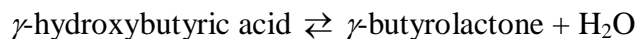


## Problem 2-04 Reversible first-order reactions, calculation of rate and equilibrium constants

Reaction



takes place in an aqueous solution. The forward reaction follows first-order kinetics, the backward reaction in the aqueous solution is pseudo-unimolecular.

The kinetic measurements revealed that the concentration of hydroxybutyric acid decreased after 102 minutes from the initial value of  $18.25 \text{ mmol dm}^{-3}$  to  $10.25 \text{ mmol dm}^{-3}$  and in equilibrium its concentration was  $5 \text{ mmol dm}^{-3}$ . Find both rate constants and the equilibrium constant of the above mentioned reaction.

$$[K_c = 2.65 ; k_{c1} = 6.59 \cdot 10^{-3} \text{ min}^{-1}, k_{c2} = 2.487 \cdot 10^{-3} \text{ min}^{-1}]$$

**Solution:**

H stands for hydroxybutyric acid, B for butyrolactone

- $\tau = 0 \dots c_{\text{H}0} = 18.25 \text{ mmol dm}^{-3}$

- Equilibrium:  $K_c = \frac{c_{\text{B, equil}}}{c_{\text{H, equil}}}$

$$c_{\text{H, equil}} = c_{\text{H}0} - x_{\text{equil}} = 5 \text{ mmol dm}^{-3}$$

$$c_{\text{B, equil}} = x_{\text{equil}} = c_{\text{H}0} - c_{\text{H, equil}} = 18.25 - 5 = 13.25 \text{ mmol dm}^{-3}$$

$$K_c = \frac{13.25}{5} = 2.65$$

- $\tau = 102 \text{ min}$

$$c_{\text{H}} = c_{\text{H}0} - x = 10.25, \quad dc_{\text{H}} = -dx$$

$$c_{\text{B}} = x = c_{\text{H}0} - c_{\text{H}} = 18.25 - 10.25 = 8 \text{ mmol dm}^{-3}$$

$$\sum c_i = c_{\text{H}0}$$

$$-\frac{dc_{\text{H}}}{d\tau} = k_{c1} \cdot c_{\text{H}} - k_{c2} \cdot c_{\text{B}}$$

$$\frac{dx}{d\tau} = k_{c1} \cdot (c_{\text{H}0} - x) - k_{c2} \cdot x = k_{c1} \cdot \left( c_{\text{H}0} - x \cdot \frac{K_c + 1}{K_c} \right)$$

$$-\ln \frac{c_{\text{H}0} - x \cdot \left( \frac{K_c + 1}{K_c} \right)}{c_{\text{H}0}} = k_{c1} \cdot \frac{K_c + 1}{K_c} \cdot \tau$$

$$k_{c1} = -\frac{K_c}{(K_c + 1) \cdot \tau} \cdot \ln \left( 1 - \frac{x}{c_{\text{H}0}} \cdot \frac{K_c + 1}{K_c} \right) = -\frac{2.65}{(2.65 + 1) \cdot 102} \cdot \ln \left( 1 - \frac{8}{18.25} \cdot \frac{2.65 + 1}{2.65} \right)$$

$$k_{c1} = 6.59 \cdot 10^{-3} \text{ min}^{-1}$$

$$k_{c2} = \frac{k_{c1}}{K_c} = \frac{6.59 \cdot 10^{-3}}{2.65} = 2.487 \cdot 10^{-3} \text{ min}^{-1}$$