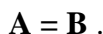


Problem 6-04 Equilibrium constant, equilibrium conversion degree, reaction enthalpy and entropy

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



- (a) Calculate the equilibrium constant of the isomeration (standard state infinite dilution at given temperature and pressure, $c^{\text{st}} = 1 \text{ mol dm}^{-3}$) 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) $\alpha_{(b)} = 0.4681$; $c_A = 0.0851 \text{ mol dm}^{-3}$, the conversion ad (b) is larger; (c) $\Delta_r H^\ominus = 11950.743 \text{ J mol}^{-1}$; $\Delta_r S^\ominus = 40 \text{ J K}^{-1} \text{ mol}^{-1}$]

Solution:

- (a) $t_1 = 48^\circ\text{C}$

$$T_1 = 321.15 \text{ K}$$

$$V = 8 \text{ dm}^3$$

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

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

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

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

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

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

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

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

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

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

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

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

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

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

- (c) $t_2 = 28^\circ\text{C}$

$$T_2 = 301.15 \text{ K}$$

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

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

$$\Sigma c = c_{A0}$$

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

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

$$\Delta_r G^\ominus = -RT \ln K = \Delta_r H^\ominus - T \cdot \Delta_r S^\ominus$$

$$\Delta_r S^\ominus = \frac{\Delta_r H^\ominus + RT_1 \ln K_1}{T_1} = \frac{11950.743 + 8.314 \cdot 321.15 \cdot \ln 1.4}{321.15} = 40.0098 \text{ J K}^{-1} \text{ mol}^{-1}$$

or

$$\Delta_r S^\ominus = \frac{\Delta_r H^\ominus + RT_2 \ln K_2}{T_2} = \frac{11950.743 + 8.314 \cdot 301.15 \cdot \ln 1.04}{301.15} = 40.0098 \text{ J K}^{-1} \text{ mol}^{-1}$$