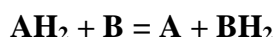


**Problem 6-02** Equilibrium constant, equilibrium mixture composition, temperature dependence

Transhydrogenation, schematically written as



is one of the reactions catalyzed by oxidoreductases.

At concentrations 0.02 mol  $\text{AH}_2$  and 5 mmol B in 1  $\text{dm}^3$  of initial mixture the equilibrium mixture contained 3 mol. % of  $\text{BH}_2$ . The experiment took place at constant temperature of 25.5 °C.

- Calculate the equilibrium constant for the standard state infinite dilution at given temperature and pressure,  $c^{\text{st}} = 1 \text{ mol dm}^{-3}$ . Assume that all activity coefficients are equal to one.
- Calculate how much of the substrate  $\text{AH}_2$  (in mmol  $\text{dm}^{-3}$ ) will be left in the equilibrium mixture if the initial mixture contained equal amounts of both substrates  $\text{AH}_2$  and B, 0.04 mol  $\text{dm}^{-3}$ .
- Calculate the reaction enthalpy of transhydrogenation if you know that at the temperature of 33 °C and equal initial concentrations, 65 mmol  $\text{dm}^{-3}$ , 9.75 mol of A was found in 1  $\text{dm}^3$  of the equilibrium mixture.

$$[(a) K_1 = 6.8755 \cdot 10^{-3}; (b) c_{\text{AH}_2} = 0.03694 \text{ mol dm}^{-3}; (c) \Delta_r H^\ominus = 153106 \text{ J mol}^{-1} (K_2 = 3.1142 \cdot 10^{-2})]$$

**Solution:**

$$(a) \quad T_1 = 298.65 \text{ K}$$

$$(c_{\text{AH}_2})_0 = 0.02 \text{ mol dm}^{-3}$$

$$c_{\text{B}0} = 0.005 \text{ mol dm}^{-3}$$

$$c_{\text{AH}_2} = (c_{\text{AH}_2})_0 - x$$

$$c_{\text{B}} = c_{\text{B}0} - x$$

$$c_{\text{A}} = c_{\text{BH}_2} = x$$

$$\Sigma c = (c_{\text{AH}_2})_0 + c_{\text{B}0} = 0.02 + 0.005 = 0.025$$

$$\frac{c_{\text{BH}_2}}{\Sigma c} = 0.03 = \frac{x}{\Sigma c} \Rightarrow x = 0.03 \cdot 0.025 = 0.00075$$

$$c_{\text{AH}_2} = 0.02 - 0.00075 = 0.01925$$

$$c_{\text{B}} = 0.005 - 0.00075 = 0.00425$$

$$c_{\text{A}} = c_{\text{BH}_2} = 0.00075$$

$$K_1 = \frac{a_{\text{A}} \cdot a_{\text{BH}_2}}{a_{\text{B}} \cdot a_{\text{AH}_2}} = \frac{c_{\text{A}} \cdot c_{\text{BH}_2}}{c_{\text{B}} \cdot c_{\text{AH}_2}} = \frac{0.00075^2}{0.01925 \cdot 0.00425} = 6.8755 \cdot 10^{-3}$$

$$(b) \quad (c_{\text{AH}_2})_0 = c_{\text{B}0} = 0.04 \text{ mol dm}^{-3}$$

$$c_{\text{AH}_2} = 0.04 - x$$

$$c_{\text{B}} = 0.04 - x$$

$$c_{\text{A}} = c_{\text{BH}_2} = x$$

$$\Sigma c = c_{\text{AH}_2} + c_{\text{B}} + c_{\text{A}} = (c_{\text{AH}_2})_0 + c_{\text{B}0} = 0.04 + 0.04 = 0.08$$

$$K_1 = \frac{c_{\text{A}} \cdot c_{\text{BH}_2}}{c_{\text{B}} \cdot c_{\text{AH}_2}} = \frac{x^2}{(0.04 - x)^2} = 6.8755 \cdot 10^{-3}$$

$$\frac{x}{0.04 - x} = \sqrt{6.8755 \cdot 10^{-3}} \Rightarrow x = \frac{0.04 \cdot \sqrt{6.8755 \cdot 10^{-3}}}{1 + \sqrt{6.8755 \cdot 10^{-3}}} = 0.003063 \text{ mol dm}^{-3}$$

$$c_{\text{AH}_2} = 0.04 - 0.003063 = 0.03694 \text{ mol dm}^{-3}$$

$$(c) \quad T_2 = 306.15 \text{ K} \quad , \quad \Delta_r H^\ominus = ?$$

$$(c_{\text{AH}_2})_0 = c_{\text{B}0} = 0.065 \text{ mol dm}^{-3}$$

$$c_{\text{AH}_2} = c_{\text{B}} = 0.065 - x = 0.065 - 0.00975 = 0.05525 \text{ mol dm}^{-3}$$

$$c_{\text{A}} = c_{\text{BH}_2} = x = 0.00975 \text{ mol dm}^{-3}$$

$$K_2 = \frac{c_{\text{A}} \cdot c_{\text{BH}_2}}{c_{\text{B}} \cdot c_{\text{AH}_2}} = \frac{0.00975^2}{0.05525^2} = 3.1142 \cdot 10^{-2}$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta_r H^\ominus}{R} \cdot \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

$$\Delta_r H^\ominus = \frac{R \cdot \ln \frac{K_2}{K_1}}{\frac{1}{T_1} - \frac{1}{T_2}} = \frac{8.314 \cdot \ln \frac{3.1142 \cdot 10^{-2}}{6.8755 \cdot 10^{-3}}}{\frac{1}{298.65} - \frac{1}{306.15}} = 153106 \text{ J mol}^{-1}$$