Problem 2-08 Parallel reactions

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

$$(1) \qquad R \xrightarrow{k_1} 2\,B + ½\,S$$

$$(2) \qquad R \xrightarrow{k_2} 3\,M$$

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

(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.

(a) $r = r_R = -\dfrac{dc_R}{d\tau} = (k_1 + k_2)\cdot c_R$, $r_B = \dfrac{dc_B}{d\tau} = 2k_1 \cdot c_R$, $r_S = \dfrac{dc_S}{d\tau} = 0.5\ k_1 \cdot c_R$, $r_M = \dfrac{dc_M}{d\tau} = 3k_2 \cdot c_R$

(b) 39.424 mol. % R; 10.202 mol. % B; 2.550 mol. % S; 47.824 mol. % M

Solution:

$k_1 = 2.4{\cdot}10^{-5}\ s^{-1}$

$k_2 = 0.27\ h^{-1} = 0.27{\cdot}(3600\ s)^{-1} = 7.5{\cdot}10^{-5}\ s^{-1}$

The dimensions of the rate constants imply that both reactions are of the first order.

Balance:

$$c_R = c_{R0} - x_1 - x_2 \qquad (1)$$

$$c_B = 2x_1 \qquad dc_B = 2\ dx_1 \qquad (2)$$

$$c_S = 0.5x_1 \qquad dc_S = 0.5\ dx_1 \qquad (3)$$

$$c_M = 3x_2 \qquad dc_M = 3\ dx_2 \qquad (4)$$

$$\Sigma c = c_R + c_B + c_S + c_M = c_{R,0} + 1.5x_1 + 2x_2 \qquad (5)$$

Diferential rate laws:

$$r = r_R = -\frac{dc_R}{d\tau} = (k_1 + k_2)\cdot c_R \quad \text{reaction rate = rate of the R decrease} \qquad (6)$$

$$r = \frac{dc_B}{2\,d\tau} = k_1 \cdot c_R\ ; \qquad (7) \qquad \text{rate of B increase: } r_B = \frac{dc_B}{d\tau} = 2k_1 \cdot c_R \qquad (8)$$

$$r = \frac{dc_S}{0.5\,d\tau} = k_1 \cdot c_R\ ; \qquad (9) \qquad \text{rate of S increase: } r_S = \frac{dc_S}{d\tau} = 0.5\ k_1 \cdot c_R \qquad (10)$$

$$r = \frac{dc_M}{3\,d\tau} = k_2 \cdot c_R\ ; \qquad (11) \qquad \text{rate of M increase: } r_M = \frac{dc_M}{d\tau} = 3k_2 \cdot c_R \qquad (12)$$

Integration of Eq. (6), $\tau = 72\ \text{min} = 72{\cdot}60\ \text{s}$:

$$c_R = c_{R0}\cdot e^{-(k_1+k_2)\cdot\tau} = c_{R0}\cdot e^{-(2.4\cdot10^{-5}+7.5\cdot10^{-5})\cdot72\cdot60} = 0.652\,c_{R0} \qquad (13)$$

From the balance (1): $c_R = c_{R0} - x_1 - x_2 = 0.652\,c_{R0} \quad \Rightarrow \quad x_1 + x_2 = 0.348\,c_{R0}$ (14)

Another equation for x_1 and x_2 we get from Eqs. (8) and (12), using balance equations (2) and (3):

$$\left.\begin{aligned} r_B &= \frac{2\,dx_1}{d\tau} = 2k_1 \cdot c_R \\ r_M &= \frac{3\,dx_2}{d\tau} = 3k_2 \cdot c_R \end{aligned}\right\} \quad \frac{r_B}{r_M} = \frac{2\ dx_1}{3\ dx_2} = \frac{2k_1 \cdot c_R}{3k_2 \cdot c_R} \Rightarrow \frac{dx_1}{dx_2} = \frac{k_1}{k_2} \Rightarrow \frac{x_1}{x_2} = \frac{k_1}{k_2} \qquad (15)$$

(14) and (15): $\frac{k_1}{k_2}x_2 + x_2 = 0.348\,c_{R0} \quad \Rightarrow \quad x_2 = \frac{0.348}{\frac{2.4\cdot 10^{-5}}{7.5\cdot 10^{-5}}+1}\cdot c_{R0} = 0.26364\,c_{R0}$

$$x_1 = \frac{k_1}{k_2}x_2 = \frac{2.4\cdot 10^{-5}}{7.5\cdot 10^{-5}}\cdot 0.26364\ c_{R0} = 0.08436\ c_{R0}$$

Concentrations of components in reaction mixture:

$c_R = c_{R0} - x_1 - x_2 = 0.652\,c_{R0}$

$c_B = 2\,x_1 = 2\cdot 0.08436\,c_{R0} = 0.16872\,c_{R0}$

$c_S = 0.5\,x_1 = 0.5\cdot 0.08436\,c_{R0} = 0.04218\,c_{R0}$

$c_M = 3\,x_2 = 3\cdot 0.26364\,c_{R0} = 0.79092\,c_{R0}$

$\Sigma c = c_{R0} + 1.5\,x_1 + x_2 = c_{R0} + 1.5\cdot 0.08436\,c_{R0} + 2\cdot 0.26364\,c_{R0} = 1.65382\,c_{R0}$

The composition of the reaction mixture:

mol. % R = $\frac{c_R}{\Sigma c}\cdot 100 = \frac{0.652\,c_{R0}}{1.65382\,c_{R0}}\cdot 100 =$ 39.424 %

mol. % B = $\frac{c_B}{\Sigma c}\cdot 100 = \frac{0.16872\,c_{R0}}{1.65382\,c_{R0}}\cdot 100 =$ 10.202 %

mol. % S = $\frac{c_S}{\Sigma c}\cdot 100 = \frac{0.04218\,c_{R0}}{1.65382\,c_{R0}}\cdot 100 =$ 2.550 %

mol. % M = $\frac{c_M}{\Sigma c}\cdot 100 = \frac{0.79092\,c_{R0}}{1.65382\,c_{R0}}\cdot 100 =$ 47.824 %