Problem 6-04 Equilibrium constant, equilibrium conversion degree, reaction enthalpy and entropy

The smallest class of enzymes represent isomerases, the task of which is to keep the equilibrium between two isomers A and B:

$$\mathbf{A = B}\ .$$

(a) Calculate the equilibrium constant of the isomeration (standard state infinite dilution at given temperature and pressure, $c^{st} = 1$ mol dm^{-3}) from these data: At the temperature of 48 °C the initial solution contained 1.28 mol A and 0.048 mol B in 8 dm^3, in equilibrium was left 0.72 mol A from the initial amount of A (activity coefficients: $\gamma_A = 0.62$; $\gamma_B = 1.028$).

(b) Calculate the equilibrium degree of conversion and the equilibrium concentration of A if the initial solution contains only A in the same concentration as ad (a). Activity coefficients have the values $\gamma_A = 0.66$ and $\gamma_B = 1.05$ in this case. Which conversion degree will be larger, $\alpha_{(a)}$ or $\alpha_{(b)}$?

(c) At 28 °C The equilibrium mixture of isomers contains 65 mol. % of A ($\gamma_A = 0.58$; $\gamma_B = 1.12$). Calculate the standard reaction enthalpy $\Delta_r H^{\ominus}$ and entropy $\Delta_r S^{\ominus}$ of isomerization. Assume that in the temperature interval under consideration these quantities are independent of temperature.

[(a) $K_1 = 1.4$; $\alpha_{(a)} = 0.4375$; (b) $\alpha_{(b)} = 0.4681$; $c_A = 0.0851$ mol dm^{-3}, the conversion ad (b) is larger; (c) $\Delta_r H^{\ominus} = 11950.743$ J mol^{-1}; $\Delta_r S^{\ominus} = 40$ J K^{-1} mol^{-1}]

Solution:

(a) $t_1 = 48°C$

$T_1 = 321.15$ K

$V = 8$ dm^3

$n_{A0} = 1.28$ mol A , $c_{A0} = 1.28/8 = 0.16$ mol dm^{-3}

$n_A = 0.72$ mol A , $c_A = 0.72/8 = 0.09$ mol dm^{-3} ; $\gamma_A = 0.62$

$n_{B0} = 0.048$ mol B , $c_{B0} = 0.048/8 = 0.006$ mol dm^{-3}

$c_A = c_{A0} - x \Rightarrow x = c_{A0} - c_A = 0.16 - 0.09 = 0.07$ mol dm^{-3}

$c_B = c_{B0} + x = 0.006 + 0.07 = 0.076$ mol dm^{-3} ; $\gamma_B = 1.028$

$$K_1 = \frac{a_B}{a_A} = \frac{\gamma_B \cdot c_B}{\gamma_A \cdot c_A} = \frac{1.028 \cdot 0.076}{0.62 \cdot 0.09} = 1.4$$

conversion degree: $\alpha_{(a)} = x/c_{A0} = 0.07/0.16 = 0.4375$

(b) $c_{A0} = 0.16$ mol dm^{-3}

$c_A = c_{A0} - \alpha\, c_{A0}$, $\gamma_A = 0.66$

$c_B = \alpha\, c_{A0}$, $\gamma_B = 1.05$

$$K_1 = 1.4 = \frac{\gamma_B \cdot \alpha \cdot c_{A0}}{\gamma_A \cdot c_{A0} \cdot (1-\alpha)} = \frac{1.05 \cdot \alpha}{0.66 \cdot (1-\alpha)}$$

$0.924 \cdot (1 - \alpha) = 1.05\ \alpha$

$$\alpha_{(b)} = \frac{0.924}{0.924+1.05} = 0.468085$$

$c_A = 0.16\,(1 - 0.468085) = 0.0851$ mol dm^{-3}

(c) $t_2 = 28°C$

$T_2 = 301.15$ K

$c_A = c_{A0} - x = 0.65\ c_{A0}$, $\gamma_A = 0.58$

$\underline{c_B = x = 0.35\ c_{A0}\qquad ,}$ $\gamma_B = 1.12$

$\Sigma c = c_{A0}$

$$K_2 = \frac{1.12 \cdot (0.35\, c_{A0})}{0.58 \cdot (0.65\, c_{A0})} = 1.04$$

$$\Delta_r H^\ominus = \frac{\boldsymbol{R} \cdot \ln \dfrac{K_2}{K_1}}{\dfrac{1}{T_1} - \dfrac{1}{T_2}} = \frac{8.314 \cdot \ln \dfrac{1.04}{1.4}}{\dfrac{1}{321.15} - \dfrac{1}{301.15}} = 11950.743 \text{ J mol}^{-1}$$

$$\Delta_r G^\ominus = -\boldsymbol{R}T \ln K = \Delta_r H^\ominus - T \cdot \Delta_r S^\ominus$$

$$\Delta_r S^\ominus = \frac{\Delta_r H^\ominus + \boldsymbol{R}T_1 \ln K_1}{T_1} = \frac{11950.743 + 8.314 \cdot 321.15 \cdot \ln 1.4}{321.15} = 40.0098 \text{ J K}^{-1} \text{ mol}^{-1}$$

or

$$\Delta_r S^\ominus = \frac{\Delta_r H^\ominus + \boldsymbol{R}T_2 \ln K_2}{T_2} = \frac{11950.743 + 8.314 \cdot 301.15 \cdot \ln 1.04}{301.15} = 40.0098 \text{ J K}^{-1} \text{ mol}^{-1}$$