Problem 2-02 Reversible first-order reactions, reaction time

Reversible isomerization **A(ℓ)** $\rightleftarrows$ **B(ℓ)** takes place in liquid phase at the temperature of 32 °C with the forward rate constant $k_{c1} = 4 \cdot 10^{-3}$ h^{-1}. The equilibrium mixture contains 25 mol.% of A. Calculate the time needed to reach the conversion of isomer A into isomer B equal to 60 % of the equilibrium value, if the reactor was originally filled with pure isomer A. You can assume that all activity coefficients are equal to unity.

[171.8 h]

Solution

$k_{c1} = 4 \cdot 10^{-3}$ h^{-1}

Balance: $x = \dfrac{c_A - c_{A0}}{(-1)}$ or $\alpha = \dfrac{c_{A0} - c_A}{c_{A0}}$

$c_A = c_{A0} - x = c_{A0}\,(1 - \alpha)$

$c_B = c_{B0} + x = c_{B0} + c_{A0}\,\alpha \quad , \quad c_{B0} = 0$

$\Sigma c = c_{A0}$

Equilibrium constant K_c :

Equilibrium mixture contains 25 mol.% of A:

$$\frac{c_{A,equil}}{\Sigma c} = 0.25 \Rightarrow c_{A,equil} = 0.25\, c_{A0}$$

$$c_{B,equil} = \alpha_{equil}\, c_{A0} = 0.75\, c_{A0}$$

$$\alpha_{equil} = 0.75$$

$$K_c = \frac{c_{B,equil}}{c_{A,equil}} = \frac{\alpha_{equil}}{1-\alpha_{equil}} = \frac{0.75}{0.25} = 3$$

In time τ = ?

conversion A to B …. $x = c_{A0} - c_A \cdot \alpha = 0.6\, x_{equil} = 0.6 \cdot 0.75 \cdot c_{A0}$

$\alpha = 0.45$

Rate laws:

$$-\frac{dc_A}{d\tau} = k_{c+} \cdot c_A - k_{c-} \cdot c_B$$

$$c_{A0} \cdot \frac{d\alpha}{d\tau} = k_{c+} \cdot c_{A0} \cdot (1-\alpha) - k_{c-} \cdot c_{A0} \cdot \alpha = k_{c+} \cdot c_{A0} \cdot \left(1 - \alpha \cdot \frac{K_c + 1}{K_c}\right)$$

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

$$\tau = \frac{\ln\left(1 - \alpha \cdot \frac{K_c+1}{K_c}\right)}{-k_{c+} \cdot \frac{K_c+1}{K_c}} = \frac{\ln\left(1 - 0.45 \cdot \frac{3+1}{3}\right)}{\left(-4 \cdot 10^{-3} \cdot \frac{3+1}{3}\right)} = 171{,}8 \text{ h}$$