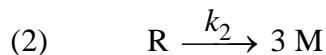
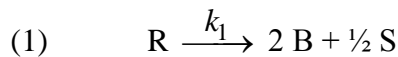


Problem 2-08 Parallel reactions

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.

$$\left[\begin{array}{l} \text{(a) } r = r_{\text{R}} = -\frac{dc_{\text{R}}}{d\tau} = (k_1 + k_2) \cdot c_{\text{R}}, \quad r_{\text{B}} = \frac{dc_{\text{B}}}{d\tau} = 2k_1 \cdot c_{\text{R}}, \quad r_{\text{S}} = \frac{dc_{\text{S}}}{d\tau} = 0.5 k_1 \cdot c_{\text{R}}, \quad r_{\text{M}} = \frac{dc_{\text{M}}}{d\tau} = 3k_2 \cdot c_{\text{R}} \\ \text{(b) } 39.424 \text{ mol. \% R; } 10.202 \text{ mol. \% B; } 2.550 \text{ mol. \% S; } 47.824 \text{ mol. \% M} \end{array} \right]$$

Solution:

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

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

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

Balance:

$$c_{\text{R}} = c_{\text{R}0} - x_1 - x_2 \quad (1)$$

$$c_{\text{B}} = 2x_1 \quad dc_{\text{B}} = 2dx_1 \quad (2)$$

$$c_{\text{S}} = 0.5x_1 \quad dc_{\text{S}} = 0.5dx_1 \quad (3)$$

$$c_{\text{M}} = 3x_2 \quad dc_{\text{M}} = 3dx_2 \quad (4)$$

$$\Sigma c = c_{\text{R}} + c_{\text{B}} + c_{\text{S}} + c_{\text{M}} = c_{\text{R}0} + 1.5x_1 + 2x_2 \quad (5)$$

Differential rate laws:

$$r = r_{\text{R}} = -\frac{dc_{\text{R}}}{d\tau} = (k_1 + k_2) \cdot c_{\text{R}} \quad \text{reaction rate} = \text{rate of the R decrease} \quad (6)$$

$$r = \frac{dc_{\text{B}}}{2d\tau} = k_1 \cdot c_{\text{R}} ; \quad (7) \quad \text{rate of B increase: } r_{\text{B}} = \frac{dc_{\text{B}}}{d\tau} = 2k_1 \cdot c_{\text{R}} \quad (8)$$

$$r = \frac{dc_{\text{S}}}{0.5d\tau} = k_1 \cdot c_{\text{R}} ; \quad (9) \quad \text{rate of S increase: } r_{\text{S}} = \frac{dc_{\text{S}}}{d\tau} = 0.5 k_1 \cdot c_{\text{R}} \quad (10)$$

$$r = \frac{dc_{\text{M}}}{3d\tau} = k_2 \cdot c_{\text{R}} ; \quad (11) \quad \text{rate of M increase: } r_{\text{M}} = \frac{dc_{\text{M}}}{d\tau} = 3k_2 \cdot c_{\text{R}} \quad (12)$$

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

$$c_{\text{R}} = c_{\text{R}0} \cdot e^{-(k_1+k_2)\tau} = c_{\text{R}0} \cdot e^{-(2.4 \cdot 10^{-5} + 7.5 \cdot 10^{-5}) \cdot 72 \cdot 60} = 0.652 c_{\text{R}0} \quad (13)$$

$$\text{From the balance (1): } c_{\text{R}} = c_{\text{R}0} - x_1 - x_2 = 0.652 c_{\text{R}0} \Rightarrow x_1 + x_2 = 0.348 c_{\text{R}0} \quad (14)$$

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

$$\left. \begin{array}{l} r_{\text{B}} = \frac{2dx_1}{d\tau} = 2k_1 \cdot c_{\text{R}} \\ r_{\text{M}} = \frac{3dx_2}{d\tau} = 3k_2 \cdot c_{\text{R}} \end{array} \right\} \quad \frac{r_{\text{B}}}{r_{\text{M}}} = \frac{2dx_1}{3dx_2} = \frac{2k_1 \cdot c_{\text{R}}}{3k_2 \cdot c_{\text{R}}} \Rightarrow \frac{dx_1}{dx_2} = \frac{k_1}{k_2} \Rightarrow \frac{x_1}{x_2} = \frac{k_1}{k_2} \quad (15)$$

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

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

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:

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

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

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

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