Foundations of Chemical Kinetics

Lecture 28: Diffusion-influenced reactions, Part I

Marc R. Roussel

Department of Chemistry and Biochemistry
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.
Diffusion-influenced reactions (continued)

- 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,

\[
k[B] = -4\pi r^2 J_B(r)
\]
Diffusion-influenced reactions (continued)

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

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

where \([B]_r\) is the concentration of B at distance \(r\) from a molecule of A.

- Using \(U(r) = z_B e V(r)\), we get

\[ J_B = -D_{AB} \left[ \frac{d[B]_r}{dr} + \frac{1}{k_B T} [B]_r \frac{dU}{dr} \right] \]
Diffusion-influenced reactions (continued)

- The steady state condition becomes

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

- 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:

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

- Therefore,

\[ k[B] = 4\pi r^2 D_{AB} \exp \left( -\frac{U(r)}{k_B T} \right) \frac{d}{dr} \left[ [B] \exp \left( \frac{U(r)}{k_B T} \right) \right] \]
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 \([B]_r \rightarrow [B]\) and \(U(r) \rightarrow 0\) as \(r \rightarrow \infty\):
  \[
  \int_{r=R_{AB}}^{\infty} d \left[ [B]_r \exp \left( \frac{U(r)}{k_B T} \right) \right] = \int_{R_{AB}}^{\infty} \frac{k[B]}{4\pi r^2 D_{AB}} \exp \left( \frac{U(r)}{k_B T} \right) \, dr
  \]

  \[
  \therefore [B]_r \exp \left( \frac{U(r)}{k_B T} \right) \bigg|_{R_{AB}}^{\infty} = \frac{k[B]}{4\pi D_{AB}} \int_{R_{AB}}^{\infty} \frac{1}{r^2} \exp \left( \frac{U(r)}{k_B T} \right) \, dr
  \]
Diffusion-influenced reactions (continued)

- Applying the limits, we get

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

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

\[ \nu = k_R[A][B]_{R_{AB}} = k[A][B] \]

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

- 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
  \[ k = \frac{4\pi LD_{AB}\beta k_R}{k_R + 4\pi D_{AB}\beta \exp \left( \frac{U(R_{AB})}{k_B T} \right)} \rightarrow 4\pi D_{AB}\beta \]
- This quantity is the diffusion-limited rate constant:
  \[ k_D = 4\pi LD_{AB}\beta \]
- 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
  \[
  k_D = 4\pi LD_{AB} R_{AB}
  \]
  and the diffusion-influenced rate constant is
  \[
  k = \frac{k_D k_R}{k_R + k_D}
  \]
The diffusion-limited rate constant
The Coulomb interaction

- If we have a reaction between ions,

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

where \( \epsilon \) is the permittivity of the solvent.
Note: The textbook writes this formula in cgs units, which is why the factor of \( 4\pi \) doesn’t appear in their formula.
Moreover, in their formula, \( \epsilon \) is the dielectric constant, not the permittivity.

- For this potential, we get

\[ \beta = \frac{z_A z_B e^2}{4\pi \epsilon k_B T \left[ \exp \left( \frac{z_A z_B e^2}{4\pi \epsilon k_B T R_{AB}} \right) - 1 \right]} \]
The diffusion-limited rate constant
The Coulomb interaction (continued)

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

▫ 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.