Problem 2-01 Reversible first-order reactions, conversion

The rate constants of the racemization of optically active bromide,

$$\text{D-R}_1\text{R}_2\text{R}_3\text{CBr} \rightleftarrows \text{L-R}_1\text{R}_2\text{R}_3\text{CBr},$$

in the forward and backward directions are of the same values, $k_1 = k_2 = 1.9\cdot10^{-6}\ \text{s}^{-1}$.

(a) What time is needed to accomplish 10 % conversion of D-bromide to L-bromide?

(b) Calculate the conversion of D-bromide to L-bromide in 48 hours, if the initial solution contains only D-bromide?

[(a) $\tau = 16.3$ h, (b) $\alpha = 0.241$]

Solution:

Balance: $c_D = c_{D0} - x = c_{D0}\,(1 - \alpha)$

$c_L = x = c_{D0}\,\alpha$

Rate laws:

$$-\frac{dc_D}{d\tau} = k_{c1}\cdot c_D - k_{c2}\cdot c_L$$

$$c_{D0}\cdot\frac{d\alpha}{d\tau} = k_{c1}\cdot c_{D0}\cdot(1-\alpha) - k_{c2}\cdot c_{D0}\cdot\alpha = k_{c1}\cdot c_{D0}\cdot\left(1-\alpha\cdot\frac{K_c+1}{K_c}\right)$$

$$\ln\left(1-\alpha\cdot\frac{K_c+1}{K_c}\right) = -k_{c1}\cdot\frac{K_c+1}{K_c}\cdot\tau$$

$$\left(K_c = \frac{k_{c1}}{k_{c2}} = K = 1\right)\ ,\quad k_{c1} = 1.9\cdot10^{-6}\ \text{s}^{-1}$$

(a) $x = c_{D0}\ \alpha = 0.1\ c_{D0}$

$\alpha = 0.1$

$$\tau = -\frac{1}{k_{c1}}\cdot\frac{K_c}{K_c+1}\cdot\ln\left(1-\alpha\cdot\frac{K_c+1}{K_c}\right) = -\frac{1}{1.9\cdot10^{-6}}\cdot\frac{1}{1+1}\cdot\ln\left(1-0.1\cdot\frac{1+1}{1}\right) = 58722\ \text{s}$$

$= 16.31$ h

(b) $\tau = 48$ hod , $x = c_{D0}\ \alpha = 0.1\ c_{D0}$

$$1-\alpha\cdot\frac{K+1}{K} = \exp\left(-k_{c1}\cdot\tau\cdot\frac{K+1}{K}\right) = \exp\left(-1.9\cdot10^{-6}\cdot48\cdot3600\cdot\frac{1+1}{1}\right) = 0.51859$$

$$\alpha = \frac{1}{1+1}\cdot(1-0.51859) = 0.241$$