

## 2. SIMULTANEOUS REACTIONS

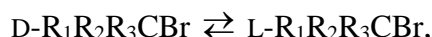
<b>Reactions</b>	<b>Diferential rate laws</b>	<b>Integrated rate laws</b>
<b>Reversible</b> $A \xrightleftharpoons[k_2]{k_1} B$	$-\frac{d c_A}{d \tau} = k_1 \cdot c_A - k_2 \cdot c_B$	$\ln \left( \frac{c_{A0} \cdot K_c - c_{B0}}{c_{A0} \cdot K_c - c_{B0} - x \cdot (K_c + 1)} \right) = k_1 \cdot \frac{K_c + 1}{K_c} \cdot \tau$
<b>Parallel branched</b> $A \begin{array}{l} \xrightarrow{k_1} S \\ \xrightarrow{k_2} R \end{array}$	$-\frac{d c_A}{d \tau} = (k_1 + k_2) \cdot c_A$	$c_A = c_{A0} \cdot e^{-(k_1 + k_2) \cdot \tau}$
	$\frac{d c_S}{d \tau} = k_1 \cdot c_A$	$c_S = c_{S0} + \frac{k_1 \cdot c_{A0}}{k_1 + k_2} \left[ 1 - e^{-(k_1 + k_2) \cdot \tau} \right]$
	$\frac{d c_R}{d \tau} = k_2 \cdot c_A$	$c_R = c_{R0} + \frac{k_2 \cdot c_{A0}}{k_1 + k_2} \left[ 1 - e^{-(k_1 + k_2) \cdot \tau} \right]$
<b>Consecutive</b> $A \xrightarrow{k_1} B \xrightarrow{k_2} R$	$-\frac{d c_A}{d \tau} = k_1 \cdot c_A$	$c_A = c_{A0} \cdot e^{-k_1 \cdot \tau}$
	$\frac{d c_B}{d \tau} = k_1 \cdot c_A - k_2 \cdot c_B$	$c_B = c_{B0} \cdot e^{-k_2 \cdot \tau} + \frac{k_1 \cdot c_{A0}}{k_2 - k_1} \left[ e^{-k_1 \cdot \tau} - e^{-k_2 \cdot \tau} \right]$
	$\frac{d c_R}{d \tau} = k_2 \cdot c_B$	$c_R = c_{R0} + c_{B0} \cdot \left( 1 - e^{-k_2 \cdot \tau} \right) +$ $\quad + \frac{c_{A0}}{k_2 - k_1} \left[ k_2 \cdot \left( 1 - e^{-k_1 \cdot \tau} \right) - k_1 \cdot \left( 1 - e^{-k_2 \cdot \tau} \right) \right]$
$A \xrightarrow{k} B \xrightarrow{k} R$	$-\frac{d c_A}{d \tau} = k \cdot c_A$	$c_A = c_{A0} \cdot e^{-k \cdot \tau}$
	$\frac{d c_B}{d \tau} = k \cdot c_A - k \cdot c_B$	$c_B = e^{-k \cdot \tau} \cdot (c_{B0} + k \cdot c_{A0} \cdot \tau)$
	$\frac{d c_R}{d \tau} = k_2 \cdot c_B$	$c_R = c_{R0} + c_{A0} \left[ 1 - (1 + k \cdot \tau) \cdot e^{-k \cdot \tau} \right] + c_{B0} \left[ 1 - e^{-k \cdot \tau} \right]$

## Reversible reactions

### Problem 2-01 Reversible first-order reactions, conversion

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The rate constants of the racemization of optically active bromide,



in the forward and backward directions are of the same values,  $k_1 = k_2 = 1.9 \cdot 10^{-6} \text{ s}^{-1}$ .

- (a) What time is needed to accomplish 10 % conversion of D-bromide to L-bromide?  
(b) Calculate the conversion of D-bromide to L-bromide in 48 hours, if the initial solution contains only D-bromide?

$$[(a) \tau = 16.3 \text{ h}, (b) \alpha = 0.241]$$

### Problem 2-02 Reversible first-order reactions, reaction time

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Reversible isomerization  $\mathbf{A(l)} \rightleftharpoons \mathbf{B(l)}$  takes place in liquid phase at the temperature of  $32^\circ\text{C}$  with the forward rate constant  $k_{c1} = 4 \cdot 10^{-3} \text{ h}^{-1}$ . The equilibrium mixture contains 25 mol.% of A. Calculate the time needed to reach the conversion of isomer A into isomer B equal to 60 % of the equilibrium value, if the reactor was originally filled with pure isomer A. You can assume that all activity coefficients are equal to unity.

$$[171.8 \text{ h}]$$

### Problem 2-03 Reversible first-order reactions, reaction time

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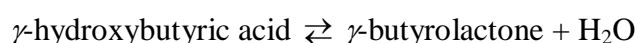
The reversible first-order reaction  $\mathbf{S(aq)} \rightleftharpoons \mathbf{R(aq)}$  takes place at  $321 \text{ K}$  in aqueous solution. The standard reaction Gibbs energy at this temperature is  $\Delta_r G^\ominus = -830.4 \text{ J mol}^{-1}$  and the rate constant of the backward reaction is  $k_2 = 1.15 \cdot 10^{-4} \text{ s}^{-1}$ . Calculate how long from the beginning of the reaction it will take before the reaction mixture will contain 18 mol. % of the product R.

$$[22.9 \text{ min}]$$

### Problem 2-04 Reversible first-order reactions, calculation of rate and equilibrium constants

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Reaction



takes place in an aqueous solution. The forward reaction follows first-order kinetics, the backward reaction in the aqueous solution is pseudo-unimolecular.

The kinetic measurements revealed that the concentration of hydroxybutyric acid decreased after 102 minutes from the initial value of  $18.25 \text{ mmol dm}^{-3}$  to  $10.25 \text{ mmol dm}^{-3}$  and in equilibrium its concentration was  $5 \text{ mmol dm}^{-3}$ . Find both rate constants and the equilibrium constant of the above mentioned reaction.

$$[K_c = 2.65 ; k_{c1} = 6.59 \cdot 10^{-3} \text{ min}^{-1}, k_{c2} = 2.487 \cdot 10^{-3} \text{ min}^{-1}]$$

### Problem 2-05 Reversible first-order reactions, calculation of rate and equilibrium constants

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Izomeration of *cis*-1,2-dimethylcyclopropane to *trans*-1,2-dimethylcyclopropane at the temperature of  $450^\circ\text{C}$  follow the first order kinetics in both directions. Use experimental data given in the following table to calculate the equilibrium constant and the rate constant of the forward and backward reaction.

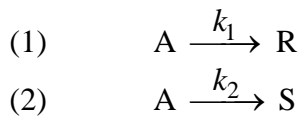
$\tau$ (s)	0	225	equilibrium
<i>cis</i> -form (%)	100	62.3	32.0

$$[K_c = 2.125 ; k_{c1} = 2.443 \cdot 10^{-3} \text{ s}^{-1} ; k_{c2} = 1.15 \cdot 10^{-3} \text{ s}^{-1}]$$

## Parallel reactions

### Problem 2-06 Parallel reactions

Substance A decomposes simultaneously by two first-order unidirectional to products R and S:

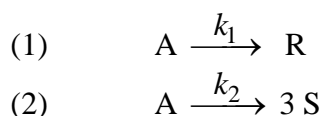


At the beginning the reactor contained only pure substance A. 10 minutes after the initialization of the reaction the reaction mixture contained 56 mol. % A and 11 mol. % R. What is the composition of the reaction mixture (in molar per cents) after another 20 minutes?

$$[17.552 \text{ mol. \% A; } 20.612 \text{ mol. \% R; } 61.836 \text{ mol. \% S; } (k_1 = 0.0145 \text{ min}^{-1}, k_2 = 0.0435 \text{ min}^{-1})]$$

### Problem 2-07 Parallel reactions

Two side first-order reactions



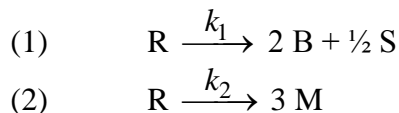
take place in a constant-volume vessel at constant temperature of 350 K. In 20.2 minutes from the beginning of the reaction the concentration of the product R reached 40 % of initial concentration of the reactant A and that of the product S 66 % of initial concentration of the reactant A.

- (a) What is the concentration of A in this instant (in per cents of initial amount of A).  
(b) Calculate the values of both rate constants.

$$[(a) c_A = 0.38 c_{A,0}, (b) k_1 = 0.0309 \text{ min}^{-1}, k_2 = 0.017 \text{ min}^{-1}]$$

### Problem 2-08 Parallel reactions

The rate constants of two first-order side reactions, following the scheme



have the values  $k_1 = 2.4 \cdot 10^{-5} \text{ s}^{-1}$  and  $k_2 = 0.27 \text{ h}^{-1}$ .

- (a) Write the differential rate laws describing the decrease or increase of all components.  
(b) Calculate the composition of the reaction mixture after 72 minutes from the beginning of the reaction, if the reaction vessel initially contained only pure component R.

$$\left[ \begin{array}{l} (a) \quad r = r_R = -\frac{dc_R}{d\tau} = (k_1 + k_2) \cdot c_R, \quad r_B = \frac{dc_B}{d\tau} = 2k_1 \cdot c_R, \quad r_S = \frac{dc_S}{d\tau} = 0.5 k_1 \cdot c_R, \quad r_M = \frac{dc_M}{d\tau} = 3k_2 \cdot c_R \\ (b) \quad 39.424 \text{ mol. \% R; } 10.202 \text{ mol. \% B; } 2.550 \text{ mol. \% S; } 47.824 \text{ mol. \% M} \end{array} \right]$$

### Problem 2-09 Parallel reactions, temperature dependence

Catalytic decomposition of formic acid in the gaseous phase can take place by these two reactions



The rate constants at the temperature of 510 K have these values:

$$k_1 = 4.7 \cdot 10^{-5} \text{ s}^{-1} \quad \text{and} \quad k_2 = 2.5 \cdot 10^{-6} \text{ s}^{-1}$$

Assuming that the activation energies,  $E_1^* = 50.2 \text{ kJ mol}^{-1}$  and  $E_2^* = 102.5 \text{ kJ mol}^{-1}$  are temperature independent, find such temperature at which the decomposition of formic acid gives an equimolar mixture of water vapour, carbon monoxide, hydrogen, and carbon dioxide

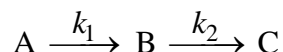
$$[T = 669.2 \text{ K}]$$

## Consecutive reactions

### Problem 2-10 Consecutive reactions, intermediate maximal concentration

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The rate constants of the two first-order consecutive reactions



are  $k_1 = 3.09 \cdot 10^{-4} \text{ s}^{-1}$  and  $k_2 = 6.18 \cdot 10^{-3} \text{ min}^{-1}$ . Calculate what time is needed to reach the maximal concentration of the intermediate B and the value of this concentration in case that the initial concentration of A was  $c_{A0} = 0.2 \text{ mol dm}^{-3}$ .

$$[ \tau_{\max} = 1.48 \text{ h} , c_{B\max} = 0.1155 \text{ mol dm}^{-3} ]$$

### Problem 2-11 Consecutive reactions, maximal intermediate concentration

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Substance A decomposes by the following consecutive reactions



The rate constants of these first-order reactions have the values  $k_1 = 3 \cdot 10^{-3} \text{ s}^{-1}$  and  $k_2 = 1.5 \cdot 10^{-3} \text{ s}^{-1}$ . Assuming that at the beginning the system contains pure substance A,

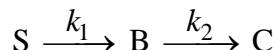
- Calculate the composition of the reaction mixture in mol. % after 15 minutes from the beginning of the reaction.
- Find out if the concentration of the intermediate B is still rising or if it is already decreasing.
- Calculate the maximum concentration of B and determine in what time it is reached.

$$[ \text{(a) } 6.72 \text{ mol. \% A, } 38.41 \text{ mol. \% B, } 54.87 \text{ mol. \% R, (b) } dc_B/d\tau < 0, \text{ the slope is negative, } \\ \text{the intermediate concentration already decreases, (c) } \tau_{\max} = 7.7 \text{ min, } c_{B\max} = 0.5 c_{A,0} ]$$

### Problem 2-12 Consecutive reactions, maximal intermediate concentration

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Substance S decomposes by consecutive reactions



with rate constants  $k_1 = 0.031 \text{ s}^{-1}$  and  $k_2 = 2.4 \text{ min}^{-1}$ . Initial solution contained all three components in concentrations  $c_{S0} = 1.195 \text{ mol dm}^{-3}$ ,  $c_{B0} = 0.1 \text{ mol dm}^{-3}$ , and  $c_{C0} = 0.1 \text{ mol dm}^{-3}$ .

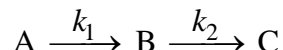
- Calculate the composition of the reaction mixture (in mol. %) after 30 s from the beginning of the reaction.
- Find out if the concentration of the intermediate B is still rising or if it is already decreasing.

$$[ \text{(a) } 33.8 \text{ mol. \% S; } 29.7 \text{ \% mol. \% B; } 36.5 \text{ \% mol. \% C ;} \\ \text{(b) } dc_B/d\tau = -1.956 \cdot 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1} - \text{the slope is negative, } c_B \text{ decreases} ]$$

### Problem 2-13 Consecutive reactions, composition of reaction mixture

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Saponification of glycol diacetate occurs as the consecutive first-order reactions



at 18°C. For the rate constants the following values were found:

the saponification to the first degree .....  $k_1 = 8.364 \cdot 10^{-7} \text{ s}^{-1}$ ,

the saponification to the second degree .....  $k_2 = 2.574 \cdot 10^{-5} \text{ min}^{-1}$

What is the composition of reaction mixture (in mol. %) after 100 hours from the beginning of the reaction when the system contained only glycol diacetate.

$$[ 74 \text{ mol. \% A, } 24 \text{ mol. \% B, } 2 \text{ mol. \% C} ]$$