Chemical kinetics

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

Homogeneous reactions: balance
0 → \( \sum \gamma_i A_i \)
Constant volume: balance in concentrations \( x = x(t) = V/t \):
\[ c_i = c_i(0) + \gamma_i x \]
Degree of conversion \( k = \text{key compound} \to \gamma_i \leq 0 \):
\[ \alpha = \frac{c_i(0) - c_i(t)}{c_i(0)} = \frac{\ln x}{\ln \gamma_i} \]
It holds \( 0 \leq \alpha \leq 1 \)

Example. Nitril fluoride is produced in gas phase by reaction:
\[ 2 \text{NO}_2(g) + F_2(g) \rightarrow 2 \text{NO}_2F(g) \]
The reaction is of the 1st order with respect to both \text{NO}_2 and \text{F}_2. Write the kinetic equation if the reaction proceeds in constant volume. The initial concentrations are \([\text{NO}_2]/[\text{F}_2]_0\), respectively, and the kinetic constant \(k\).

\[ \langle x - 0 \rangle = \langle x - 0 \rangle \text{[CON]} = \frac{12}{15} \frac{\text{mol}}{\text{g}} = \frac{12}{15} \frac{\beta_{\text{CON}}}{\beta_{\text{x}}} \]

Reactions:
- homogeneous (one phase)
- heterogeneous
- enzyme
- isothermal – adiabatic
- isobaric – isochoric

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

Rate of reaction
- Net change in the concentration of species (relative): \( r = \frac{\partial c}{\partial t} \)
- Concentration: \( \frac{c_i}{c_i(0)} = \frac{r}{V} = \frac{1}{V} \frac{dc}{dt} \)
- Stoichiometric coefficient: \( \alpha \) changes to the concentration:
  \[ \frac{c_i}{c_i(0)} = \frac{\alpha_i}{c_i(0)} \]
- Dimensionality of \( k \): \( (\text{mol} \cdot \text{dm}^{-3})^{1-n} \text{g}^{-1} \)
- Half life of reaction: \( c_A \) decreases to one half
  \[ c_A(t_{1/2}) = \frac{c_A(0)}{2} \]

Solution (integrated form):

\[ c_A(t) = \frac{c_A(0)}{1 + \frac{c_A(0) - c_A(t)}{c_A(0) - c_A(0)}} \]

Reaction A → P
- Rate equation:
  \[ \frac{dc_A}{dt} = -k c_A \text{ for } c_A > 0 \]
  \[ = 0 \text{ for } c_A = 0 \]
- Initial condition: \( c_A(0) = c_{A0} \)

Solution (integrated form):

\[ c_A(t) = \frac{c_A(0)}{1 + \frac{c_A(0) - c_A(t)}{c_A(0) - c_A(0)}} \]

Reactions:
- \( \text{NO}_2 + \text{H}_2 \rightarrow \text{NO}_2\text{H}_2 \)
- \( \text{NO}_2\text{H}_2 + \text{NO}_2 \rightarrow \text{NO}_2\text{H}_2 \text{NO}_2 \)
- \( \text{NO}_2\text{H}_2 \text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_2\text{H}_2 \text{NO}_2 \text{NO}_2 \)
- \( \text{NO}_2\text{H}_2 \text{NO}_2 \text{NO}_2 + \text{NO}_2 \rightarrow \text{NO}_2\text{H}_2 \text{NO}_2 \text{NO}_2 \text{NO}_2 \)

Kinetic measurements
- Differential data: rates \( dc_i/dt \): symbol * means “proportional to”
- Fast reaction: lasers
- Proxies to \( c_A(t) \): pressure (in g), density, optical activity, extinction, index of refraction, . . .
Determining the reaction order

(Plot/[kintfit.sh] 9/16

- integral method: fitting (regression, correlation) of data to theoretical equation $c_A = f(c_{A0}, k, n, t)$ preferred now.
- integral method “by hand” (for $A \rightarrow P$):
  \[
  k = \left\{ \begin{array}{ll}
  \frac{c_A^n}{(n-1)(n-2)c_{A0}^n} & n \neq 1 \\
  \frac{n}{(n-2)c_{A0}^n} & n = 1
  \end{array} \right.
  \]
- differential method: rate known at two times
  \[
  n = \frac{\ln(c_{A1}/c_{A2})}{\ln(t_{1}/t_2)}
  \]
- half-life method:
  \[
  n = 1 \ln(t_{1/2.1}/t_{1/2.2})/ \ln(c_{A01}/c_{A02})
  \]
- Ostwald isolation method:
  \[
  \tau = \frac{k_c c_B^\beta}{c_A} \quad c_B \gg c_A \quad (B \text{ in excess}) \Rightarrow \tau = k_c^\gamma c_A
  \]

Order of reaction graphically

(Plot/[sintg1.sh] 10/16

Now obsolete!

- integral method
  1. order: $\ln c_A = \ln c_{A0} - k t$ straight line in $(t, \ln c_A)$
  2. order: $-1/c_A = -1/c_{A0} - k t$ straight line in $(t, -1/c_A)$
  2. \(1/2\) order: $-1/2 c_A^{1/2} = -1/2 c_{A0}^{1/2} - k t$ straight line in $(t, -2/c_A^{1/2})$
- differential method
  - tangent to $c_A(t) \Rightarrow$ derivative $\tau(c_A)$
  - $\ln r = \ln k + n \ln c_A$ straight line in $(\ln c_A, \ln r)$

Consecutive reactions of the 1st order

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A $k_1$ B $k_2$ C

Kinetic equations:

- $\frac{dc_A}{dt} = -k_1 c_A$
- $\frac{dc_B}{dt} = k_1 c_A - k_2 c_B$
- $\frac{dc_C}{dt} = k_2 c_B$

Initial conditions:

$c_A(0) = c_{A0}, c_B(0) = 0, c_C(0) = 0$

Solution:

$c_A = c_{A0} e^{-k_1 t}$
$c_B = \frac{k_1 c_{A0}}{k_2} [e^{-k_2 t} - e^{-k_1 t}]$ for $k_1 \neq k_2$
$c_C = \frac{k_2 c_{A0}}{k_1}$

Max. concentration:

$t_{\text{max}} = \frac{\ln(k_1/k_2)}{k_2 - k_1}$ for $k_1 \neq k_2$

- $t_{\text{max}} = k_1 t_1/k_2$ for $k_1 = k_2$
- radioactivity decay
- pharmacokinetics
- $k_1$ = absorption const.
- $k_2$ = elimination const.

Concurrent reactions

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Example. Both reactions of the first order:

A $k_1$ B $k_2$

Rate equations:

- $\frac{dc_A}{dt} = -k_1 c_A - k_2 c_A$
- $\frac{dc_B}{dt} = k_1 c_A$
- $\frac{dc_C}{dt} = k_2 c_A$

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

$c_A = c_{A0} e^{-k_1 t}$
$c_B = \frac{k_1 c_{A0}}{k_2} [1 - e^{-k_1 t}]$
$c_C = \frac{k_2 c_{A0}}{k_1} [1 - e^{-k_1 t}]$

Variants: A+B→, A+C→, A≫B,C

Reversible reactions

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Example. Both reactions of the 1st order:

A $k_1$ B $k_2$

Rate equation:

$\frac{dc_A}{dt} = -k_1 c_A + k_2 c_B$

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

$c_A + c_B = c_{A0}$

Solution:

$c_A = c_{A0} \left( \frac{k_2}{k_1 + k_2} \right) + \frac{k_1}{k_1 + k_2} c_B$

Equilibrium:

$\lim_{t \to \infty} c_A = \frac{k_1}{k_1 + k_2} c_{A0}$

Equilibrium constant: $c_A(\infty) = \frac{k_1}{k_1 + k_2} = K$

Law of mass action

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Guldberg-Waage:

Let both reactions in

A + B $\rightarrow$ C + D

are elementary (of 1st order wrt all compounds)

Rate equation:

$\frac{dc_A}{dt} = -k_1 c_A c_B + k_2 c_C c_D$

Equilibrium: $\frac{dc_A}{dc_B} = 0$

$c_{CCD} c_{A0} = \frac{k_1}{k_1 + k_2}$

where K si the equilibrium constant

Potential energy surface (PES)

(Plot/[rocoord.sh] 15/16

Nuclei are much heavier than electrons $\Rightarrow$ 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 $\Rightarrow$ over the saddle point (better close to it) = transition state

Transition state theory (Eyring): $k = (RT/\Delta H^\circ) \exp[-(\Delta G^\circ - G_0^\text{actants}/RT)]$

$\Delta G^\circ = E^*/RT$

$E^*$: activation energy, $\Delta H^*$ = prefactor

T-dependence of the reaction rate (Arrhenius)

$\frac{\ln k}{RT} = \frac{\Delta H^\circ - \Delta H^\circ_{\text{act}}}{RT} = \frac{k_0 e^{-\Delta H^\circ_{\text{act}}/RT}}{A e^{\Delta H^\circ/RT}}$

$k = A e^{-\Delta H^\circ/RT}$

$E^* = \text{activation energy, } \Delta H^\circ = \text{prefactor}$

$\Delta H^\circ = E^* - E^*_{\text{act}}$

Typical $E^*$: 50–110 kJ mol⁻¹

Rule of the thumb: 1.5–3× per 10°C

$\Delta H^\circ_{\text{act}} = E^* - E^*_{\text{act}}$

$\Delta H^\circ_{\text{act}} = E^* - E^*_{\text{act}}$

Kinetik theory of gases (Boltzmann): $k = 2N_A e(\Delta H^\circ/RT)^{1/2} \exp(-\Delta G^\circ/RT)$

$\Delta G^\circ = E^*/RT$