6. EQUILIBRIUM CONSTANT, EQUILIBRIUM CONVERSION, TEMPERATURE DEPENDENCE

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:

$$\mathbf{A_2B_2 = 2\,AB}\ .$$

(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]

Problem 6-02 Equilibrium constant, equilibrium mixture composition, temperature dependence

Transhydrogenation, schematically written as

$$\mathbf{AH_2 + B = A + BH_2}$$

is one of the reactions catalyzed by oxidoreductases.

At concentrations 0.02 mol AH_2 and 5 mmol B in 1 dm^3 of initial mixture the equilibrium mixture contained 3 mol. % of BH_2. The experiment took place at constant temperature of 25.5 °C.

(a) Calculate the equilibrium constant for the standard state infinite dilution at given temperature and pressure, c^{st} = 1 mol dm^{-3}. Assume that all activity coefficients are equal to one.

(b) Calculate how much of the substrate AH_2 (in mmol dm^{-3}) will be left in the equilibrium mixture if the initial mixture contained equal amounts of both substrates AH_2 and B, 0.04 mol dm^{-3}.

(c) Calculate the reaction enthalpy of transhydrogenation if you know that at the temperature of 33 °C and equal initial concentrations, 65 mmol dm^{-3}, 9.75 mol of A was found in 1 dm^3 of the equilibrium mixture.

[(a) $K_1 = 6.8755{\cdot}10^{-3}$; (b) c_{AH2} = 0.03694 mol dm^{-3}; (c) $\Delta_r H^\ominus$ = 153106 J mol^{-1} ($K_2 = 3.1142{\cdot}10^{-2}$)]

Problem 6-03 Equilibrium constant, equilibrium mixture composition, temperature dependence

Lyases are enzymes catalyzing non-hydrolytic decompositions of substrates into two components:

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

(a) Calculate the equilibrium constant of this reaction at the temperature of 25 °C for standard state infinite dilution at given temperature and pressure, c^{st} = 1 mol dm^{-3} if you know that in the solution initially containing 0.4 mol AB and 0.1 mol B in 1 dm^3, in equilibrium was found 22.4 mmol of A in 1 dm^3. You can assume that all activity coefficients are equal to one.

(b) What would be the values of equilibrium concentrations of AB, A, and B, if the initial solution contained only AB in concentration 7.6 mmol dm^{-3}?

(c) The reaction enthalpy has the value of 42.8 kJ mol^{-1}, and it can be taken as constant at the temperature interval under consideration. At which temperature will be the reaction yield twice larger than that reached ad (a) – i.e. at 25 °C?

[(a) $K_1 = 7.261{\cdot}10^{-3}$; (b) $c_A = c_B$ = 0.004638 mol dm^{-3} , c_{AB} = 0.002963 mol dm^{-3}, (c) T_2 = 315 K]

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:

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

(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}]

Problem 6-05 Equilibrium in liquid and gaseous phases

Standard Gibbs energy of the reaction

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

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]