Problem 6-05 Equilibrium in liquid and gaseous phases

Standard Gibbs energy of the reaction

$$\text{myoglobin (aq)} + O_2\ (g) \rightarrow \text{oxymyoglobin (aq)}$$

at the temperature of 25 °C is $\Delta_r G_m^{\ominus} = -30$ kJ mol^{-1} standard state infinite dilution at given temperature and pressure, $c^{st} = 1$ mol dm^{-3}). Henry constant of oxygen solution in water at the same conditions has the value $K_H = 769$ bar (mol kg^{-1})$^{-1}$. What amount of myoglobin (%) will be present in equilibrium in the form of oxymyoglobin at the pressure of 1 bar? Take that the air contains 21 vol. % of oxygen.

[98 % myoglobin is in the form of oxymyoglobin]

Solution:

Concentration of oxygen dissolved in water – from Henry law $p_{O2} = \underline{m}_{O2} \cdot K_H$

Partial pressure of oxygen above the liquid is

$p_{O2} = y_{O2} \cdot p$, where $y_{O2} = 0.21$ (in air), $p = 1$ bar (= 100 kPa)

$$\underline{m}_{O2} \cong \frac{y_{O2} \cdot p}{K_H} = \frac{0.21 \cdot 1}{769} = 0.000273 \text{ mol kg}^{-1}$$

$$\underline{m}_{O2} \cong c_{O2} = 0.000273 \text{ mol dm}^{-3}$$

$$K = \exp\left(-\frac{\Delta_r G^{\ominus}}{\boldsymbol{R}T}\right) = \exp\left(-\frac{(-30 \cdot 10^3)}{8.314 \cdot 298.15}\right) = 180328.786$$

$$K = \frac{\dfrac{c_{\text{oxymyoglobin}}}{c^{st}}}{\dfrac{c_{\text{myoglobin}}}{c^{st}} \cdot \dfrac{c_{O2}}{c^{st}}} = \frac{x}{[(c_{\text{myoglobin}})_0 - x] \cdot c_{O2}} \quad , \quad c^{st} = 1 \text{ mol dm}^{-3}$$

where $c_{\text{myoglobin}} = (c_{\text{myoglobin}})_0 - x$

$c_{\text{oxymyoglobin}} = x$

$$\frac{c_{\text{oxymyoglobin}}}{c_{\text{myoglobin}}} = \frac{x}{(c_{\text{myoglobin}})_0 - x} = K \cdot c_{O2} = 180328.786 \cdot 0.000273 = 49.23$$

$$\frac{x}{(c_{\text{myoglobin}})_0} = 0.98$$

98 % of myoglobin is in the form of oxymyoglobin