

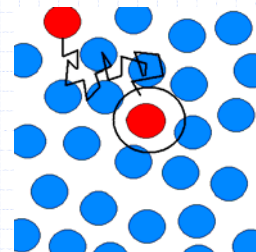
# Physical Chemistry

## Lecture 8

Reactions in solution and relaxation methods in fast kinetics

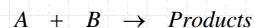
# The cage effect

- ◆ 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

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

- ◆ Typical size of diffusion-controlled rate constant

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

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

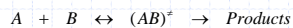
# Rate constants for bimolecular reactions in solution

Reaction	k (298 K) / (dm <sup>3</sup> mol <sup>-1</sup> s <sup>-1</sup> )
H <sup>+</sup> + HS <sup>-</sup> → H <sub>2</sub> S	7.5 × 10 <sup>10</sup>
H <sup>+</sup> + CH <sub>3</sub> OH → CH <sub>3</sub> OH <sub>2</sub> <sup>+</sup>	1 × 10 <sup>9</sup>
OH <sup>-</sup> + HCO <sub>3</sub> <sup>-</sup> → CO <sub>3</sub> <sup>2-</sup> + H <sub>2</sub> O	6 × 10 <sup>9</sup>
OH <sup>-</sup> + CH <sub>3</sub> OH → CH <sub>3</sub> O <sup>-</sup> + H <sub>2</sub> O	3 × 10 <sup>9</sup>
OH <sup>-</sup> + p-C <sub>6</sub> H <sub>4</sub> (COOC <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> → p-C <sub>6</sub> H <sub>4</sub> OOCC <sub>2</sub> H <sub>5</sub> COO <sup>-</sup> + H <sub>2</sub> O	5.4 × 10 <sup>2</sup>
hemoglobin + 3 O <sub>2</sub> → hemoglobin + 4 O <sub>2</sub>	2 × 10 <sup>7</sup>

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



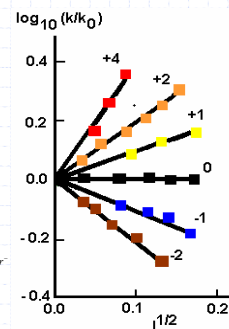
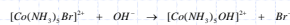
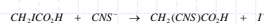
$$k(T) = \frac{k_B T}{h C^{\ddagger}} \left( \frac{\gamma_A \gamma_B}{\gamma_{AB}^{\ddagger}} \right) e^{\Delta S^{\ddagger}} e^{-\Delta H^{\ddagger} / RT}$$

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

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

# Ionic reactions in solution

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

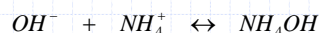
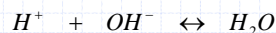


## Relaxation methods

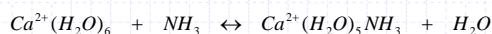
- ◆ For reactions that happens so fast it is not possible to mix reactants uniformly before the reaction is substantially done, one cannot use typical methods of kinetics
- ◆ Alternative is **relaxation method** to determine rate constants
  - Perturb the system from equilibrium
  - Observe the return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

## Examples of fast reactions

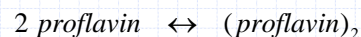
### ◆ Recombinations



### ◆ Substitution reactions

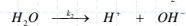
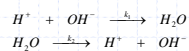


### ◆ Dimerizations



## Relaxation methods

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



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

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

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

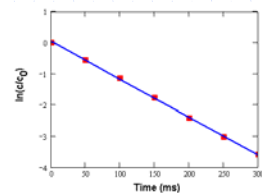
$$[OH^-] = \overline{[OH^-]} - x$$

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

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

## 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.

## 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