Chemical kinetics

- rate of reactions, dependence on conditions
- calculate the composition as a function of time
- reaction mechanisms
Chemical kinetics

Reactions:
- homogeneous (one phase)
- heterogeneous
- enzyme

Activation:
- catalyst
- heat, other reaction, microwaves
- light (VIS, UV, X), ultrasound . . .
Rate of reaction

\[ 0 \to \sum_i \nu_i A_i \]

Rate of reaction \((\xi = \text{extent of reaction}, \ [\xi] = \text{mol})\):

\[ J = \frac{d\xi}{d\tau} = \frac{1}{\nu_i} \frac{dn_i}{d\tau} \]

Usually per unit volume (intensive quantity):

\[ r = \frac{J}{V} = \frac{1}{\nu_i} \frac{dc_i}{d\tau} \]

\( r \) depends on stoichiometry:

\[ r(2A \to A_2) = \frac{1}{2} r(A \to \frac{1}{2}A_2) \]

reactants: \( \nu_i < 0 \)
products: \( \nu_i > 0 \)

concentration:
\[ c_i = [A_i] = n_i/V \]
dimensionless (relative) concentration:
\[ c_i^{\text{rel}} = \{A_i\} = c_i/c^{\text{st}} \]
**Simple reaction** is given by one reaction and one kinetic equation (not necessarily elementary)

Generally:

\[ r = f(c_A, c_B, \ldots, T) \]

Often:

\[ r = k(T) c_A^\alpha c_B^\beta \ldots \]

\[ \text{pak} \]

- \( k(T) = \) rate constant (kinetic constant)
- \( \alpha, \beta = \) partial orders of reaction (elem.r. = integers)
- \( n = \alpha + \beta \cdots = \) (total) reaction order

Dimensional(\( k \)) = \( (\text{mol dm}^{-3})^{1-n} \text{s}^{-1} \)

Often dimensionless \( c_i^{\text{rel}} = c_i/c^\text{st} \), then dimension(\( k \)) = \( \text{s}^{-1} \)

**Half life of reaction:** \( c_A \) decreases to one half

\[ c_A(\tau_{1/2}) = \frac{c_A(0)}{2} \]
Homogeneous reactions: balance

\[ 0 \rightarrow \sum_i \nu_i A_i \]

Constant volume: balance in concentrations \((x = x(\tau) = \xi/V)\):

\[ c_i = c_{i,0} + \nu_i x \]

Degree of conversion \((k = \text{key compound} \Rightarrow \nu_k < 0)\):

\[ \alpha = \frac{c_{k,0} - c_k}{c_{k,0}} = \frac{\nu_k x}{c_{k,0}} \]

It holds \(0 \leq \alpha \leq 1\)

**Example.** Nitryl fluoride is produced in gas phase by reaction:

\[ 2 \text{NO}_2(g) + \text{F}_2(g) \rightarrow 2 \text{NO}_2\text{F}(g) \]

The reaction is of the 1st order with respect to both NO\(_2\) and F\(_2\). Write the kinetic equation if the reaction proceeds in constant volume. The initial concentrations are \([\text{NO}_2]_0\) a \([\text{F}_2]_0\), respectively, and the kinetic constant \(k\).

\[ (x - 0[\text{F}]) (x \text{F} - 0[\text{NO}]) \chi = \frac{1p}{[\text{F}] \text{NO} \chi p} = \frac{1p}{[\text{NO}] \text{F} \chi p} = \frac{1p}{[\text{F}]*\chi p} \]
Reaction A → P

Rate equation:
\[
\frac{dc_A}{d\tau} = -kc_A^n \quad \text{for } c_A > 0
\]
\[
= 0 \quad \text{for } c_A = 0
\]

Initial condition: \( c_A(0) = c_A0 \)

Solution (integrated form):

<table>
<thead>
<tr>
<th>( n )</th>
<th>( c_A(\tau) )</th>
<th>conditions</th>
<th>( \tau_{1/2} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>( c_A0 - k\tau )</td>
<td>( \tau &lt; c_A0/k ) &lt;br&gt;( \tau \geq c_A0/k )</td>
<td>( \frac{c_A0}{2k} )</td>
</tr>
<tr>
<td>1</td>
<td>( c_A0 e^{-k\tau} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>( \frac{1}{1/c_A0+k\tau} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(1, ( \infty ))</td>
<td>( [c_A0^{1-n} - (1-n)k\tau]^{1/(1-n)} )</td>
<td></td>
<td></td>
</tr>
<tr>
<td>[0, 1)</td>
<td>( [c_A0^{1-n} - (1-n)k\tau]^{1/(1-n)} )</td>
<td>( \tau &lt; c_A0^{1-n}/[(1-n)k] ) ( \tau \geq c_A0^{1-n}/[(1-n)k] )</td>
<td></td>
</tr>
</tbody>
</table>
Both partial orders $\alpha = \beta = 1$ (total order $= 2$)

Rate equation:

$$\frac{dx}{d\tau} = kc_Ac_B = k(c_{A0} - x)(c_{B0} - x)$$

Initial condition:

$$x(0) = 0 \text{ or } c_A(0) = c_{A0}, \ c_B(0) = c_{B0},$$

Solution (integrated form):

- $c_{A0} = c_{B0}$: the same as previous slide
- $c_{A0} \neq c_{B0}$: $(c_{A0} - c_{B0})k\tau = \ln \left( \frac{c_{A0} - x}{c_{B0} - x} \right) = \ln \left( \frac{c_A}{c_B} \frac{c_{B0}}{c_{A0}} \right)$

$$c_A = (c_{A0} - c_{B0}) \frac{c_{A0} \epsilon}{c_{A0} \epsilon - c_{B0}}$$

$$c_B = (c_{A0} - c_{B0}) \frac{c_{B0}}{c_{A0} \epsilon - c_{B0}} \quad \text{where } \epsilon = \exp[(c_{A0} - c_{B0})k\tau]$$

Example: $\text{NO}_2^-(aq.) + \text{NH}_4^+(aq.) \rightarrow \text{N}_2(g) + 2 \text{H}_2\text{O}(l)$
Kinetic measurements

- Integral data: $c_i(\tau)$

- Differential data: rates $dc_i/d\tau$:
  - flow reactor (steady state) $dc_i/d\tau \propto c_i^{in} - c_i^{out}$
  - initial reaction rate (small extent)

- Fast reaction: lasers

- Proxies to $c_i(\tau)$: pressure (in g), density, optical activity, extinction, index of refraction, ...
Determining the reaction order

- integral method: fitting (regression, correlation) of data to theoretical equation \( c_A = f(c_{A0}, k, n; \tau) \) – preferred now

- integral method “by hand” (for \( A \rightarrow P \)):

\[
k = \begin{cases} 
\frac{c_A^{1-n} - c_A^{1-n}}{(n-1)(\tau_1 - \tau_2)} & n \neq 1 \\
- \ln\left(\frac{c_{A1}}{c_{A2}}\right) \div \tau_1 - \tau_2 & n = 1
\end{cases}
\]

- differential method: rate known at two times

\[
n = \frac{\ln(r_1/r_2)}{\ln(c_{A1}/c_{A2})}
\]

- half-life method:

\[
n = 1 - \frac{\ln(\tau_{1/2,1}/\tau_{1/2,2})}{\ln(c_{A0,1}/c_{A0,2})}
\]

- Ostwald isolation method:

\[
r = kc_A^\alpha c_B^\beta : c_B \gg c_A \text{ (B in excess)} \Rightarrow r = k'c_A^\alpha
\]
Now obsolete!

- **integral method**
  1. **order**: \( \ln c_A = \ln c_{A0} - k \tau \) \( \Rightarrow \) straight line in \((\tau, \ln c_A)\)
  2. **order**: \( -1/c_A = -1/c_{A0} - k \tau \) \( \Rightarrow \) straight line in \((\tau, -1/c_A)\)
  3. **order**: \( -2/c_A^{1/2} = -2/c_{A0}^{1/2} - k \tau \) \( \Rightarrow \) straight line in \((\tau, -2/c_A^{1/2})\)

- **differential method**
  - tangent to \( c_A(\tau) \) \( \Rightarrow \) derivative \( r(\tau) \)
  - \( \ln r = \ln k + n \ln c_A \) \( \Rightarrow \) straight line in \((\ln c_A, \ln r)\)
Consecutive reactions of the 1st order

\[ A \xrightarrow{k_1} B \xrightarrow{k_2} C \]

**Kinetic equations:**

\[
\frac{dc_A}{d\tau} = -k_1 c_A
\]

\[
\frac{dc_B}{d\tau} = k_1 c_A - k_2 c_B
\]

\[
\frac{dc_C}{d\tau} = k_2 c_B
\]

**Initial conditions:**

\[ c_A(0) = c_{A0}, \quad c_B(0) = 0, \quad c_C(0) = 0 \]

**Solution:**

\[ c_A = c_{A0} e^{-k_1 \tau} \]

\[ c_B = \frac{k_1}{k_2 - k_1} c_{A0} \left[ e^{-k_1 \tau} - e^{-k_2 \tau} \right] \quad \text{for} \quad k_1 \neq k_2 \]

\[ = k_1 c_{A0} \tau e^{-k_1 \tau} \quad \text{for} \quad k_1 = k_2 \]

\[ c_C = c_{A0} - c_A - c_B \]

**Max. concentration:**

\[ \tau_{\text{max}} = \frac{\ln(k_1/k_2)}{k_1 - k_2} \quad \text{for} \quad k_1 \neq k_2 \]

\[ = 1/k_1 \quad \text{for} \quad k_1 = k_2 \]

- radioactive decay
- pharmacokinetics:
  \[ k_1 = \text{absorption const.} \]
  \[ k_2 = \text{elimination const.} \]
Concurrent reactions

**Example.** Both reactions of the first order

\[
\begin{align*}
  A & \overset{k_1}{\rightarrow} B \\
  A & \overset{k_2}{\rightarrow} C
\end{align*}
\]

Rate equations:

\[
\begin{align*}
  \frac{dc_A}{d\tau} &= -k_1 c_A - k_2 c_A \\
  \frac{dc_B}{d\tau} &= k_1 c_A \\
  \frac{dc_C}{d\tau} &= k_2 c_A
\end{align*}
\]

Solution for \( c_A(0) = c_{A0}, \ c_B(0) = 0, \ c_C(0) = 0 \):

\[
\begin{align*}
  c_A &= c_{A0} \exp\left[-(k_1 + k_2)\tau\right] \\
  c_B &= c_{A0} \frac{k_1}{k_1 + k_2} \left\{ 1 - \exp[-(k_1 + k_2)\tau] \right\} \\
  c_C &= c_{A0} \frac{k_2}{k_1 + k_2} \left\{ 1 - \exp[-(k_1 + k_2)\tau] \right\}
\end{align*}
\]

Variants: \( A+B \rightarrow, \ A+C \rightarrow, \ A \gg B,C \)
Reversible reactions

Example. Both reactions of the 1st order:

\[ A \xrightleftharpoons{k_1, k_{-1}} B \]

Rate equation:

\[
\frac{dc_A}{d\tau} = -k_1 c_A + k_{-1} c_B
\]

Balance for \( c_A(0) = c_{A0}, \) \( c_B(0) = 0 \):

\[ c_A + c_B = c_{A0} \]

Solution:

\[
c_A = \frac{c_{A0}}{k_1 + k_{-1}} \left[ k_1 e^{-(k_1+k_{-1})\tau} + k_{-1} \right]
\]

Equilibrium:

\[
\lim_{\tau \to \infty} c_A = \frac{k_{-1}}{k_1 + k_{-1}} c_{A0}
\]

Equilibrium constant:

\[
\frac{c_B(\infty)}{c_A(\infty)} = \frac{k_1}{k_{-1}} = K
\]
Law of mass action

Guldberg-Waage:

Let both reactions in

\[ A + B \xleftrightarrow{\k_1} \ k_{-1} C + D \]

are elementary (of 1st order wrt all compounds)

Rate equation:

\[ \frac{dc_A}{d\tau} = -k_1 c_A c_B + k_{-1} c_C c_D \]

Equilibrium: \[ \frac{dc_A}{d\tau} = 0 \] or

\[ \frac{c_C c_D}{c_A c_B} = \frac{k_1}{k_{-1}} = K \]

where K is the equilibrium constant
Nuclei are much heavier than electrons ⇒ electrons are faster (Born–Oppenheimer approximation): electrons follow nuclei

**Potential energy surface:** energy as a function of coordinates of all nuclei

Better: after removing redundant coordinates because of symmetry (rotations, translations)

A reaction proceeds by the least obstacle way = over the saddle point (better: close to it) = **transition state**

Transition state theory (Eyring): $k = \frac{RT}{N_A h} \exp\left(-\frac{G_m^\ddagger - G_{m_{\text{reactants}}}}{RT}\right)$
T-dependence of the reaction rate (Arrhenius)

\[
\frac{d \ln K}{dT} = \frac{\Delta r H_m^\phi}{RT^2} \quad \Delta r H_m^\phi = \text{const}
\]

\[
K = K_0 e^{-\frac{\Delta r H_m^\phi}{RT}} = \frac{k_1}{k_-} = \frac{A_1 e^{-\frac{E^*_1}{RT}}}{A_2 e^{-\frac{E^*_{-1}}{RT}}}
\]

\[
\Rightarrow \quad k = A e^{-\frac{E^*}{RT}}
\]

\( E^* = \text{activation energy} \), \( A = \text{prefactor} \)

\( \Delta r H_m^\phi = E^*_{1} - E^*_{-1} \)

Typical \( E^* \):
\( 50–110 \text{ kJ mol}^{-1} \)

Rule of the thumb:
\( 1.5–3 \times \text{ per } 10 \degree \text{C} \)

Kinetic theory of gases (Boltzmann):
\( k = 2N_A \sigma (RT/\pi M)^{1/2} \exp(-E^*/RT) \)