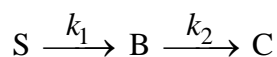


Problem 2-12 Consecutive reactions, maximal intermediate concentration

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 $c_{C0} = 0.1 \text{ mol dm}^{-3}$.

(a) Calculate the composition of the reaction mixture (in mol. %) after 30 s 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.

[(a) 33.8 mol. % S; 29.7 % mol. % B; 36.5 % mol. % C ;

(b) $dc_B/d\tau = -1.956 \cdot 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1}$ – the slope is negative, c_B decreases]

Solution:

$$k_1 = 0.031 \text{ s}^{-1}$$

$$k_2 = 2.4 \text{ min}^{-1} = 0.04 \text{ s}^{-1}$$

$$c_{S0} = 1.195 \text{ mol dm}^{-3}, c_{B0} = 0.1 \text{ mol dm}^{-3}, c_{C0} = 0.1 \text{ mol dm}^{-3}$$

$$\tau = 30 \text{ s}$$

$$c_S = c_{S0} \cdot e^{-k_1 \cdot \tau} = 1.195 \cdot \exp(-0.031 \cdot 30) = 0.4715 \text{ mol dm}^{-3}$$

$$\begin{aligned} c_B &= c_{B0} \cdot e^{-k_2 \cdot \tau} + \frac{k_1 \cdot c_{A0}}{k_2 - k_1} [e^{-k_1 \cdot \tau} - e^{-k_2 \cdot \tau}] \\ &= 0.1 \cdot \exp(-0.04 \cdot 30) + \frac{0.031 \cdot 1.195}{0.04 - 0.031} [\exp(-0.031 \cdot 30) - \exp(-0.04 \cdot 30)] = \\ &= 0.0301194 + 0.384278 = 0.4144 \text{ mol dm}^{-3} \end{aligned}$$

$$c_S = c_{S0} - x_1$$

$$c_B = c_{B0} + x_1 - x_2$$

$$c_C = c_{C0} + x_2$$

$$\Sigma c = \underbrace{c_S + c_B + c_C}_{= c_{S0} + c_{B0} + c_{C0}}$$

$$\begin{aligned} c_C &= c_{S0} + c_{B0} + c_{C0} - c_S - c_B = 1.195 + 0.1 + 0.1 - 0.4715 - 0.4144 \\ &= 0.5091 \text{ mol dm}^{-3} \end{aligned}$$

Composition of the reaction mixture in mol. %: $\Sigma c = 1.195 + 0.1 + 0.1 = 1.395$

$$100 \cdot 0.4715 / 1.395 = 33.8 \text{ mol. \% S}$$

$$100 \cdot 0.4144 / 1.395 = 29.7 \text{ \% mol. \% B}$$

$$100 \cdot 0.5091 / 1.395 = 36.5 \text{ \% mol. \% C}$$

(b) The slope of $c_B = f(\tau)$:

$$\begin{aligned} \frac{dc_B}{d\tau} &= -k_2 \cdot c_{B0} \cdot e^{-k_2 \cdot \tau} + \frac{k_1 \cdot c_{A0}}{k_2 - k_1} [-k_1 \cdot e^{-k_1 \cdot \tau} - (-k_2) \cdot e^{-k_2 \cdot \tau}] = \\ &= (-0.04) \cdot 0.1 \cdot \exp(-0.04 \cdot 30) + \\ &\quad + \frac{0.031 \cdot 1.195}{0.04 - 0.031} [(-0.031) \cdot \exp(-0.031 \cdot 30) - (-0.04) \cdot \exp(-0.04 \cdot 30)] \end{aligned}$$

$$\frac{dc_B}{d\tau} = -1.956 \cdot 10^{-3} \text{ mol dm}^{-3} \text{ s}^{-1} \text{ – the slope is negative, } c_B \text{ decreases}$$