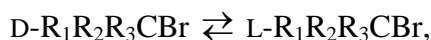


### Problem 2-01 Reversible first-order reactions, conversion

The rate constants of the racemization of optically active bromide,



in the forward and backward directions are of the same values,  $k_1 = k_2 = 1.9 \cdot 10^{-6} \text{ s}^{-1}$ .

(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)  $\tau = 16.3 \text{ h}$ , (b)  $\alpha = 0.241$  ]

Solution:

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

Rate laws:

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

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

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

$$(K_c = \frac{k_{c1}}{k_{c2}} = K = 1) \text{ , } k_{c1} = 1.9 \cdot 10^{-6} \text{ s}^{-1}$$

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

$$\tau = -\frac{1}{k_{c1}} \cdot \frac{K_c}{K_c + 1} \cdot \ln \left(1 - \alpha \cdot \frac{K_c + 1}{K_c}\right) = -\frac{1}{1.9 \cdot 10^{-6}} \cdot \frac{1}{1+1} \cdot \ln \left(1 - 0.1 \cdot \frac{1+1}{1}\right) = 58722 \text{ s}$$

$= 16.31 \text{ h}$

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

$$1 - \alpha \cdot \frac{K+1}{K} = \exp \left(-k_{c1} \cdot \tau \cdot \frac{K+1}{K}\right) = \exp \left(-1.9 \cdot 10^{-6} \cdot 48 \cdot 3600 \cdot \frac{1+1}{1}\right) = 0.51859$$

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