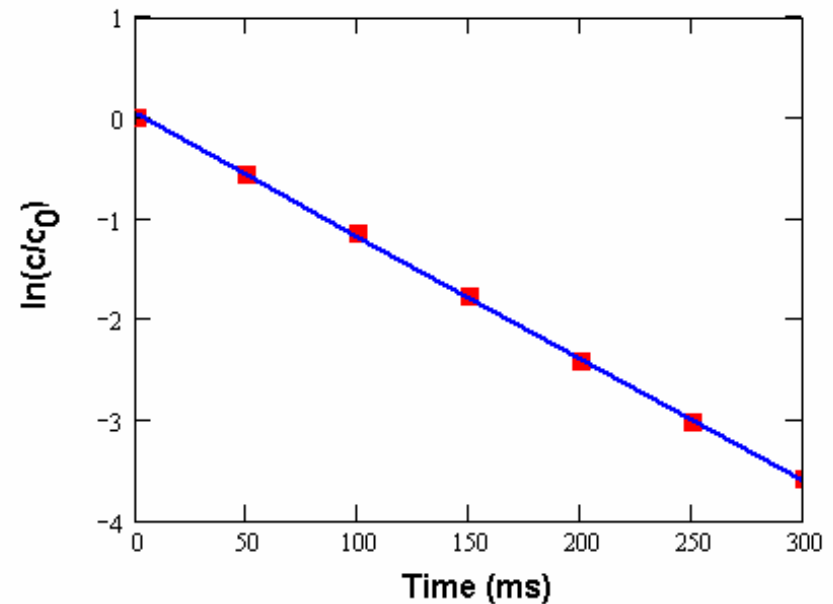
$$[OH^-] = \overline{[OH^-]} - x$$

$$\frac{dx}{dt} \cong -\left(k_1(\overline{[H^+]} + \overline{[OH^-]}) + k_2\right)x = -\frac{1}{\tau}x$$

$$x(t) = x(0) \exp(-t/\tau)$$

Example relaxation method

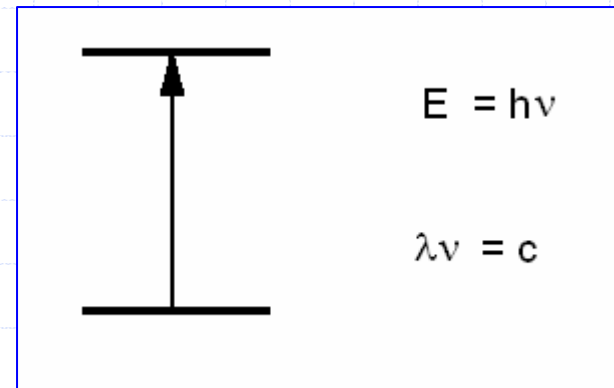
- ◆ Refolding of a decanucleotide at 32.4°C
- ◆ Determined optically through absorption of UV light
- ◆ Slope of line $\equiv -\tau^{-1}$
- ◆ Time scale of milliseconds



From Porschke, Uhlenbeck, and Martin, 1973.

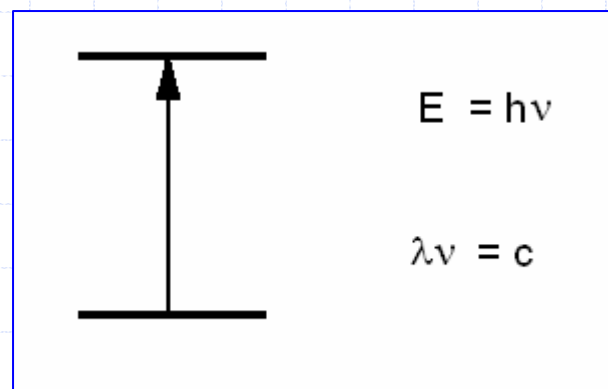
Photochemistry

- ◆ Absorption of light causes change of state
- ◆ Energy of transition related to frequency of light (and therefore wavelength)



Photochemistry

- ◆ Absorption of light causes change of state
- ◆ Total energy is conserved in a transition
 - Measure absorbed energy (or intensity) by difference
- ◆ Transmitted intensity determined by Beer-Lambert Law



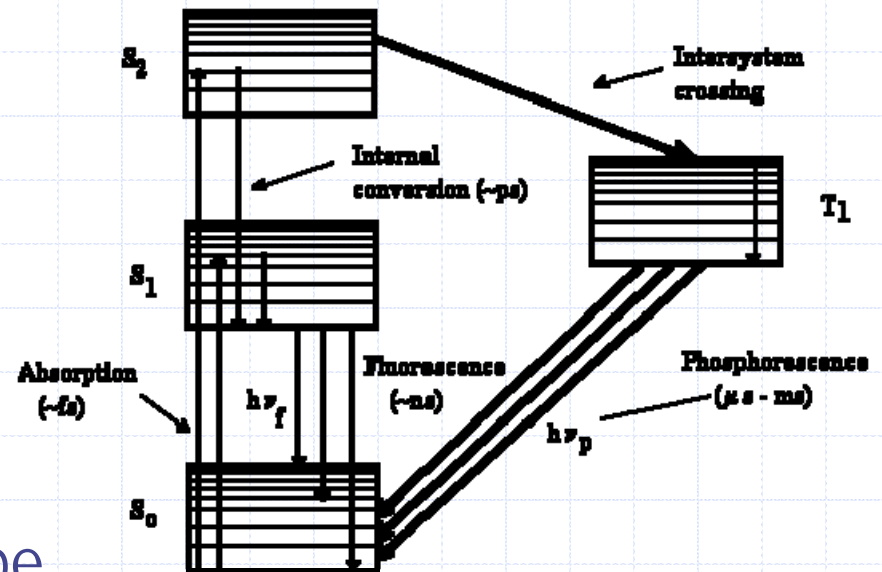
$$I_0 = I_{abs} + I_{trans}$$

$$I_{trans} = I_0 e^{-2.303\epsilon l[A]}$$

$$I_{abs} = I_0 \left(1 - e^{-2.303\epsilon l[A]}\right)$$

Types of photophysical processes

- ◆ Radiative transitions
 - Fluorescence
 - Phosphorescence
- ◆ Intersystem crossing
- ◆ Internal conversion
- ◆ Kinetics apply
 - Usually considered to be of first order
 - Often described by a lifetime, rather than a rate constant



Summary

- ◆ Solution reactions are complicated because of the interaction with solvent
- ◆ Diffusion control gives an estimate of the fastest solution reaction rates (**cage effect**)
 - Reactive species such as HS⁻ show reaction rate constants that imply total diffusion control
 - Other reactions show slower reaction rates
- ◆ Ionic reactions show a dependence on
 - Ionic strength
 - Charge on ions
 - Debye-Hueckel theory prediction
- ◆ Fast reactions may be studied by relaxation techniques
 - Modern techniques can even study processes on scales of picoseconds and femtoseconds