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:

$$A_2B_2 = 2\ AB\ .$$

(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 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^{st} = 1 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 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 kJ mol^{-1}; (b) 44.7°C]

Solution:

(a) V = 150 cm^3 = 0.15 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:
$c_{A2B2} = c_0 - c_0\,\alpha$
$c_{AB} = 2\,c_0\,\alpha$

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

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

(b) α_2 = 0.197/2 = 0.0985

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

T_1 = 298.15 K

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

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

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

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

T_2 = 317.87 K

t_2 = 44.72°C