1 - CHEMICAL KINETICS – SIMPLE REACTIONS

$$J = \frac{d\xi}{d\tau} \quad , \quad d\xi = \frac{dn_i}{\nu_i} \quad , \quad r = \frac{J}{V} = \frac{d\xi}{V \cdot d\tau} = \frac{1}{V} \cdot \frac{1}{\nu_i} \cdot \frac{dn_i}{d\tau} \quad , \quad [V] \quad r = \frac{1}{\nu_i} \cdot \frac{dc_i}{d\tau}$$

$$r = k_c \cdot c_A^{\alpha} \cdot c_B^{\beta} \cdots \qquad n = \alpha + \beta + \cdots \quad , \quad [k_c] = \text{concentration}^{(1-n)} \text{ time}^{-1}$$

$$x = \frac{\xi}{V} = \frac{c_i - c_{i0}}{\nu_i} \qquad c_i = c_{i0} + \nu_i \cdot x$$

$$\text{or} \quad r = \frac{1}{\nu_i} \cdot \frac{dp_i}{d\tau} \quad , \quad r = k_p \cdot p_A^{\alpha} \cdot p_B^{\beta} \cdots \qquad n = \alpha + \beta + \cdots \quad , \quad [k_p] = \text{pressure}^{(1-n)} \text{ time}^{-1}$$

$$y = \frac{p_i - p_{i0}}{\nu_i} \qquad p_i = p_{i0} + \nu_i \cdot y \quad , \quad (y = x \cdot RT)$$

$$\frac{d \ln k}{dT} = \frac{E^*}{RT^2} \qquad , \qquad \frac{d \ln k}{dT} > 0$$

$$k = A \cdot e^{-E^*/RT} \quad , \quad \ln \frac{k_2}{k_1} = \frac{E^*}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \quad , \quad \ln k = \ln A - \frac{E^*}{RT}$$

Order	Reaction	Differential rate law	Integrated rate law	Half-life
0	$a\,A \rightarrow$ products	$\dfrac{dc_A}{(-a)\,d\tau} = k_c$	$c_A = c_{A0} - a \cdot k_c \cdot \tau$	$\dfrac{c_{A0}}{2\,a\,k_c}$
1st	$a\,A \rightarrow$ products	$\dfrac{dc_A}{(-a)\,d\tau} = k_c \cdot c_A$	$\ln\dfrac{c_A}{c_{A0}} = -a \cdot k_c \cdot \tau$	$\dfrac{\ln 2}{a\,k_c}$
2nd	$a\,A \rightarrow$ products $a\,A + b\,B \rightarrow$ products $\alpha = \beta = 1,\ c_{A0} = c_{B0}$	$\dfrac{dc_A}{(-a)\,d\tau} = k_c \cdot c_A^2$	$\dfrac{1}{c_A} - \dfrac{1}{c_{A0}} = a \cdot k_c \cdot \tau$	$\dfrac{1}{c_{A0} \cdot a \cdot k_c}$
	$a\,A + b\,B \rightarrow$ products $\alpha = \beta = 1,\ \dfrac{c_{A0}}{a} = \dfrac{c_{B0}}{b}$	$\dfrac{dc_A}{(-a)\,d\tau} = \dfrac{dc_B}{(-b)\,d\tau} = k_c \cdot c_A^2$	$\dfrac{1}{c_A} - \dfrac{1}{c_{A0}} = b\,k_c \cdot \tau$ $\dfrac{1}{c_B} - \dfrac{1}{c_{B0}} = a \cdot k_c \cdot \tau$	$\dfrac{1}{c_{A0} \cdot b \cdot k_c} =$ $= \dfrac{1}{c_{B0} \cdot a \cdot k_c}$
	$a\,A + b\,B \rightarrow$ products $\alpha = \beta = 1,\ \dfrac{c_{A0}}{a} \neq \dfrac{c_{B0}}{b}$	$\dfrac{dc_A}{(-a)\,d\tau} = \dfrac{dc_B}{(-b)\,d\tau} = k_c \cdot c_A \cdot c_B$	$\ln\dfrac{c_{B0} \cdot c_A}{c_{A0} \cdot c_B} =$ $= k_c \cdot (b\,c_{A0} - a\,c_{B0}) \cdot \tau$	$\dfrac{\ln\left(2 - \dfrac{a\,c_{B0}}{b\,c_{A0}}\right)}{k_c \cdot (b\,c_{A0} - a\,c_{B0})}$
n	$a\,A \rightarrow$ products	$\dfrac{dc_A}{(-a)\,d\tau} = k_c \cdot c_A^n$	$c_A^{1-n} - c_{A0}^{1-n} = a \cdot (n-1) \cdot k_c \cdot \tau$	$\left[\dfrac{2^{n-1} - 1}{a\,(n-1) \cdot k_c}\right] \cdot c_{A0}^{1-n}$

Note:
In the gaseous systems the forms of equations are the same, only instead of concentrations the partial pressures are used and k_c [concentration^{1-n} time^{-1}] $\rightarrow k_p$ [pressure^{1-n} time^{-1}]:

Problem 1-01 Reaction rate

The decomposition of nitrous acid is described by the following stoichiometric equation:
$$3\,HNO_2 = H^+ + NO_3^- + 2\,NO + H_2O$$
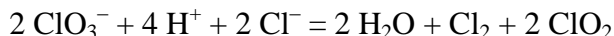For the reaction rate in certain moment from the beginning of the reaction we have found the value $J = 0.15$ mol min^{-1}. Calculate the rate of change of mole number of
(a) HNO_2, (b) NO, (c) H_2O.

[(a) –0.45 mol min^{-1} , (b) +0.30 mol min^{-1} , (c) +0.15 mol min^{-1}]

Problem 1-02 Reaction rate expressed by the rate of change of mole number

The time change of the mole number of chloride ions in the course of the reaction
$$2\,ClO_3^- + 4\,H^+ + 2\,Cl^- = 2\,H_2O + Cl_2 + 2\,ClO_2$$
is $dn_{Cl^-}/d\tau = -0.025$ mol s^{-1}. Calculate
(a) reaction rate J, corresponding to the stoichiometry given above,
(b) rate of change of mole number of (i) H^+, (ii) H_2O,
(c) rate of change of total mole number.

$$\left[\begin{array}{l} \text{(a) } J = +0.0125 \text{ mol s}^{-1}, \text{ (b)(i) } dn_{H^+}/d\tau = +0.05 \text{ mol s}^{-1}, \text{ (ii) } dn_{H_2O}/d\tau = +0.025 \text{ mol s}^{-1}, \\ \hspace{5cm} \text{(c) } dn/d\tau = +0.0375 \text{ mol s}^{-1} \end{array} \right]$$

Problem 1-03 First-order reactions

Consider a first-order unidirectional reaction

A → products

If you know that 30 per cent of this reaction is accomplished in 45 minutes, calculate how long it will take to change 80 per cent of initial amount of A to products.

[$k_c = 1.321 \cdot 10^{-4}$ s^{-1} ; $\tau_2 = 3.384$ h]

Problem 1-04 First-order reactions

The rate constant of the first-order reaction **2A → products** was found to be $k_c = 0.005$ min^{-1}. Determine what is the amount of A (in per cents of initially present A) remains unreacted after 3 hours from the beginning of the reaction.

[16.53 % A remains unchanged]

Problem 1-05 First-order reactions- radioactive decomposition

The age of water or aqueous solutions can be determined from the content of the radioactive tritium, arising in nature by the action of the cosmic rays. Calculate the age of the cognac showing ten times lower radioactivity than freshly made sample. Your cognac was stored in the place shaded from the cosmic rays. The half-life of the tritium is 12.5 years.

[$\tau = 41.524$ years]

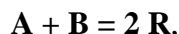## Problem 1-06 Second-order reactions

An unidirectional reaction **A → B** takes place in aqueous solution with the rate constant $k_c = 0.0125$ dm^3 mol^{-1} s^{-1}. How many minutes will it take to reach the concentration of the product B the value of 0.09 mol dm^{-3}, if the initial concentration of A is $c_{A0} = 0.35$ mol dm^{-3}?

[$\tau = 660.3$ s = 11 min]

Problem 1-07 Second-order reaction, equal initial concentrations of the components

The value of the rate constant of the unidirectional second-order reaction (first order in A and first-order in B), represented by a scheme
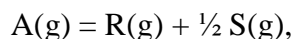
A + B = 2 R,

is $k_c = 4 \cdot 10^{-3}$ m^3 mol^{-1} h^{-1}. Determine how long it will take before 80 % of initially present A will be left in the reaction mixture. The initial concentrations of both reactants are the same, $c_{A0} = c_{B0} = 0.05$ mol dm^{-3}.

[$\tau = 1.25$ h]

Problem 1-08 Second-order reactions[*V*]

An unidirectional reaction between ideal gases,

$$A(g) = R(g) + \tfrac{1}{2} S(g),$$

takes place in the reactor of constant volume at the temperature of 337 K. The rate constant is $k_c = 0.035$ dm^3 mol^{-1} min^{-1}. What will be the concentration of A (mol dm^{-3}) in the reaction mixture if the reactor, initially filled by pure A to a pressure of 109 kPa, was tempered for one hour to a temperature of 337 K?

[$c_A = 0.03596$ mol dm^{-3}]

Problem 1-09 Second-order reactions [*V*], temperature dependence

The steel autoclave was filled by equimolar mixture of gaseous A and B. The initial pressure was 92 kPa. In the course of the second-order reaction, schematically written as **A + B → *products***, which takes place in the gaseous mixture at constant temperature of 313 K, one half of each of reactants was consumed during 108.7 minutes. Calculate
(a) the value of the rate constant at the temperature of 313 K,
(b) the half-life of this reaction at the temperature of 323 K, if the initial mixture is the same as in the preceding case and the activation energy has the value $E^* = 63$ kJ mol^{-1}.

[(a) $k_{p1} = 2 \cdot 10^{-4}$ kPa^{-1} min^{-1}; (b) $(\tau_{1/2})_2 = 51.37$ min ($k_{p2} = 4.2318 \cdot 10^{-4}$ kPa^{-1} min^{-1})]

Problem 1-10 Second-order reactions [*V*], temperature dependence

The rate constant of the second-order reaction in solution, described by stoichiometry **3 A → B**, has the value $k_c = 0.0967$ dm^3 mol^{-1} min^{-1} at 380 K and its activation energy is $E^* = 74$ kJ mol^{-1}. What time is needed to decompose 28 % of the reactant A at the temperature of 420 K, if its initial concentration is $c_{A0} = 0.023$ mol dm^{-3}.

[$\tau = 6.262$ min]

Problem 1-11 Second-order reaction [*V*], half-life, temperature dependence

A second-order reaction between ideal gases, described by stoichiometry $^5/_2$ **A(g) → 2 R(g) + C(g)**, is realized in a closed reactor of constant volume at 434 K. If the reactor was filled by pure A to a pressure of 40 kPa, the half-life of 25 min was obtained.
(a) Calculate the rate constant of this reaction at the temperature of 434 K.
(b) What will be the partial pressure of A in the reaction mixture at this temperature after one hour and 12 minutes from the initiation of the reaction?
(c) Calculate the rate constant at the temperature of 390 K. Activation energy is $E^* = 68$ kJ mol^{-1}.

[(a) $k_{p1} = 4 \cdot 10^{-4}$ kPa^{-1} min^{-1}; (b) $p_A = 10.309$ kPa; (c) $k_{p2} = 4.772 \cdot 10^{-5}$ kPa^{-1} min^{-1}]

Problem 1-12 First-order reaction [*V*], temperature dependence

The rate constant of the unidirectional decomposition   A = R + 2 S   at the temperature of 400 K is $5 \cdot 10^{-4}$ min^{-1}. The activation energy of this reaction has the value of 50 kJ mol^{-1}. Determine
(a) what is the percentage of A decomposed at 400 K in 50 minutes from the beginning of the reaction,
(b) to which temperature should be warmed the system in order that ten times greater amount of A than at 400 K was decomposed during the same time interval

[(a) 2.47 % A is decomposed; (b) $T_2 = 477.1$ K ($k_{c2} = 5.6738 \cdot 10^{-3}$ min^{-1})]

Problem 1-13 Half-life, activation energy

Thermal decomposition of a hydrocarbon is a second-order reaction. At the temperature of 500 °C the value of the half-life was found to be 8.7 min and at 548 °C the half of the same initial hydrocarbon amount was decomposed in 3.9 min. Calculate the activation energy of the decomposition reaction.

[$E^* = 88.23$ kJ mol^{-1}]