Foundations of Chemical Kinetics

Lecture 28:
Diffusion-influenced reactions, Part I

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The encounter pair

- One of the major differences between gas-phase and solution-phase kinetics is solvent caging.
  - In the gas phase, a collision is a single event with a very short lifetime.
  - In solution, once two molecules have come into direct contact with each other, they may stay in contact for a long time because the solvent molecules that surround them need to move in order to allow them to move away from each other.
- A pair of molecules that are in contact and surrounded by solvent is called an encounter pair.

Diffusion-influenced reactions

- In solution, the rate of reaction will in general depend both on the intrinsic reaction rate and on the rate at which molecules diffuse into close proximity.
- We then say that the reaction is diffusion-influenced.
- In what follows, we will consider a reaction

$$A + B \xrightarrow{k} \text{product(s)}$$
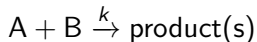
with rate

$$v = k[A][B]$$

Diffusion-influenced reactions (continued)

- ▶ For simplicity, assume spherical molecules.
- ▶ The molecules need to touch in order to react.
- ▶ They touch when their centres are a distance $R_{AB} = R_A + R_B$ apart.
- ▶ We focus on one particular A molecule, and assume the solution is sufficiently dilute that the distribution of B molecules around one A molecule does not affect the distribution around the others.
- ▶ We assume that the A molecules are stationary. We can compensate for this by replacing D_B by the relative diffusion coefficient $D_{AB} = D_A + D_B$.
- ▶ If the concentration of encounter pairs is in a steady state, the rate at which B molecules reach a distance R_{AB} from the centre of an A molecule balances the rate of reaction.

- The flux at $r = R_{AB}$ is the rate of arrival of molecules of B at a sphere of radius R_{AB} centered on a given A molecule per unit area.

- Therefore, the steady-state condition becomes

$$v/[A] = k[B] = -4\pi R_{AB}^2 J_B(r = R_{AB})$$

- In a steady state, because the concentration between any two shells of arbitrary radii r_1 and r_2 is constant, the flux through a shell of any r must be the same. Thus,

$$k[B] = -4\pi r^2 J_B(r)$$

▶ The steady-state distribution of B around a given A should be (on average) spherical. Thus,

$$J_B = -\left[D_{AB} \frac{d[\text{B}]_r}{dr} + \frac{z_B e}{k_B T} D_{AB} [\text{B}]_r \frac{dV}{dr} \right]$$

where $[\text{B}]_r$ is the concentration of B at distance r from a molecule of A.

▶ Using $U(r) = z_B e V(r)$, we get

$$J_B = -D_{AB} \left[\frac{d[\text{B}]_r}{dr} + \frac{1}{k_B T} [\text{B}]_r \frac{dU}{dr} \right]$$

► The steady state condition becomes

$$k[B] = 4\pi r^2 D_{AB} \left[\frac{d[B]_r}{dr} + \frac{1}{k_B T}[B]_r \frac{dU}{dr} \right]$$

► In this equation [B] is the average concentration of B in the solution, which is also the expected concentration of B far from any given A molecule.

► Note:

$$\frac{d}{dr}\left[[B]_r \exp\left(\frac{U(r)}{k_B T} \right) \right] = \exp\left(\frac{U(r)}{k_B T} \right) \left[\frac{d[B]_r}{dr} + \frac{1}{k_B T}[B]_r \frac{dU}{dr} \right]$$

► Therefore,

$$k[B] = 4\pi r^2 D_{AB} \exp\left(-\frac{U(r)}{k_B T} \right) \frac{d}{dr}\left[[B]_r \exp\left(\frac{U(r)}{k_B T} \right) \right]$$

Diffusion-influenced reactions (continued)

▶ Rearranging, we get

$$\frac{d}{dr}\left[[B]_r \exp\left(\frac{U(r)}{k_B T}\right)\right] = \frac{k[B]}{4\pi r^2 D_{AB}} \exp\left(\frac{U(r)}{k_B T}\right)$$

▶ We can solve this equation by separation of variables subject to the boundary conditions $[B]_r \to [B]$ and $U(r) \to 0$ as $r \to \infty$:

$$\int_{r=R_{AB}}^{\infty} d\left[[B]_r \exp\left(\frac{U(r)}{k_B T}\right)\right] = \int_{R_{AB}}^{\infty} \frac{k[B]}{4\pi r^2 D_{AB}} \exp\left(\frac{U(r)}{k_B T}\right) dr$$

$$\therefore \left[[B]_r \exp\left(\frac{U(r)}{k_B T}\right)\right]_{R_{AB}}^{\infty} = \frac{k[B]}{4\pi D_{AB}} \int_{R_{AB}}^{\infty} \frac{1}{r^2} \exp\left(\frac{U(r)}{k_B T}\right) dr$$

Diffusion-influenced reactions (continued)

- Applying the limits, we get

$$[B] - [B]_{R_{AB}} \exp\left(\frac{U(R_{AB})}{k_B T}\right) = \frac{k[B]}{4\pi D_{AB}\beta} \tag{1}$$

where

$$\beta^{-1} = \int_{R_{AB}}^{\infty} \frac{1}{r^2} \exp\left(\frac{U(r)}{k_B T}\right) \, dr$$

- There is some intrinsic rate constant for reaction when A and B are in contact, k_R, such that

$$v = k_R[A][B]_{R_{AB}} = k[A][B]$$
$$\therefore [B]_{R_{AB}} = k[B]/k_R$$

- The next step is to substitute for $[B]_{R_{AB}}$ in equation (1) and solving for k.

Diffusion-influenced reactions (continued)

▸ The result is

$$k = \frac{4\pi D_{AB}\beta k_R}{k_R + 4\pi D_{AB}\beta \exp\left(\frac{U(R_{AB})}{k_B T}\right)}$$

▸ In order to get a rate constant in molar units, we need to multiply this equation by L:

$$k = \frac{4\pi L D_{AB}\beta k_R}{k_R + 4\pi D_{AB}\beta \exp\left(\frac{U(R_{AB})}{k_B T}\right)}$$

▸ This equation allows us to calculate the rate constant for a diffusion-influenced reaction, provided we know the intrinsic rate constant k_R, the potential energy $U(r)$, and the diffusion coefficients and radii of A and B.

The diffusion-limited rate constant

- Suppose that k_R is very large, i.e. that A and B react nearly every time they meet in solution.
  We then say that the reaction is diffusion-limited.

- For k_R very large, we get

$$k = \frac{4\pi L D_{AB}\beta k_R}{k_R + 4\pi D_{AB}\beta \exp\left(\frac{U(R_{AB})}{k_B T}\right)} \to 4\pi D_{AB}\beta$$

- This quantity is the diffusion-limited rate constant:

$$k_D = 4\pi L D_{AB}\beta$$

- The diffusion-influenced rate constant can consequently be written

$$k = \frac{k_D k_R}{k_R + k_D \exp\left(\frac{U(R_{AB})}{k_B T}\right)}$$

The diffusion-limited rate constant
Weak intermolecular forces

- If intermolecular forces between A and B are weak, then $U(r) \approx 0$, except when A and B are very close.
- In this case,

$$\beta^{-1} = \int_{R_{AB}}^{\infty} \frac{1}{r^2} \exp\left(\frac{U(r)}{k_B T}\right) \, dr \approx \int_{R_{AB}}^{\infty} \frac{1}{r^2} \, dr = \frac{1}{R_{AB}}$$

  or $\beta = R_{AB}$.
- The diffusion-limited rate constant becomes

$$k_D = 4\pi L D_{AB} R_{AB}$$

  and the diffusion-influenced rate constant is

$$k = \frac{k_D k_R}{k_R + k_D}$$

▶ If we have a reaction between ions,

$$U(r) = \frac{z_A z_B e^2}{4\pi\epsilon r}$$

where ϵ is the permittivity of the solvent.
Note: The textbook writes this formula in cgs units, which is why the factor of 4π doesn't appear in their formula.
Moreover, in their formula, ϵ is the dielectric constant, not the permittivity.

▶ For this potential, we get

$$\beta = \frac{z_A z_B e^2}{4\pi\epsilon k_B T \left[\exp\left(\frac{z_A z_B e^2}{4\pi\epsilon k_B T R_{AB}}\right) - 1\right]}$$

$$\beta = \frac{z_A z_B e^2}{4\pi\epsilon k_B T \left[\exp\left(\frac{z_A z_B e^2}{4\pi\epsilon k_B T R_{AB}}\right) - 1\right]}$$

- For $z_A z_B > 0$, putting in some typical numbers, you would find $\beta \ll R_{AB}$.
  Thus, as you might expect, k_D is decreased due to Coulomb repulsion.

- Conversely, for $z_A z_B < 0$, $\beta > R_{AB}$, so k_D is increased when the reactants are subject to an attractive potential.