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

Substance A decomposes by the following consecutive reactions

$$A \rightarrow B \quad (1) \quad , \quad B \rightarrow R \quad (2)$$

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

(a) Calculate the composition of the reaction mixture in mol. % after 15 minutes from the beginning of the reaction.

(b) Find out if the concentration of the intermediate B is still rising or if it is already decreasing.

(c) Calculate the maximum concentration of B and determine in what time it is reached.

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

**Solution:**

(a) The time change of A concentration is given by the relation

$$-\frac{\mathrm{d}\,c_A}{\mathrm{d}\,\tau} = k_1 \cdot c_A\,, \qquad \text{in integrated form} \qquad c_A = c_{A0} \cdot \exp(-k_1 \cdot \tau) \tag{3}$$

where $c_{A,0}$ and $c_A$ are the concentrations of A in $\tau = 0$ and $\tau$, respectively. The time change of B concentration:

$$\frac{\mathrm{d}\,c_B}{\mathrm{d}\,\tau} = k_1 \cdot c_A - k_2 \cdot c_B \tag{4}$$

$$c_B = \frac{k_1 \cdot c_{A,0}}{k_2 - k_1}\,(\mathrm{e}^{-k_1\tau} - \mathrm{e}^{-k_2\tau}) \tag{5}$$

The balance $\qquad \Sigma c = c_A + c_B + c_R = c_{A0} \qquad (6)$

leads to the time change of R concentration

$$c_R = c_{A,0} \cdot \left(1 - \frac{k_2}{k_2 - k_1} \cdot \mathrm{e}^{-k_1\tau} + \frac{k_1}{k_2 - k_1} \cdot \mathrm{e}^{-k_2\tau}\right) \tag{7}$$

Inserting the values

$$k_1 = 3{\cdot}10^{-3}\ \mathrm{s}^{-1},\quad k_2 = 1.5{\cdot}10^{-3}\ \mathrm{s}^{-1},\quad \tau = 15{\cdot}60 = 900\ \mathrm{s}$$

into (3), (5) a (7) we get the values of instantaneous concentrations of all componenets in $\tau$ = 15 min

$$c_A = 0.0672\ c_{A0}\ ,\quad c_B = 0.3841\ c_{A0}\ ,\quad c_R = 0.5487\ c_{A0}$$

Considering the mass balance (6) the composition of the reaction mixture is

6.72 mol.% A, 38.41 mol.% B and 54.87 mol.% R.

(b) From the derivative $\mathrm{d}c_B/\mathrm{d}\tau$ , which represents the slope of the dependence $c_B = c_B(\tau)$, can be determined, whether the concentration of B in certain time moment falls or rises:

$$\frac{\mathrm{d}\,c_B}{\mathrm{d}\,\tau} = \frac{k_1 \cdot c_{A,0}}{k_2 - k_1}(-k_1 \cdot \mathrm{e}^{-k_1\cdot\tau} + k_2 \cdot \mathrm{e}^{-k_2\cdot\tau}) =$$

$$= \frac{3{\cdot}10^{-3} \cdot c_{A0}}{3{\cdot}10^{-3} - 1.5{\cdot}10^{-3}}\left(-3{\cdot}10^{-3} \cdot \mathrm{e}^{-3\cdot10^{-3}\cdot15\cdot60} - 1.5{\cdot}10^{-3} \cdot \mathrm{e}^{-1.5\cdot10^{-3}\cdot15\cdot60}\right) =$$

$$= -3.745{\cdot}10^{-3} \cdot c_{A,0} \tag{14}$$

The slope of the curve $c_B = c_B(\tau)$ is negative, i.e. the concentration of B is already decreasing.

(c) The position of the maximum on the curve $c_B = c_B(\tau)$ is given by the condition $\mathrm{d}c_B/\mathrm{d}\tau = 0$:

$$\tau_{max} = \frac{1}{k_1 - k_2} \ln \frac{k_1}{k_2} = \frac{1}{3 \cdot 10^{-3} - 1.5 \cdot 10^{-3}} \ln \frac{3 \cdot 10^{-3}}{1.5 \cdot 10^{-3}} = 462\ \mathrm{s} = \underline{7.7\ \mathrm{min}} \qquad (16)$$

and

$$c_{Bmax} = c_{A,0} \cdot \left(\frac{k_1}{k_2}\right)^{\left(\frac{k_2}{k_2 - k_1}\right)} = c_{A,0} \cdot \left(\frac{3 \cdot 10^{-3}}{1.5 \cdot 10^{-3}}\right)^{[1.5 \cdot 10^{-3}/(1.5 \cdot 10^{-3} - 3 \cdot 10^{-3})]} = \underline{0.5\ c_{A,0}}$$

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