Problem 2-07 Parallel reactions

Two side first-order reactions

$$(1) \qquad A \xrightarrow{k_1} R$$

$$(2) \qquad A \xrightarrow{k_2} 3\,S$$

take place in a constant-volume vessel at constant temperature of 350 K. In 20.2 minutes from the beginning of the reaction the concentration of the product R reached 40 % of initial concentration of the reactant A and that of the product S 66 % of initial concentration of the reactant A.
(a) What is the concentration of A in this instant (in per cents of initial amount of A).
(b) Calculate the values of both rate constants.

[(a) $c_A = 0.38\ c_{A,0}$, (b) $k_1 = 0.0309\ \text{min}^{-1}$, $k_2 = 0.017\ \text{min}^{-1}$]

Solution:

$\tau = 20.2$ min , $c_R = 0.4\ c_{A0}$, $c_S = 0.66\ c_{A0}$

Balance:

$$c_A = c_{A0} - x_1 - x_2$$

$c_R = x_1$ ..... $x_1 = 0{,}4\ c_{A0}$

$c_S = 3\ x_2$ ..... $x_2 = \frac{c_S}{3} = \frac{0.66}{3}\ c_{A0} = 0.22\ c_{A0}$

$$\Sigma c = c_A + c_R + c_S = c_{A0} + 2\,x_2$$

(a) $c_A = c_{A0} - 0.4 c_{A0} - 0.22 c_{A0} = 0.38\ c_{A0}$

(b) $r = r_A = -\frac{\mathrm{d}c_A}{\mathrm{d}\tau} = (k_1 + k_2)\cdot c_A$

$$\ln\frac{c_{A0}}{c_A} = (k_1 + k_2)\cdot\tau \text{ .....} \quad k_1 + k_2 = \frac{1}{\tau}\cdot\ln\frac{c_{A0}}{c_A} = \frac{1}{20.2}\cdot\ln\frac{c_{A0}}{0.38\,c_{A0}} = 0.0479\,\text{min}^{-1}$$

$$\left.\begin{aligned} r &= \frac{\mathrm{d}c_R}{\mathrm{d}\tau} = k_1\cdot c_A \\ r &= \frac{\mathrm{d}c_S}{3\,\mathrm{d}\tau} = k_2\cdot c_A \end{aligned}\right\} \quad \frac{\mathrm{d}c_S}{\mathrm{d}c_R} = \frac{3k_2}{k_1} \quad \Rightarrow \quad \frac{k_2}{k_1} = \frac{c_S}{3c_R} = \frac{0.66}{3\cdot 0.4} = 0.55$$

$$k_1 + 0.55 k_1 = 0.0479\ \text{min}^{-1}$$

$$k_1 = \frac{0.0479}{1.55} = 0.0309\,\text{min}^{-1}$$

$$k_2 = 0.55\ k_1 = 0.017\,\text{min}^{-1}$$