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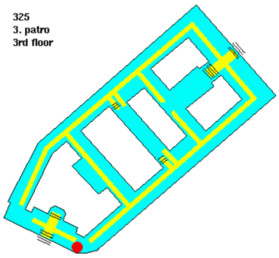

Chemical kinetics

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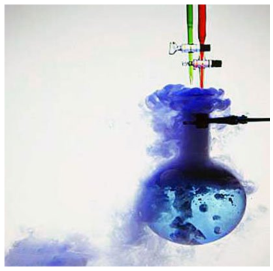
- rate of reactions, dependence on conditions
- calculate the composition as a function of time
- reaction mechanisms



credit: people.bath.ac.uk/ch3mw/photo3.gif

Chemical kinetics

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Reactions:

- homogeneous (one phase)
- heterogeneous
- enzyme

- isothermal – adiabatic
- isobaric – isochoric

Activation:

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

Rate of reaction

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$$0 \to \sum_i \nu_i A_i$$

reactants: $\nu_i < 0$
products: $\nu_i > 0$

Rate of reaction (ξ = extent of reaction, $[\xi]$ = mol):

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

Usually per unit volume (intensive quantity):

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

concentration:
$c_i = [A_i] = n_i/V$
unit:
$\mathrm{mol\,dm^{-3} = mol/L = M}$

dimensionless (relative) concentration:
$c_i^{\rm rel} = \{A_i\} = c_i/c^{\rm st}$

- r depends on stoichiometry:

$$r(2\,\mathrm{A} \to \mathrm{A}_2) = \tfrac{1}{2} r(\mathrm{A} \to \tfrac{1}{2}\mathrm{A}_2)$$

Example. Hydrogen peroxide decomposes in the presence of a catalyst by rate $d[H_2O_2]/d\tau = -0.02\,\mathrm{mol\,L^{-1}\,min^{-1}}$. Deretmine the rate of the reaction

$$2\,H_2O_2 \to 2\,H_2O + O_2$$

$0.01\,\mathrm{mol\,L^{-1}\,min^{-1}}$

Rate (kinetic) equation

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Simple reaction is given by one reaction and one kinetic equation (not necessarily elementary)

Generally:

$$r = f(c_A, c_B, \ldots, T)$$

Often:

$$r = k(T)\, c_A^{\alpha} c_B^{\beta} \cdots$$

where

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

Dimensionality(k) = $(\mathrm{mol\,dm^{-3}})^{1-n}\mathrm{s^{-1}}$
Often dimensionless $c_i^{\rm rel} = c_i/c^{\rm st}$, then dimension($k$) = $\mathrm{s^{-1}}$

Half life of reaction: c_A decreases to one half

$$c_A(\tau_{1/2}) = \frac{c_A(0)}{2}$$

Homogeneous reactions: balance

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$$0 \to \sum_i \nu_i A_i$$

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

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

Degree of conversion (k = 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 $0 \le \alpha \le 1$

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

$$2\,NO_2(g) + F_2(g) \to 2\,NO_2F(g)$$

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 $[NO_2]_0$ a $[F_2]_0$, respectively, and the kinetic constant k.

$$\frac{dx}{d\tau} = -\frac{d[F_2]}{d\tau} = -\frac{1}{2}\frac{d[NO_2]}{d\tau} = \frac{1}{2}\frac{d[NO_2F]}{d\tau} = k([NO_2]_0 - 2x)([F_2]_0 - x)$$

Reaction A → P

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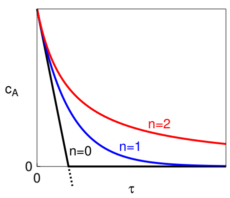
Rate equation:

$$\begin{aligned} \frac{dc_A}{d\tau} &= -k c_A^n \quad \text{for } c_A > 0 \\ &= 0 \quad \text{for } c_A = 0 \end{aligned}$$

Initial condition: $c_A(0) = c_{A0}$



Solution (integrated form):

n	$c_A(\tau)$	conditions	$\tau_{1/2}$
0	$c_{A0} - k\tau$	$\tau < c_{A0}/k$	$\frac{c_{A0}}{2k}$
	0	$\tau \ge c_{A0}/k$	
1	$c_{A0}\,e^{-k\tau}$		$\ln 2/k$
2	$\frac{1}{1/c_{A0}+k\tau}$		$\frac{1}{kc_{A0}}$
$(1,\infty)$	$[c_{A0}^{1-n} - (1-n)k\tau]^{1/(1-n)}$		$\frac{2^{n-1}-1}{(n-1)k}\, c_{A0}^{1-n}$
$[0,1)$	$[c_{A0}^{1-n} - (1-n)k\tau]^{1/(1-n)}$	$\tau < c_{A0}^{1-n}/[(1-n)k]$	
	0	$\tau \ge c_{A0}^{1-n}/[(1-n)k]$	

Reaction A + B → P (1st order to both A and B)

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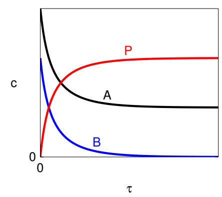
Both partial orders $\alpha = \beta = 1$ (total order = 2)

Rate equation:

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

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
- $c_{A0} \ne c_{B0}$: $(c_{A0} - c_{B0})k\tau = \ln\left(\frac{c_{A0} - x}{c_{B0} - x}\frac{c_{B0}}{c_{A0}}\right) = \ln\left(\frac{c_A}{c_B}\frac{c_{B0}}{c_{A0}}\right) \Rightarrow$

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

$\exp x = e^x$

Example: $NO_2^-(aq) + NH_4^+(aq) \to N_2(g) + 2\,H_2O(l)$

Kinetic measurements

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

symbol $\propto$ means "proportional to"

Proxies to $c_i(\tau)$:

- mechanical:
  (g): pressure (manometry) / volume (volumetry)
  (l): difference of volume (dillatometry), densitometry
  (s/g): mass (gravimetry)
  (l/g): vapor pressure
- optical: spectrophotometry, refractometry, polarimetry
- electric: conductometry, potentiometry, polarography
- chromatography, mass spectrometry

Determining the order and rate constant

Example. For reaction A → P with rate equation $dc/d = -kc^n$

- **Fitting** (correlation, regression): the integrated form of the kinetic equation, $c_A = c_A(c_{A0}, k, n; \tau)$, is fitted to the data by the **least square method**

  The sum of squares is minimized over 3 unknowns parameters c_{A0}, k, n

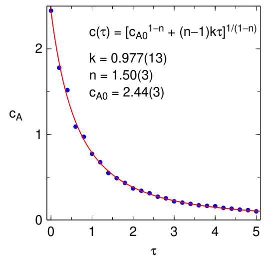
τ/min	c/mol L^{-1}	τ/min	c/mol L^{-1}	τ/min	c/mol L^{-1}	τ/min	c/mol L^{-1}
0.0	2.446	1.4	0.549	2.8	0.253	4.2	0.141
0.2	1.779	1.6	0.489	3.0	0.218	4.4	0.132
0.4	1.518	1.8	0.433	3.2	0.203	4.6	0.121
0.6	1.091	2.0	0.369	3.4	0.188	4.8	0.115
0.8	0.972	2.2	0.341	3.6	0.172	5.0	0.101
1.0	0.773	2.4	0.313	3.8	0.165		
1.2	0.675	2.6	0.272	4.0	0.161		

Mathematically:

$$s^2 = \min_{c_{A0},k,n} \frac{1}{N-3} \sum_{i=1}^{N} \left[\frac{c_A(c_{A0}, k, n; \tau) - c_i}{\sigma_i}\right]^2$$

where σ_i = standard error[a] of conc. $c_{A,i}$ (its estimate); for large N then $s^2 = 1$. If σ_i are not known, they can be calculated from $s^2 = 1$ assuming that all σ_i are the same.

[a] or uncertainty – called differently in statistics and in metrology



Old fashined methods. . .

- **Integral method** trial-and-error: For several orders n, we calculate the rate constant from pairs $c(\tau_1), c(\tau_2)$.
  For A → P:

$$k = \begin{cases} \dfrac{c_{A1}^{1-n} - c_{A2}^{1-n}}{(n-1)(\tau_1 - \tau_2)} & n \neq 1 \\ -\dfrac{\ln(c_{A1}/c_{A2})}{\tau_1 - \tau_2} & n = 1 \end{cases}$$

Example (see previous data):

τ_1	τ_2	$n=1$	$n=2$	$n=1.5$
0	1	1.152	0.885	0.996
1	2	0.739	1.416	1.018
2	3	0.526	1.877	0.991
3	4	0.303	1.624	0.701
4	5	0.466	3.690	1.309

- **Differential method**: rates for two times (or compositions) known

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

- **Isolation method** (Ostwald):

$$r = kc_A^\alpha c_B^\beta: \ c_B \gg c_A \text{ (surplus B)} \ \Rightarrow \ r = k' c_A^\alpha$$

Order of reaction graphically

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 $(\tau, -1/c_A)$
  $\frac{3}{2}$. 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:

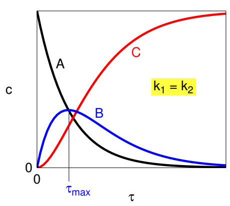
$$\frac{dc_A}{d\tau} = -k_1 c_A$$
$$\frac{dc_B}{d\tau} = k_1 c_A - k_2 c_B$$
$$\frac{dc_C}{d\tau} = k_2 c_B$$

Initial conditions:

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

Solution:

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



Max. concentration:

$\tau_{\max} =$

$\dfrac{\ln(k_1/k_2)}{k_1 - k_2}$ for $k_1 \neq k_2$

$1/k_1$ for $k_1 = k_2$

- radioactive decay
- pharmacokinetics:
  k_1 = absorption const.
  k_2 = elimination const.

Application to pharmacokinetics

Distribution volume V_d is the volume of water in which the dissolved drug would have the same concentration as it has in blood plasma.

$$V_d = \frac{\text{mass of drug}}{\text{mass conc. in plasma}}$$

Often give per 1 kg of patient's weight

$$V_d = \frac{\text{mass of drug}}{\text{(mass conc. in plasma)} \times \text{(mass of patient)}}$$

volume	$V_d/(\text{L kg}^{-1})$	
water total	0.6	children more, seniors less
intracellular	0.4	
extracellular	0.2	
blood total	0.08	
plasma	0.04–0.05	

- water-soluble compound, permeates through membranes, does not bind to anything: $V_d \approx 0.6\,\text{L kg}^{-1}$ (e.g., ethanol)
- lipophilic compound: higher (even hundreds)
- slow permeation through membranes etc.: more compartments needed

Application to pharmacokinetics

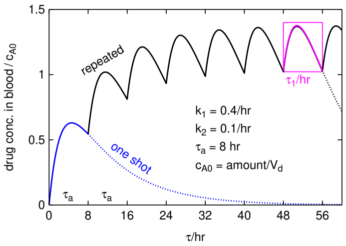
Simplification:

- one compartment
- 1st order kinetics (other options: 0th order, Michaelis–Menten)
- absorption k_1, elimination k_2
- "initial" weight concentration:

$$c_{A0} = \frac{\text{mass of drug}}{\text{mass of patient} \times V_d}$$

One shot
see "consecutive reactions"

Repeated shots
k-times by τ_a
(in times 0, τ_a, $2\tau_a$, . . . $(k-1)\tau_a$)



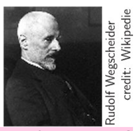
After many cycles (∞ series) for $\tau_1 = \tau - (k-1)\tau_a$ = time from the last shot:

$$c_B = \frac{k_1 c_{A0}}{k_2 - k_1}\left[\frac{e^{-k_1\tau_1}}{1 - e^{-k_1\tau_a}} - \frac{e^{-k_2\tau_1}}{1 - e^{-k_2\tau_a}}\right], k_1 \neq k_2$$
$$= \frac{k_1 c_{A0} e^{-k_1\tau_1}}{1 - e^{-k_1\tau_a}}\left[\tau + \frac{\tau_a e^{-k_1\tau_a}}{1 - e^{-k_1\tau_a}}\right], k_1 = k_2$$

Concurrent reactions

Example. Both reactions of the first order

$$A \xrightarrow{k_1} B$$
$$A \xrightarrow{k_2} C$$



Rate equations:

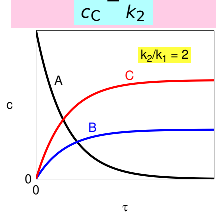
$$\frac{dc_A}{d\tau} = -k_1 c_A - k_2 c_A$$
$$\frac{dc_B}{d\tau} = k_1 c_A$$
$$\frac{dc_C}{d\tau} = k_2 c_A$$

if both reactions are of the same order: Wegscheider principle:

$$\frac{c_B}{c_C} = \frac{k_1}{k_2}$$

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

$$c_A = c_{A0} \exp[-(k_1 + k_2)\tau]$$
$$c_B = c_{A0} \frac{k_1}{k_1 + k_2}\{1 - \exp[-(k_1 + k_2)\tau]\}$$
$$c_C = c_{A0} \frac{k_2}{k_1 + k_2}\{1 - \exp[-(k_1 + k_2)\tau]\}$$

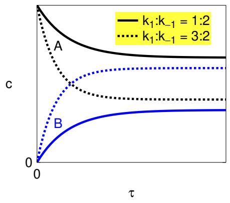


Variants: A+B→, A+C→, A≫B,C

Reversible reactions

Example. Both reactions of the 1st order:

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{B}$$



Rate equation:

$$\frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}\tau} = -k_1 c_\mathrm{A} + k_{-1} c_\mathrm{B}$$

Balance for $c_\mathrm{A}(0) = c_{\mathrm{A}0}$, $c_\mathrm{B}(0) = 0$:

$$c_\mathrm{A} + c_\mathrm{B} = c_{\mathrm{A}0}$$

Solution:

$$c_\mathrm{A} = \frac{c_{\mathrm{A}0}}{k_1 + k_{-1}} \left[k_1 \mathrm{e}^{-(k_1+k_{-1})\tau} + k_{-1} \right]$$

Equilibrium:

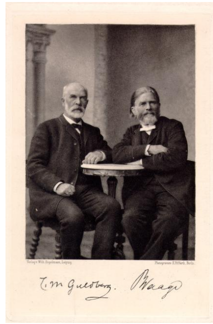
$$\lim_{\tau\to\infty} c_\mathrm{A} = \frac{k_{-1}}{k_1 + k_{-1}} c_{\mathrm{A}0}$$

Equilibrium constant: $\dfrac{c_\mathrm{B}(\infty)}{c_\mathrm{A}(\infty)} = \dfrac{k_1}{k_{-1}} = K$

racemization (1 chiral C): $K = 1$

Law of mass action

Guldberg-Waage:



credit: Wikipedia

Let both reactions in

$$\mathrm{A} + \mathrm{B} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{C} + \mathrm{D}$$

are elementary (of 1st order wrt all compounds)

Rate equation:

$$\frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}\tau} = -k_1 c_\mathrm{A} c_\mathrm{B} + k_{-1} c_\mathrm{C} c_\mathrm{D}$$

Equilibrium: $\frac{\mathrm{d}c_\mathrm{A}}{\mathrm{d}\tau} = 0$ or

$$\frac{c_\mathrm{C} c_\mathrm{D}}{c_\mathrm{A} c_\mathrm{B}} = \frac{k_1}{k_{-1}} = K$$

where K si the equilibrium constant

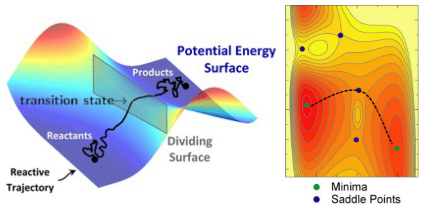
Potential energy surface (PES)

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 redundand coordinates because of symmetry (rotations, translations)

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



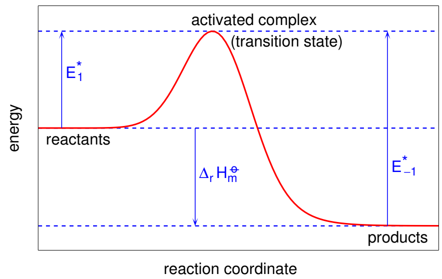
credits: http://www.ucl.ac.uk/~ucecmst/publications.html, http://theory.cm.utexas.edu/henkelman/research/ltd/

Transition state theory (Eyring): $k = (RT/N_\mathrm{A}h)\exp(-[G^\ddagger_\mathrm{m} - G^\mathrm{reactants}_\mathrm{m}]/RT)$

T-dependence of the reaction rate (Arrhenius)

$$\frac{\mathrm{d}\ln K}{\mathrm{d}T} = \frac{\Delta_\mathrm{r}H^\ominus_\mathrm{m}}{RT^2} \overset{\Delta_\mathrm{r}H^\ominus_\mathrm{m}=\mathrm{const}}{\Rightarrow} K = K_0 \mathrm{e}^{-\frac{\Delta_\mathrm{r}H^\ominus_\mathrm{m}}{RT}} = \frac{k_1}{k_{-1}} = \frac{A_1 \mathrm{e}^{-\frac{E^*_1}{RT}}}{A_2 \mathrm{e}^{-\frac{E^*_{-1}}{RT}}} \text{ “}\Rightarrow\text{” } k = A\mathrm{e}^{-\frac{E^*}{RT}}$$

E^* = **activation energy**, A = prefactor



$\Delta_\mathrm{r}H^\ominus_\mathrm{m} = E^*_1 - E^*_{-1}$

Typical E^*:
50–110 kJ mol^{-1}

Rule of the thumb:
1.5–3× per 10 °C

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