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

Reaction

$$\gamma\text{-hydroxybutyric acid} \rightleftarrows \gamma\text{-butyrolactone} + H_2O$$

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 mmol dm^{-3} to 10.25 mmol dm^{-3} and in equilibrium its concentration was 5 mmol dm^{-3}. Find both rate constants and the equilibrium constant of the above mentioned reaction.

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

Solution:

H stands for hydroxybutyric acid, B for butyrolactone

- $\tau = 0$ ….. $c_{H0} = 18.25$ mmol dm^{-3}

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

$c_{H,\text{ equil}} = c_{H0} - x_{\text{equil}} = 5$ mmol dm^{-3}

$c_{B,\text{ equil}} = x_{\text{equil}} = c_{H0} - c_{H,\text{ equil}} = 18.25 - 5 = 13.25$ mmol dm^{-3}

$$K_c = \frac{13.25}{5} = 2{,}65$$

- $\tau = 102$ min

$c_H = c_{H0} - x = 10.25$, $\mathrm{d}c_H = -\mathrm{d}x$

$c_B = x = c_{H0} - c_H = 18.25 - 10.25 = 8$ mmol dm^{-3}

$\Sigma c_i = c_{H0}$

$$-\frac{\mathrm{d}c_H}{\mathrm{d}\tau} = k_{c1} \cdot c_H - k_{c2} \cdot c_B$$

$$\frac{\mathrm{d}x}{\mathrm{d}\tau} = k_{c1} \cdot (c_{H0} - x) - k_{c2} \cdot x = k_{c1} \cdot (c_{H0} - x \cdot \frac{K_c + 1}{K_c})$$

$$-\ln \frac{c_{H0} - x \cdot (\frac{K_c + 1}{K_c})}{c_{H0}} = k_{c1} \cdot \frac{K_c + 1}{K_c} \cdot \tau$$

$$k_{c1} = -\frac{K_c}{(K_c + 1) \cdot \tau} \cdot \ln\left(1 - \frac{x}{c_{H0}} \cdot \frac{K_c + 1}{K_c}\right) = -\frac{2.65}{(2.65 + 1) \cdot 102} \cdot \ln\left(1 - \frac{8}{18.25} \cdot \frac{2.65 + 1}{2.65}\right)$$

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

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