

Chemical Kinetics

Rate of reaction for the process $aA + bB + \dots \rightarrow rR + sS + \dots$ is expressed as:

$$r = -\frac{1}{a} \frac{dc_A}{d\tau} = -\frac{1}{b} \frac{dc_B}{d\tau} = \dots = \frac{1}{r} \frac{dc_R}{d\tau} = \frac{1}{s} \frac{dc_S}{d\tau} = \dots$$

where c_i are concentrations of reaction species, ν_i stoichiometric coefficients and τ time.

Kinetic equation is a differential equation connecting the concentration of reactants and time

$$r = -\frac{dc_A}{d\tau} = kc_A^\alpha c_B^\beta \dots$$

Exponents α, β are **reaction orders for reactants A, B...**, respectively. Sum of exponents $n = \alpha + \beta + \dots$ is the **(total) reaction order**. Parameter k is the **rate constant**. Units of rate constant follow from the reaction order.

Half-time of reaction $\tau_{1/2}$ is time when the concentration of selected reactant drops to one half of the initial value. Following table summarizes the integrals of zeroth-order, first-order and second-order kinetic equations

n	reactants	kinetic equation	integral	$\tau_{1/2}$
0	aA	$-\frac{dc_A}{d\tau} = k$	$k\tau = c_A^\circ - c_A$	$\tau_{1/2} = \frac{c_A^\circ}{2k}$
1	aA	$-\frac{dc_A}{d\tau} = kc_A$	$k\tau = \ln\left(\frac{c_A^\circ}{c_A}\right)$	$\tau_{1/2} = \frac{\ln 2}{k}$
n	aA	$-\frac{dc_A}{d\tau} = kc_A^n$	$k\tau = \frac{1}{n-1} \left(\frac{1}{c_A^{n-1}} - \frac{1}{(c_A^\circ)^{n-1}} \right)$	$\tau_{1/2} = (c_A^\circ)^{1-n} \frac{2^{n-1} - 1}{(n-1)k}$

With more than one reactant in the reaction, their concentrations are connected by mass balance with the help of the extent of reaction. More complicated kinetic equations require numerical solution.

Orders of reaction for individual reactants are often determined with the help of **Ostwald isolation method**: kinetic experiment is performed with the surplus of all reactants but one, allowing determination of the order of reaction for this single reactant. Since the order of reaction is an exponent, the kinetic equation is typically subject to linearization and the derivatives are calculated numerically from the experimental data. After a series of experiments with different limiting species we obtain the orders of reaction for each of them.

Simultaneous Reactions

Simultaneous reactions proceed in the same system at the same time with (at least) one shared reactant. Basic types include **parallel** reactions (reactant enter two or more reaction pathways with different products); **reversible** reactions (proceeding in both directions); **consecutive** reactions (include reaction intermediates).

Reaction Mechanism, Elementary Reaction

Stoichiometric chemical reactions in most cases fail to capture the actual progress of reaction at the molecular level. Such molecular-level processes are described by **elementary reactions**. Stoichiometric reactions are typically a succession of elementary reactions, called **reaction mechanism**.

Control Process

Part of reaction mechanism with the largest influence on the (overall) reaction rate is called control process. Control process is typically the fastest reaction (in parallel mechanism) or the slowest reaction (in consecutive mechanism).

Bodenstein Principle

Frequent type of reaction intermediates are radicals, “activated molecules“, or „activated complexes“. Their concentration is very low and almost constant over the timescale of the reaction.

Temperature dependence of the rate of reaction is hidden in the rate constant and often described by the **Arrhenius Equation**

$$k = A e^{-\frac{E_a}{RT}}$$

where A and E_a are temperature-independent constants. Parameter A is **frequency factor**, parameter E_a is **activation energy**. Both parameters are positive except for radioactive decay where $E_a = 0$.

Catalyst is a compound that enters the reaction, changes reaction mechanism and exits the reaction unchanged. Catalyst affects the rate of reaction (but has no effect on chemical equilibrium). Catalyst can be either in the same phase as reactants (**homogeneous catalysis**) or in a different phase (**heterogeneous catalysis** – typically solid catalyst and fluid reactants). Kinetic model of heterogeneous catalysis must include all reaction steps: transport of reactants to the catalyst, their adsorption, chemical reaction, desorption of products and their transport from the surface of the catalyst. Each of these steps may be a control process in the (overall) procedure.

One example is **enzyme catalysis**, corresponding to a mechanism:



ES is enzyme-substrate complex. Applying the Bodenstein principle ($\frac{dc_{ES}}{d\tau} = 0$) we find the kinetic equation

$$\frac{dc_p}{d\tau} = \frac{k_3 k_1}{k_2 + k_3} c_E c_S = \frac{k_3 c_E^0 c_S}{K_M + c_S}$$

where $c_E^0 = c_E + c_{ES}$ is the initial enzyme concentration, $K_M = (k_2 + k_3)/k_1$ is the **Michaelis-Menten constant**.

Industrial chemical processes are carried out in reactors, operating in either batch or flow regimes. **Batch reactors** are described by the kinetic equation of the reaction. In **flow reactor with laminar flow** the feed of reactants is $F = dV/d\tau$ with the integral $F = V_R / \tau_z$, where V_R is reactor volume and τ_z the retardation time. It

follows from kinetic equation that $dc_A/dV = r/F$ and, after integration, $V_R = F \int_{c_A^0}^{c_A} dc_A / r$. In **flow reactor with**

turbulent flow the concentrations and the rate of reaction are the same in every part of the reactor and the final equation is simplified to $V_R = F / r(c_A - c_A^0)$.

Homework 8:

Decomposition of gaseous compound A was observed at 50°C:

τ (s)	c_A (mol/dm ³)	τ (s)	c_A (mol/dm ³)	τ (s)	c_A (mol/dm ³)
40	0,037	220	0,028	404	0,023
70	0,035	320	0,025	642	0,019

Initial concentration of compound A was 0,04 mol/dm³. Evaluate from the data the order of reaction and reaction rate.