

Foundations of Chemical Kinetics Lecture 28: Diffusion-influenced reactions

Marc R. Roussel

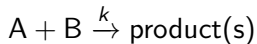
November 23, 2021

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.
- If the rate of diffusive encounters and the intrinsic reaction rate are both important in determining the rate of reaction, we say that the reaction is **diffusion-influenced**.
- In what follows, we will consider a reaction



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)

- $v/[A] = k[B]$ is the rate of reaction per molecule of A.
- Units: $(\text{molecules})\text{s}^{-1}$
- 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

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

- Unit considerations: the flux is normally in $\text{mol m}^{-2}\text{s}^{-1}$. The factor of L gives a flux in $(\text{molecules})\text{m}^{-2}\text{s}^{-1}$.

Diffusion-influenced reactions (continued)

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

- In a steady state, because the concentration between any two shells of arbitrary radii r_1 and r_2 is constant, the rate at which particles through a shell of any r (in, say, molecules per unit time) must be the same. Thus,

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

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 an A molecule.

- 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

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

- 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,

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

Diffusion-influenced reactions (continued)

- Rearranging, we get

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

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

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

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

Diffusion-influenced reactions (continued)

- Applying the limits, we get

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

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

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

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

Diffusion-influenced reactions (continued)

- The result is

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

- 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-controlled 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-controlled**.

- For k_R very large, we get

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

- This quantity is the **diffusion-controlled 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-controlled 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-controlled rate constant becomes

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

and the diffusion-influenced rate constant is

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

The diffusion-controlled 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 ϵ is the permittivity of the solvent.

- 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-controlled rate constant

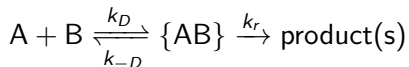
The Coulomb interaction (continued)

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

- β has units of length.
- 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.

Diffusion-influenced reactions: a second approach

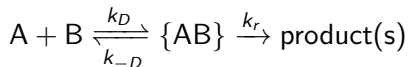
- Consider an elementary reaction $A + B \xrightarrow{k} \text{product(s)}$.
- If $\{AB\}$ is the encounter pair formed from the reactants A and B, we can break down a reaction in solution into two steps:



- An encounter pair is **not**
 - a chemical intermediate or
 - the transition state of a reaction.
- The encounter pair has a very short lifetime (to be estimated later).

We should therefore be able to apply the steady-state approximation to the encounter pair.

Diffusion-influenced reactions (continued)



$$\frac{d[\{AB\}]}{dt} = k_D[A][B] - (k_{-D} + k_r)[\{AB\}] \approx 0$$

$$\therefore [\{AB\}] \approx \frac{k_D}{k_{-D} + k_r} [A][B]$$

$$\therefore v = k_r[\{AB\}] \approx \frac{k_D k_r}{k_{-D} + k_r} [A][B]$$

- Since $v = k[A][B]$,

$$k = \frac{k_D k_r}{k_{-D} + k_r}$$

Comparison of the two approaches

- We previously derived the equation

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

for the case of weak intermolecular forces (hard-sphere potential), where k_R is the **second-order** rate constant for A reacting with B molecules that have already reached distance R_{AB} .

- We now have

$$k = \frac{k_D k_r}{k_{-D} + k_r}$$

where k_r is the **first-order** rate constant for the formation of products from the encounter pair.

Comparison of the two approaches (continued)

- These are two different ways of describing the same thing, so the two k expressions must be equal.

$$\begin{aligned} \therefore \frac{k_D k_R}{k_R + k_D \exp\left(\frac{U(R_{AB})}{k_B T}\right)} &= \frac{k_D k_r}{k_{-D} + k_r} \\ \therefore \frac{1}{1 + \frac{k_D}{k_R} \exp\left(\frac{U(R_{AB})}{k_B T}\right)} &= \frac{1}{1 + k_{-D}/k_r} \\ \therefore k_R &= \frac{k_D}{k_{-D}} \exp\left(\frac{U(R_{AB})}{k_B T}\right) k_r \end{aligned}$$

or

$$k_r = k_R \frac{1}{K_D} \exp\left(-\frac{U(R_{AB})}{k_B T}\right)$$

where $K_D = k_D/k_{-D}$ is the equilibrium constant for formation of the encounter pair.

Comparison of the two approaches (continued)

$$k_r = k_R \frac{1}{K_D} \exp\left(-\frac{U(R_{AB})}{k_B T}\right)$$

- K_D^{-1} has units of concentration.

It is a characteristic concentration scale for the equilibrium of the formation of the encounter pair.

(If $[A], [B] \sim K_D^{-1}$, then $[AB] \sim K_D^{-1}$.)

- Thus, k_R is the second-order rate constant we would get if the encounter pair were in equilibrium with A and B at the characteristic concentration.

(Compare the last equation in the previous lecture:

$$c_i(r) = c_i^\circ \exp\left(-\frac{U(r)}{k_B T}\right).$$

Comparison of the two approaches (continued)

- k_r ought in principle be evaluable from variational transition-state theory or other similar approaches.
- In either theory, the same equation for k_D holds.

Encounter pair formation and breakup

- For the special case of molecules whose intermolecular forces with the solvent are about the same as those between each other, we can estimate K_D by a statistical argument. This will also lead to an estimate of k_{-D} since we know how to calculate k_D .
- Focus again on an A molecule.
- Suppose that the **coordination number** of the reactive site of A is \mathcal{N} , i.e. that the reactive site of A makes contacts with \mathcal{N} neighboring molecules in solution.
- Let $[S]$ be the mole density of the solvent. The probability that any given molecule of S has been replaced by a B in the first solvation sphere of A is $[B]/[S]$.

Encounter pair formation and breakup

- If $[B] \ll [S]$, the probability that one of the \mathcal{N} solvent molecules around A has been replaced by a B is $\mathcal{N}[B]/[S]$.
- Another way to think about it is that $\mathcal{N}[B]/[S]$ is the fraction of A molecules that have a B molecule in their first solvation sphere.
- Therefore,

$$[\{AB\}] \approx \mathcal{N} \frac{[B]}{[S]} [A]$$

- Since

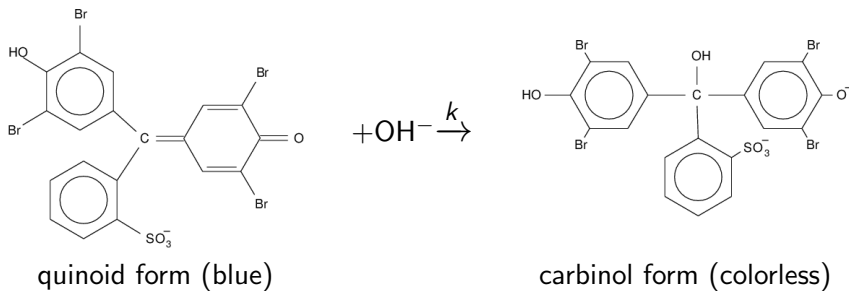
$$K_D = \frac{[\{AB\}]}{[A][B]}$$

we get

$$K_D = \frac{\mathcal{N}}{[S]}$$

Example:

Reaction of bromphenol blue with hydroxide ion



$$k = 9.30 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1} \text{ in water at } 25^\circ \text{C.}$$

To do: Estimate k_r .

Example:

Reaction of bromphenol blue with hydroxide ion

Estimate of k_D

- Given: $D_{\text{OH}^-} = 5.30 \times 10^{-9} \text{ m}^2\text{s}^{-1}$,
 $D_{\text{BPB}} = 4.4 \times 10^{-10} \text{ m}^2\text{s}^{-1}$, C-O bond length = 143 pm,
 $\kappa_{\text{H}_2\text{O}} = 78.37$ (all at 25 °C)
- Take $R_{AB} \approx$ C-O bond length.
- The two reactants are both anions with a single negative charge.

$$\epsilon = \kappa\epsilon_0 = 6.939 \times 10^{-10} \text{ C}^2\text{J}^{-1}\text{m}^{-1}$$

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

$$= 4.846 \times 10^{-12} \text{ m.}$$

Example:

Reaction of bromphenol blue with hydroxide ion

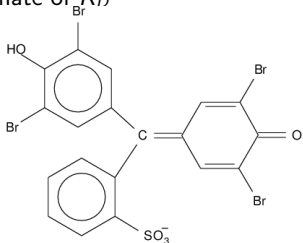
Estimate of k_D (continued)

$$\begin{aligned}\therefore k_D &= 4\pi L D_{AB} \beta \\ &= 4\pi (6.022\,141 \times 10^{23} \text{ mol}^{-1}) [(5.30 + 0.44) \times 10^{-9} \text{ m}^2 \text{ s}^{-1}] \\ &\quad \times (4.846 \times 10^{-12} \text{ m}) \\ &= 2.11 \times 10^5 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1} \equiv 2.11 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1}\end{aligned}$$

Example:

Reaction of bromphenol blue with hydroxide ion

Estimate of K_D



- For this structure, $\mathcal{N} = 2$ seems reasonable.
- The mole density of water at 25 °C is 55.33 mol L⁻¹.
- Therefore

$$K_D \approx \frac{\mathcal{N}}{[\text{H}_2\text{O}]} = \frac{2}{55.33 \text{ mol L}^{-1}} = 4 \times 10^{-2} \text{ L mol}^{-1}$$

Example:

Reaction of bromphenol blue with hydroxide ion

Estimate of k_{-D}

- Since $K_D = k_D/k_{-D}$, we have

$$k_{-D} = k_D/K_D = 6 \times 10^9 \text{ s}^{-1}$$

Aside: This value of k_{-D} implies a half-life of the encounter pair of

$$t_{1/2} = \ln 2/k_{-D} = 1 \times 10^{-10} \text{ s} \equiv 100 \text{ ps}$$

Example:

Reaction of bromphenol blue with hydroxide ion

Estimate of k_r

- By rearranging

$$k = \frac{k_D k_r}{k_{-D} + k_r}$$

we get

$$\begin{aligned} k_r &= \frac{k k_{-D}}{k_D - k} \\ &= \frac{(9.30 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1})(6 \times 10^9 \text{ s}^{-1})}{2.11 \times 10^8 \text{ L mol}^{-1} \text{ s}^{-1} - 9.30 \times 10^{-4} \text{ L mol}^{-1} \text{ s}^{-1}} \\ &= 3 \times 10^{-2} \text{ s}^{-1} \end{aligned}$$

Example:

Reaction of bromphenol blue with hydroxide ion

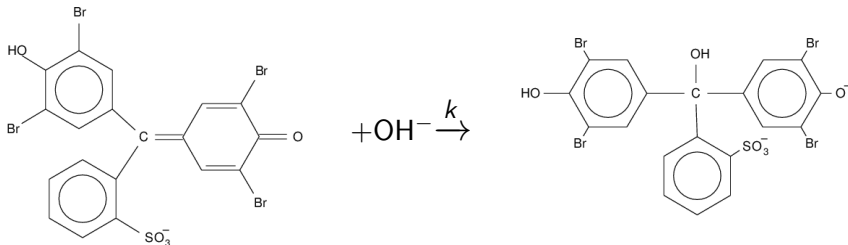
Activation-controlled reactions

- Note that $k_r \ll k_{-D}$.
- Therefore $k \approx k_r K_D$.
- Such a reaction is said to be **activation controlled**.
- Getting to the transition state is a rare event for encounter pairs.

Example:

Reaction of bromphenol blue with hydroxide ion

Activation-controlled reactions



What makes the transition state hard to reach?