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

Substance S decomposes by consecutive reactions

$$S \xrightarrow{k_1} B \xrightarrow{k_2} C$$

with rate constants $k_1$ = 0.031 s$^{-1}$ and $k_2$ = 2.4 min$^{-1}$. Initial solution contained all three components in concentrations $c_{S0}$ = 1.195 mol dm$^{-3}$, $c_{B0}$ = 0.1 mol dm$^{-3}$, and $c_{C0}$ = 0.1 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) $\mathrm{d}c_B/\mathrm{d}\tau$ = –1.956·10$^{-3}$ mol dm$^{-3}$ s$^{-1}$ – the slope is negative, $c_B$ decreases ]

Solution:

$k_1$ = 0.031 s$^{-1}$
$k_2$ = 2.4 min$^{-1}$ = 0.04 s$^{-1}$
$c_{S0}$ = 1.195 mol dm$^{-3}$ , $c_{B0}$ = 0.1 mol dm$^{-3}$ , $c_{C0}$ = 0.1 mol dm$^{-3}$
$\tau$ = 30 s

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

$$c_B = c_{B0} \cdot e^{-k_2 \cdot \tau} + \frac{k_1 \cdot c_{A0}}{k_2 - k_1}\left[e^{-k_1 \cdot \tau} - e^{-k_2 \cdot \tau}\right]$$

$$= 0.1 \cdot \exp(-0.04 \cdot 30) + \frac{0.031 \cdot 1.195}{0.04 - 0.031} \cdot \left[\exp(-0.031 \cdot 30) - \exp(-0.04 \cdot 30)\right] =$$

$$= 0.0301194 + 0.384278 = 0.4144 \text{ mol dm}^{-3}$$

$c_S = c_{S0} - x_1$
$c_B = c_{B0} + x_1 - x_2$
$c_C = c_{C0} + x_2$

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

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

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 mol.% S

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

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

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

$$\frac{\mathrm{d}c_B}{\mathrm{d}\tau} = -k_2 \cdot c_{B0} \cdot e^{-k_2 \cdot \tau} + \frac{k_1 \cdot c_{A0}}{k_2 - k_1}\left[-k_1 . e^{-k_1 \cdot \tau} - (-k_2).e^{-k_2 \cdot \tau}\right] =$$

$$= (-0.04) \cdot 0.1 \cdot \exp(-0.04 \cdot 30) +$$
$$+ \frac{0.031 \cdot 1.195}{0.04 - 0.031} \cdot \left[(-0.031) \cdot \exp(-0.031 \cdot 30) - (-0.04) \cdot \exp(-0.04 \cdot 30)\right]$$

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