SwissChO 2013 - Kinetics

Kinetics study the rate of chemical reactions and investigate the path taken by the reaction, i.e. we are interested in the *reaction mechanism* (qualitative) and the *reaction rate* (quantitative).

Reaction mechanisms

Many reactions are actually a series of reactions steps. As an example, the reaction $2\,A + B \longrightarrow D$ could be described by the reaction steps

$$A + B \longrightarrow C$$
$$A + C \longrightarrow D$$

Each of these reaction steps are called *elementary reactions.*

Rate equations

The rate of a reaction
$$aA + bB + \ldots \longrightarrow cC + dD + \ldots$$
is defined as
$$r = -\frac{1}{a}\frac{\mathrm{d}c_A}{\mathrm{d}t} = -\frac{1}{b}\frac{\mathrm{d}c_B}{\mathrm{d}t} = \frac{1}{c}\frac{\mathrm{d}c_C}{\mathrm{d}t} = \frac{1}{d}\frac{\mathrm{d}c_D}{\mathrm{d}t} = \cdots$$
r usually depends on the concentration of the different species. For elementary reactions,

$$r = kc_A^a c_B^b \ldots$$

k is the so-called *rate constant.*

Important elementary reactions

RO	Reaction	Rate law	Concentration	Half-life
1	$A \xrightarrow{k} C$	$-\frac{dc_A}{dt} = kc_A$	$c_A(t) = c_A(t_0) \cdot e^{-k \cdot (t-t_0)}$	$\frac{\ln 2}{k}$
2	$2\,A \xrightarrow{k} C$	$-\frac{1}{2}\frac{dc_A}{dt} = kc_A^2$	$\frac{1}{c_A(t)} = \frac{1}{c_A(t_0)} + 2k \cdot (t-t_0)$	$\frac{1}{2\,k\,c_A(t_0)}$
2	$A + B \xrightarrow{k} C, \; c_B = c_A$	$-\frac{dc_A}{dt} = kc_A^2$	$\frac{1}{c_A(t)} = \frac{1}{c_A(t_0)} + k \cdot (t-t_0)$	$\frac{1}{k\,c_A(t_0)}$
ps. 1	$A + B \xrightarrow{k} C, \; c_B \gg c_A$	$-\frac{dc_A}{dt} = (kc_B)c_A$	$c_A(t) = c_A(t_0) \cdot e^{-kc_B \cdot (t-t_0)}$	$\frac{\ln 2}{k\,c_B}$
0		$-\frac{dc_A}{dt} = k$	$c_A(t) = c_A(t_0) - k \cdot (t-t_0)$	-

Steady-State Approximation

For complicated reaction mechanisms consisting of many elementary reactions, one usually assumes that the concentration of the intermediates is constant during the reaction.

Arrhenius equation

Rate constants are temperature-dependent. The Arrhenius equation describes the relation between rate constant and temperature:

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

or

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

where E_a is the activation energy, R the universal gas constant $(R = 8.314\,\text{J}^{-1}\text{mol}^{-1}\text{K}^{-1})$ and T the temperature.

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Gibbs Energy

$$\Delta_{\mathrm{R}}G = \Delta_{\mathrm{R}}H - T\Delta_{\mathrm{R}}S$$

$$\Delta_{\mathrm{R}}G = \Delta_{\mathrm{R}}G^{\circ} + RT \ln Q$$

(Q is the reaction quotient)

Equilibrium

The condition for equilibrium is
$$\Delta_{\mathrm{R}}G = 0$$

Therefore,
$$\Delta_{\mathrm{R}}G^{\circ} = -RT \ln K \qquad K = e^{-\Delta_{\mathrm{R}}G^{\circ}/RT}$$

Van't Hoff equation

$$\ln \frac{K(T_2)}{K(T_1)} = -\frac{\Delta_{\mathrm{R}}H^{\circ}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Nernst Equation

$$E = E^{\circ} - \frac{RT}{zF}\ln Q$$

Clausius-Clapeyron equation

$$\ln \frac{p_2}{p_1} = -\frac{\Delta_{\mathrm{vap}}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

where p_1 and p_2 are the vapour pressures at temperatures T_1 and T_2.