Problem 2-03 Reversible first-order reactions, reaction time

The reversible first-order reaction **S(aq)** $\rightleftarrows$ **R(aq)** takes place at 321 K in aqueous solution. The standard reaction Gibbs energy at this temperature is $\Delta_r G^{\ominus} = -830.4$ J mol^{-1} and the rate constant of the backward reaction is $k_2 = 1.15 \cdot 10^{-4}$ s^{-1}. Calculate how long from the beginning of the reaction it will take before the reaction mixture will contain 18 mol. % of the product R.

[22.9 min]

Solution:

$T = 321$ K

$\Delta_r G^{\ominus} = -0.7$ kJ mol^{-1}

$k_2 = k_{c2} = 1.15 \cdot 10^{-4}$ s^{-1}

$$K = \exp\left(-\frac{\Delta_r G^{\ominus}}{\boldsymbol{R}T}\right) = \exp\left(-\frac{(-830.4)}{8.314 \cdot 321}\right) = 1.365$$

$$\frac{K+1}{K} = \frac{1{,}365+1}{1{,}365} = 1.7326 \quad , \quad K = K_c = \frac{k_{c1}}{k_{c2}} \quad , \quad k_{c1} = K \cdot k_{c2}$$

Balance:

$$c_S = c_{S0} - x = c_{S0}\,(1-\alpha)$$
$$c_R = c_{R0} + x = c_{A0}\,\alpha \quad , \quad (c_{R0} = 0)$$
$$\Sigma c = c_{S0}$$

18 mol. % of R: $\frac{c_R}{\Sigma c} = 0.18 \;\Rightarrow\; c_R = 0.18\, c_{S0} \;\Rightarrow\; \alpha = 0.18$

$$-\frac{\mathrm{d}c_S}{\mathrm{d}\tau} = k_{c1} \cdot c_S - k_{c2} \cdot c_R$$

$$c_{S0} \cdot \frac{\mathrm{d}\alpha}{\mathrm{d}\tau} = k_{c1} \cdot (1-\alpha) - k_{c2} \cdot c_{S0} \cdot \alpha = k_{c1} \cdot c_{S0} \cdot \left(1 - \alpha \cdot \frac{K_c+1}{K_c}\right)$$

$$\ln\left(1 - \alpha \cdot \frac{K+1}{K}\right) = -k_{c2} \cdot K \cdot \frac{K+1}{K} \cdot \tau = -k_{c2} \cdot (K+1) \cdot \tau$$

($K_c = K$)

$$\tau = \frac{\ln\left(1 - \alpha \cdot \frac{K+1}{K}\right)}{-k_{c2} \cdot (K+1)} = \frac{\ln\left(1 - 0.18 \cdot 1.7326\right)}{(-1.15 \cdot 10^{-4} \cdot 2.365)} = 1374.3 \text{ s} = 22.9 \text{ min}$$