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

Transhydrogenation, schematically written as

$$\mathbf{AH_2 + B = A + BH_2}$$

is one of the reactions catalyzed by oxidoreductases.

At concentrations 0.02 mol AH_2 and 5 mmol B in 1 dm^3 of initial mixture the equilibrium mixture contained 3 mol. % of BH_2. The experiment took place at constant temperature of 25.5 °C.

(a) Calculate the equilibrium constant for the standard state infinite dilution at given temperature and pressure, $c^{st} = 1$ mol dm^{-3}. Assume that all activity coefficients are equal to one.

(b) Calculate how much of the substrate AH_2 (in mmol dm^{-3}) will be left in the equilibrium mixture if the initial mixture contained equal amounts of both substrates AH_2 and B, 0.04 mol dm^{-3}.

(c) Calculate the reaction enthalpy of transhydrogenation if you know that at the temperature of 33 °C and equal initial concentrations, 65 mmol dm^{-3}, 9.75 mol of A was found in 1 dm^3 of the equilibrium mixture.

[(a) $K_1 = 6.8755\cdot 10^{-3}$; (b) $c_{AH2} = 0.03694$ mol dm^{-3}; (c) $\Delta_r H^{\ominus} = 153106$ J mol^{-1} ($K_2 = 3.1142\cdot 10^{-2}$)]

Solution:

(a) $T_1 = 298.65$ K

$(c_{AH2})_0 = 0.02$ mol dm^{-3}
$c_{B0} = 0.005$ mol dm^{-3}

$c_{AH2} = (c_{AH2})_0 - x$
$c_B = c_{B0} - x$
$c_A = c_{BH2} = x$
$\Sigma c = (c_{AH2})_0 + c_{B0} = 0.02 + 0.005 = 0.025$

$$\frac{c_{BH_2}}{\Sigma c} = 0.03 = \frac{x}{\Sigma c} \quad \Rightarrow \quad x = 0.03 \cdot 0.025 = 0.00075$$

$c_{AH2} = 0.02 - 0.00075 = 0.01925$
$c_B \;\; = 0.005 - 0.00075 = 0.00425$
$c_A = c_{BH2} = 0.00075$

$$K_1 = \frac{a_A \cdot a_{BH_2}}{a_B \cdot a_{AH_2}} = \frac{c_A \cdot c_{BH_2}}{c_B \cdot c_{AH_2}} = \frac{0.00075^2}{0.01925 \cdot 0.00425} = 6.8755\cdot 10^{-3}$$

(b) $(c_{AH2})_0 = c_{B0} = 0.04$ mol dm^{-3}

$c_{AH2} = 0{,}04 - x$
$c_B = 0{,}04 - x$
$c_A = c_{BH2} = x$
$\Sigma c = c_{AH2} + c_B + c_A = (c_{AH2})_0 + c_{B0} = 0.04 + 0.04 = 0.08$

$$K_1 = \frac{c_A \cdot c_{BH_2}}{c_B \cdot c_{AH_2}} = \frac{x^2}{(0.04 - x)^2} = 6.8755\cdot 10^{-3}$$

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

$c_{AH2} = 0.04 - 0.003063 = 0.03694$ mol dm^{-3}

(c) $T_2 = 306.15$ K , $\Delta_r H^\ominus = ?$

$(c_{AH2})_0 = c_{B0} = 0.065$ mol dm^{-3}

$c_{AH2} = c_B = 0.065 - x = 0.065 - 0.00975 = 0.05525$ mol dm^{-3}

$c_A = c_{BH2} = x = 0.00975$ mol dm^{-3}

$$K_2 = \frac{c_A \cdot c_{BH_2}}{c_B \cdot c_{AH_2}} = \frac{0.00975^2}{0.05525^2} = 3.1142 \cdot 10^{-2}$$

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

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