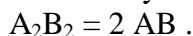


Problem 6-01 Calculation of equilibrium constant from equilibrium mixture composition, temperature dependence

Molecules of mammalian haemoglobin consist of two pairs of two types of polypeptide chains (A and B). These oligomers A_2B_2 dissociate reversibly to two AB molecules:



- (a) In one of experiments performed at the temperature of 25°C was found that in the solution initially containing 1.5 g of haemoglobin ($M = 64500 \text{ g mol}^{-1}$) in 150 cm^3 , in equilibrium 19.7 % of this amount was converted to AB. Calculate the equilibrium constant and standard reaction Gibbs energy for the standard state of infinite dilution, $c^{\text{st}} = 1 \text{ mol dm}^{-3}$ at given temperature and pressure. Assume that activity coefficients are equal to one.
- (b) The value of the standard reaction enthalpy is $\Delta_r H^\ominus = -60 \text{ kJ mol}^{-1}$. At which temperature will be the conversion degree of haemoglobin one half of that at the temperature of 25°C ?

[(a) $K = 3 \cdot 10^{-5}$; $\Delta_r G^\ominus = 25.815 \text{ kJ mol}^{-1}$; (b) 44.7°C]

Solution:

(a) $V = 150 \text{ cm}^3 = 0.15 \text{ dm}^3$

$$c_0 = \frac{m}{M \cdot V} = \frac{1.5}{64500 \cdot 0.15} = 1.55 \cdot 10^{-4} \text{ mol dm}^{-3}$$

$$\alpha_1 = 0.197$$

Balance: $c_{A_2B_2} = c_0 - c_0 \alpha$
 $c_{AB} = 2 c_0 \alpha$

$$K_1 = \frac{a_{AB}^2}{a_{A_2B_2}} = \frac{c_{AB}^2}{c_{A_2B_2} \cdot c^{\text{st}}} = \frac{(2 c_0 \alpha_1)^2}{c_0 (1 - \alpha_1)} = \frac{1.55 \cdot 10^{-4} \cdot 4 \cdot 0.197^2}{1 - 0.197} = 2.9964 \cdot 10^{-5}$$

$$\Delta_r G^\ominus = -8.314 \cdot 298.15 \cdot \ln 2.9964 \cdot 10^{-5} = 25818 \text{ J mol}^{-1}$$

(b) $\alpha_2 = 0.197/2 = 0.0985$

$$\Delta_r H^\ominus = -60 \text{ kJ mol}^{-1}$$

$$T_1 = 298.15 \text{ K}$$

$$K_2 = \frac{4 c_0 \alpha_2^2}{1 - \alpha_2} = \frac{1.55 \cdot 10^{-4} \cdot 4 \cdot 0.0985^2}{1 - 0.0985} = 6.67265 \cdot 10^{-6}$$

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

$$\frac{1}{T_2} = \frac{1}{T_1} - \frac{R}{\Delta_r H^\ominus} \cdot \ln \frac{K_2}{K_1} = \frac{1}{298.15} - \frac{8.314}{(-60000)} \cdot \ln \frac{6.67265 \cdot 10^{-6}}{2.9964 \cdot 10^{-5}} = 0.003354 - 0.000208124$$

$$= 3.1459 \cdot 10^{-3}$$

$$T_2 = 317.87 \text{ K}$$

$$t_2 = 44.72^\circ\text{C}$$