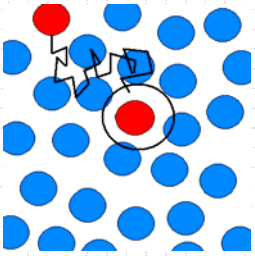
Physical Chemistry

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

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

$$A + B \rightarrow Products$$

$$v = 4\pi N_0 (D_A + D_B) d_{AB} [A][B]$$

$$k_{eff} = 4\pi N_0 (D_A + D_B) d_{AB}$$

Rate constants for bimolecular reactions in solution

Reaction	k (298 K)/ ($dm^3\ mol^{-1}\ s^{-1}$)
$H^+ + HS^- \rightarrow H_2S$	7.5×10^{10}
$H^+ + CH_3OH \rightarrow CH_3OH_2^+$	1×10^{8}
$OH^- + HCO_3^- \rightarrow CO_3^{2-} + H_2O$	6×10^{9}
$OH^- + CH_3OH \rightarrow CH_3O^- + H_2O$	3×10^{6}
$OH^- + p\text{-}C_6H_4(COOC_2H_5)_2 \rightarrow p\text{-}C_2H_5OOCC_6H_4COO^- + H_2O$	5.4×10^{-2}
hemoglobin•3 O_2 + O_2 → hemoglobin•4 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

$$A + B \leftrightarrow (AB)^{\neq} \rightarrow Products$$

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

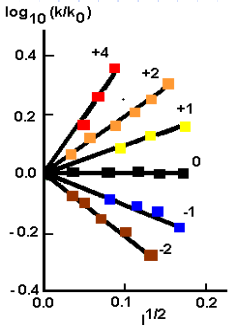
$$\ln k(T) = \ln k_0(T) + 2\alpha |z_A z_B| \sqrt{I}$$

Ionic reactions in solution

- Dependence of rate constant on
  - Ionic strength
  - Product of charges
- Example reactions

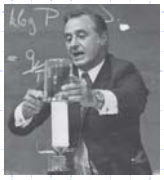
$$CH_2ICO_2H + CNS^- \rightarrow CH_2(CNS)CO_2H + I^-$$

$$[Co(NH_3)_5Br]^{2+} + OH^- \rightarrow [Co(NH_3)_5OH]^{2+} + Br^-$$



Relaxation methods

- For a reaction 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
- An alternative for determining rate constants of fast reactions is the relaxation method
  - Perturb the system from equilibrium
  - Observe the return to equilibrium
- Types of relaxation methods
  - Temperature jump
  - Pressure jump
  - Electric-field jump
  - Flash photolysis
  - Laser pump



Sir George Porter

Examples of fast reactions

- Recombinations

$$H^+ + OH^- \leftrightarrow H_2O$$

$$OH^- + NH_4^+ \leftrightarrow NH_4OH$$

- Substitution reactions

$$Ca^{2+}(H_2O)_6 + NH_3 \leftrightarrow Ca^{2+}(H_2O)_5NH_3 + H_2O$$

- Dimerizations

$$2\ proflavin \leftrightarrow (proflavin)_2$$

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

$$H^+ + OH^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} H_2O$$

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

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

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

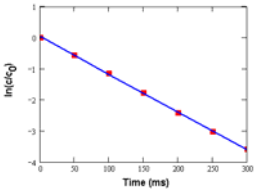
$$[OH^-] = \overline{[OH^-]} - x$$

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

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

Example relaxation method

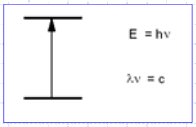
- Refolding of a decanucleotide at 32.4°C
- Determined optically through absorption of UV light
- Slope of line $\equiv -\tau^{-1}$
- Time scale of milliseconds



From Porschke, Uhlenbeck, and Martin, 1973.

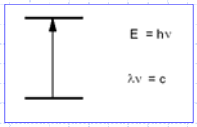
Photochemistry

- 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



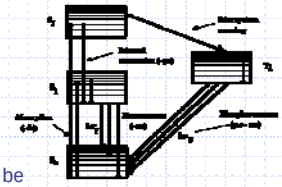
$$I_0 = I_{abs} + I_{trans}$$

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

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

Types of photphysical 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