Lecture 6: Diffusion and Reaction kinetics
12-10-2010

• Lecture plan:
  – diffusion
    • thermodynamic forces
    • evolution of concentration distribution
  – reaction rates and methods to determine them
  – reaction mechanism in terms of the elementary reaction steps
  – basic reaction types
  – problems
• Thermodynamic force

If the chemical potential depends on position, the maximum nonexpansion work

\[ dw = d\mu = \left( \frac{\partial \mu}{\partial x} \right)_{p,T} \, dx \]

Comparing with \( dw = -F \, dx \)

\[ F = -\left( \frac{\partial \mu}{\partial x} \right)_{p,T} \quad \text{Thermodynamic force} \]
• Thermodynamic force of concentration gradient

\[ \mu = \mu_0 + RT \ln a \]

For ideal solution

\[ F = -RT \left( \frac{\partial \ln a}{\partial x} \right)_{p,T} \]

\[ F = -\frac{RT}{c} \left( \frac{\partial c}{\partial x} \right)_{p,T} \]

Fick’s law of diffusion:

Particles flux: \[ J \sim drift velocity \sim F \sim \frac{\partial c}{\partial x} \]
• The Einstein relation

\[ J = -D \frac{\partial c}{\partial x} \quad J = \frac{s \Delta A t c}{A \Delta t} = sc \]

\[ sc = -D \frac{\partial c}{\partial x} \]

\[ s = -\frac{D}{c} \frac{\partial c}{\partial x} = \frac{DF}{RT} \]

In the case of charged particle (ion) in electric field we know drift speed vs force relation for ion mobility, so we can deduce diffusion constant

\[ s = uE = \frac{DzeN_A E}{RT} \quad \Rightarrow \quad D = \frac{uRT}{zF} \]

Einstein relation

For example: for \( \mu = 5 \cdot 10^{-8} \text{ m}^2 / \text{sV} \) we find \( D = 1 \cdot 10^{-9} \text{ m}^2 / \text{s} \)
Diffusion

• The Nernst-Einstein equation

Molar conductivity of ions in the solution

$$\Lambda_m = (v_+z^2D_+ + v_-z^2D_-) \frac{F^2}{RT}$$

$$\lambda = z\mu F = \frac{z^2DF^2}{RT}$$

• The Stokes-Einstein equation

$$\mu E = \frac{ezE}{f}$$

$$D = \frac{\mu RT}{zF}$$

$$D = \frac{zeRT}{fzF} = \frac{zekNA}{fzeN_A} = \frac{kT}{f}$$

Using Stokes’s law

$$D = \frac{kT}{6\pi\eta a}$$

No charge involved -> applicable to all molecules
**Diffusion equation**

- How concentration distribution evolves with time due to diffusion

\[
\frac{\partial c}{\partial t} = \frac{JAdt}{Aldt} - \frac{J'Adt}{Aldt} = \frac{J - J'}{l}
\]

\[
J - J' = -D \frac{\partial c}{\partial x} + D \frac{\partial c'}{\partial x} = -D \frac{\partial c}{\partial x} + D \frac{\partial}{\partial x} \left( c + \left( \frac{\partial c}{\partial x} \right) l \right) = Dl \frac{\partial^2 c}{\partial x^2}
\]

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2}
\]

**Diffusion with convection**

\[
\frac{\partial c}{\partial t} = \frac{JAdt}{Aldt} - \frac{J'Adt}{Aldt} = \frac{J - J'}{l}
\]

\[
J - J' = cv - c'v = \left( c - \left( c + \left( \frac{\partial c}{\partial x} \right) l \right) \right) v = vl \frac{\partial c}{\partial x}
\]

\[
\frac{\partial c}{\partial t} = v \frac{\partial c}{\partial x}
\] due to convection only

\[
\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - v \frac{\partial c}{\partial x}
\]
Solution of diffusion equation

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - \nu \frac{\partial c}{\partial x} \]

- 2nd order differential equation: two boundary condition are required for spatial dependence and single for time dependence

**Example 1:**
one surface of a container \((x=0)\) is coated with \(N_0\) molecules at time \(t=0\)

\[ c(x,t) = \frac{n_0}{A(\pi Dt)^{1/2}} e^{-x^2/4Dt} \]

**Example 2:**
dissolution infinitely small solid containing \(N_0\) molecules at time \(t=0\) in 3D solvent

\[ c(r,t) = \frac{n_0}{8(\pi Dt)^{3/2}} e^{-r^2/4Dt} \]
Diffusion probabilities

- Probability to find a particle at a given slab of thickness \( dx \) is proportional to the concentration there:
  \[
p(x) = c(x) AN_A dx / N_0
  \]

- The mean distance traveled by the particles:

  \[
  \langle x \rangle = \int_0^\infty \frac{c(x) AN_A dx}{N_0} = \frac{1}{(\pi Dt)^{1/2}} \int_0^\infty xe^{-x^2/4Dt} dx = 2 \left( \frac{Dt}{\pi} \right)^{1/2}
  \]

  \[
  \langle x^2 \rangle^{1/2} = (2Dt)^{1/2}
  \]

Diffusion in unstirred solution, \( D=5\times10^{-10} \text{ m}^2/\text{S} \)

- Diagram showing log-log plot of \( \log(\langle x^2 \rangle^{1/2}) \) vs. \( \log(t/s) \) with markers for 1 ms, 1 s, 1 h, and 1 y.
Random Walk

- Apparently diffusion can be modeled as a random walk, where particle is jumping distance \( \lambda \) in a time \( \tau \). Direction of the jump is chosen randomly.

- One dimensional walk:

\[
p = \left( \frac{2\tau}{\pi t} \right)^{1/2} e^{-x^2/2t\lambda^2}
\]

Comparing with the solution of diffusion equation

\[
D = \frac{\lambda^2}{2\tau}
\]

Einstein-Smoluchowski equation

Connection between microscopic and macroscopic parameters.
RATES OF CHEMICAL REACTIONS
Rates of chemical reactions

\[ A + 2B \rightarrow 3C + D \]

Instantaneous rate of consumption of a reactant:
\[-d[R]/dt\]

Instantaneous rate of formation of a product:
\[d[P]/dt\]

From stoichiometry
\[
\frac{d[D]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = - \frac{d[A]}{dt} = - \frac{1}{2} \frac{d[B]}{dt}
\]

Rate of the reaction:
\[v = \frac{1}{\nu_i} \frac{dn_i}{dt} = \frac{d\xi}{dt}\]

In case of heterogeneous reaction the rate will be defined as mol/m²s
Reaction order

Reaction rate is generally dependent on temperature, pressure, concentration of species, the phases where reaction occurs etc. However, an empirical relation called a rate law exists stating that:

\[ v = k[A]^a[B]^b \ldots \]

rate constant, depends only on T and not on the concentration

algebraic dependence on the reagent concentration raised to some power

reaction order with respect to species A: \( \alpha \)

overall reaction order: \( \alpha + \beta \ldots \)

The power is generally not equal to the stoichiometric coefficients, has to be determined from the experiment

Order of a reaction:

\[ v = k \]

\( \rightarrow \) Zero order. \( [M \cdot s^{-1}] \)

\[ v = k[A][B] \]

\( \rightarrow \) First order in A, first order in B, overall second order. \( [M^{-1} \cdot s^{-1}] \)

\[ v = k[A]^{1/2}[B] \]

\( \rightarrow \) Halforder in A, first order in B, overall tree-halves order.
Measuring the rates of chemical reactions

- Experimental measuring progress of the reaction
  
  - Monitoring pressure in the reaction involving gases
    
    \[ 2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g) \]
    
    \[
n(1-\alpha) \quad 2\alpha n \quad \frac{1}{2} \alpha n
    \]
    
    \[ p = (1 + \frac{3}{2} \alpha)p_0 \]

  - Absorption at particular wavelength (e.g. Br\(_2\) below)
    
    \[ H_2(g) + Br_2(g) \rightarrow 2HBr(g) \]

  - Conductance of the ionic solution
    
    \[(CH_3)_3CCl(aq) + H_2O(aq) \rightarrow (CH_3)_3COH(aq) + H^+(aq) + Cl^-(aq)\]
Measuring the Rates of chemical reactions

- Flow method
- Stopped-flow method (down to 1 ms range)
- Flash photolysis (down to 10 fs = 10^{-14} s range)
- Chemical quench flow
- Freeze quench method
Measuring the rates of chemical reactions

• Determination of the rate law

Usual technique is the **isolation method**, where all the components except one are present in large amounts (therefore their concentration is constant)

\[ v = k[A][B_0] = k'[A] \]

It usually accompanied by the **method of initial rates**, when several initial concentration of A measured (again assuming that the concentrations are constant)

\[ v_0 = k'[A_0]^a \quad \log v_0 = \log k' + a \log[A_0] \]
Measuring the rates of chemical reactions

- Example: \[ 2I(g) + Ar(g) \longrightarrow I_2(g) + Ar(g) \]
Integrated rate laws

• First order reaction.
  – Let’s find concentration of reagent A after time t

\[
\frac{d[A]}{dt} = -k[A] \quad \Rightarrow \quad \int_{A_0}^{A} \frac{d[A]}{[A]} = -k \int_{0}^{t} dt \quad \Rightarrow
\]

\[\ln \left( \frac{[A]}{[A_0]} \right) = -kt \quad \Rightarrow \quad [A] = [A_0] e^{-kt}
\]

– **Half-life** – time required for concentration to drop by \(\frac{1}{2}\).

\[
kt_{1/2} = -\ln \left( \frac{1}{2} \frac{[A_0]}{[A_0]} \right) = \ln 2 \quad t_{1/2} = \frac{\ln 2}{k}
\]

– **Time constant** – time required for concentration to drop by \(1/e\):

\[
\tau = \frac{1}{k}
\]
Integrated rate laws

• Second-order reactions

\[
\frac{d[A]}{dt} = -k[A]^2 \quad \Rightarrow \quad \int_{[A]}^{A_0} \frac{d[A]}{[A]^2} = -k \int_0^t dt \quad \Rightarrow
\]

\[
\frac{1}{[A]} - \frac{1}{[A_0]} = kt \quad \Rightarrow \quad [A] = \frac{[A_0]}{1 + kt[A_0]}
\]

– Half-life – depends on initial concentration

\[
\frac{1}{2}[A_0] = \frac{[A_0]}{1 + kt_{1/2}[A_0]} \quad t_{1/2} = \frac{1}{k[A_0]}
\]

The concentration of the reagent drops faster in the 1\textsuperscript{st} order reaction than in the 2\textsuperscript{nd} order reaction
Reaction approaching equilibrium

- Generally, most kinetics measurements are made far from equilibrium where reverse reactions are not important. **Close to equilibrium** the amount of products is significant and reverse reaction should be considered.

\[
\begin{align*}
A &\rightarrow B \quad \nu = k[A] \\
B &\rightarrow A \quad \nu = k'[B]
\end{align*}
\]

\[
\frac{dA}{dt} = -k[A] + k'[B] \quad [A] + [B] = [A]_0
\]

\[
\frac{dA}{dt} = -k[A] + k'([A]_0 - [A])
\]

\[
[A] = \frac{k' + ke^{-(k+k')t}}{k + k'}[A]_0
\]

\[
[A]_{eq} = \frac{k'}{k + k'}[A]_0, \quad [B]_{eq} = \frac{k}{k + k'}[A]_0, \quad K = \frac{[B]_{eq}}{[A]_{eq}} = \frac{k}{k'}
\]

Generally:

\[
K = \frac{k_a}{k'_a} \times \frac{k_b}{k'_b} \times \ldots
\]
The temperature dependence of reaction rate

- The rate constants of most reactions increase with the temperature.
- Experimentally, for many reactions $k$ follows the Arrhenius equation:

$$\ln k = \ln A - \frac{E_a}{RT}$$

$A$ – pre-exponential (frequency) factor,

$E_a$ – activation energy

High activation energy means that rate constants depend strongly on the temperature, zero would mean reaction independent on temperature.
The temperature dependence of reaction rate

- **Stages of reaction:**
  - Reagents
  - Activation complex
  - Product

\[ k = Ae^{-E_a / RT} \]

- Activation energy is the minimum kinetic energy reactants must have to form the products.
- Pre-exponential is rate of collisions
- Arrhenius equation gives the rate of successful collisions.

**reaction coordinate:** e.g. changes of interactomic distances or angles
Most reactions occur in a sequence of steps called **elementary reactions**. Molecularity of an elementary reaction is the number of molecules coming together to react (e.g. **uni-molecular**, **bimolecular**)

**Uni-molecular:** first order in the reactant

\[
A \rightarrow P \quad \frac{d[A]}{dt} = -k[A]
\]

**Bimolecular:** first order in the reactant

\[
A + B \rightarrow P \quad \frac{d[A]}{dt} = -k[A][B]
\]

Proportional to collision rate

\[
H + Br_2 \rightarrow HBr + Br
\]
Consecutive elementary reactions

\[ A \xrightarrow{k_a} I \xrightarrow{k_b} P \]

\[
\frac{d[A]}{dt} = -k_a[A] \\
\frac{d[I]}{dt} = k_a[A] - k_b[I] \\
\frac{d[P]}{dt} = k_b[I]
\]

Solution for A should be in a form: \[ [A] = [A]_0 e^{-k_a t} \]

\[
\frac{d[I]}{dt} + k_b[I] = k_a[A]_0 e^{-k_a t} \\
[I] = \frac{k_a}{k_b - k_a} (e^{-k_a t} - e^{-k_b t})[A]_0
\]

\[ [A] + [I] + [P] = [A]_0 \]

\[ [P] = \left(1 + \frac{k_a e^{-k_a t} - k_b e^{-k_b t}}{k_b - k_a}\right)[A]_0 \]
Consecutive elementary reactions

- The (quasi) steady-state approximation

\[
\frac{d[I]}{dt} = 0
\]

Then
\[
\frac{d[I]}{dt} = k_a[A] - k_b[I] = 0
\]

and
\[
\frac{d[P]}{dt} = k_b[I] \approx k_a[A]
\]

\[
[P] \approx \left(1 - e^{-k_a t}\right)[A]_0
\]
Consecutive elementary reactions

- Pre-equilibria

\[ A + B \xrightleftharpoons[k_a \cdot k'_a]{k_b} I \xrightarrow[k_b]{k_a} P \]

This condition arises when \( k'_a \gg k_b \).

Then

\[ K = \frac{[I]}{[A][B]} = \frac{k_a}{k'_a} \]

and

\[ \frac{d[P]}{dt} = k_b[I] = k_b K[A][B] \quad \text{Second order form with composite rate constant} \]
Unimolecular reactions

• As the molecule acquires the energy as a result of collision why the reaction is still a first order?

• Lindemann-Hinshelwood mechanism

\[ A + A \xrightarrow{k_a} A^* + A \quad \frac{d[A^*]}{dt} = k_a[A]^2 \]

\[ A + A^* \xrightarrow{k'_a} A + A \quad \frac{d[A^*]}{dt} = -k'_a[A^*][A] \]

\[ A^* \xrightarrow{k_b} P \quad \frac{d[A^*]}{dt} = -k_b[A^*] \]

If the last step is rate-limiting the overall reaction will have first order kinetics.
Lindemann-Hinshelwood mechanism

\[
\begin{align*}
A + A & \xrightarrow{k_a} A^* + A \\
A + A^* & \xrightarrow{k'} A + A \\
A^* & \xrightarrow{k_b} P
\end{align*}
\]

\[
\begin{align*}
\frac{d[A^*]}{dt} &= k_a [A]^2 \\
\frac{d[A^*]}{dt} &= -k'[A^*][A] \\
\frac{d[A^*]}{dt} &= -k_b [A^*]
\end{align*}
\]

\[
\begin{align*}
\frac{d[A^*]}{dt} &= k_a [A]^2 - k'_a [A^*][A] - k_b [A^*] \\
[A^*] &= \frac{k_a [A]^2}{k_b + k'_a [A]} \\
\frac{dP}{dt} &= k_b [A^*] = \frac{k_b k_a [A]^2}{k_b + k'_a [A]}
\end{align*}
\]

If the rate of deactivation is much higher that unimolecular decay than:

\[
\frac{dP}{dt} = \frac{k_b k_a [A]^2}{k_b + k'_a [A]} \approx \frac{k_b k_a [A]}{k'_a}
\]

The Lindemann-Hinshelwood mechanism can be tested by reducing the pressure (slowing down the activation step) so the reaction will switch to the second order.
Let’s consider Lindemann-Hinshelwood mechanism and apply Arrhenius-like temperature dependence to each rate constant

\[ k = \frac{k_ao \cdot k_bo}{k'_a} = \frac{(A_a e^{-E_a(a)/RT})(A_b e^{-E_a(b)/RT})}{(A'_a e^{-E'_a(a)/RT})} = \frac{A_a A_b}{A'_a} e^{-(E_a(a) + E_a(b) - E'_a(a))/RT} \]

Overall activation energy can be positive or negative

\[ E_a(a) + E_a(b) > E'_a(a) \]

\[ E_a(a) + E_a(b) < E'_a(a) \]
Problems

• **P20.35.** The diffusion coefficient of particular RNA molecule is \(1.0 \times 10^{-11}\) m\(^2\)/s. Estimate time required for a molecule to diffuse 1 um from nucleus to the cell wall.

• **E21.11a** The second-order rate constant for the reaction

\[
\text{CH}_3\text{COOC}_2\text{H}_5(aq) + \text{OH}^-(aq) \rightarrow \text{CH}_3\text{CO}_2^-(aq) + \text{CH}_3\text{CH}_2\text{OH}(aq)
\]

is 0.11 dm\(^3\) mol\(^{-1}\) s\(^{-1}\). What is the concentration of ester after (a) 10 s, (b) 10 min when ethyl acetate is added to sodium hydroxide so that the initial concentrations are [NaOH] = 0.050 mol dm\(^{-3}\) and [CH\(_3\)COOC\(_2\)H\(_5\)] = 0.100 mol dm\(^{-3}\)?

• **E21.17a** The effective rate constant for a gaseous reaction that has a Lindemann–Hinshelwood mechanism is \(2.50 \times 10^{-4}\) s\(^{-1}\) at 1.30 kPa and \(2.10 \times 10^{-5}\) s\(^{-1}\) at 12 Pa. Calculate the rate constant for the activation step in the mechanism.