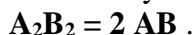


6. EQUILIBRIUM CONSTANT, EQUILIBRIUM CONVERSION, TEMPERATURE DEPENDENCE

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:

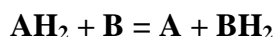


- (a) In one of experiments performed at the temperature of 25°C was found that in the solution initially containing 1.5 g of haemoglobin ($M = 64500 \text{ g mol}^{-1}$) in 150 cm^3 , in equilibrium 19.7 % of this amount was converted to AB. Calculate the equilibrium constant and standard reaction Gibbs 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 ?

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

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

Transhydrogenation, schematically written as



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, $c^{\text{st}} = 1 \text{ mol dm}^{-3}$. 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.

$$[(a) K_1 = 6.8755 \cdot 10^{-3}; (b) c_{AH_2} = 0.03694 \text{ mol dm}^{-3}; (c) \Delta_r H^\ominus = 153106 \text{ J mol}^{-1} (K_2 = 3.1142 \cdot 10^{-2})]$$

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

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

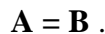


- (a) Calculate the equilibrium constant of this reaction at the temperature of 25°C for standard state infinite dilution at given temperature and pressure, $c^{\text{st}} = 1 \text{ mol dm}^{-3}$ if you know that in the solution initially containing 0.4 mol AB and 0.1 mol B in 1 dm^3 , in equilibrium 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 at (a) – i.e. at 25°C ?

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

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:

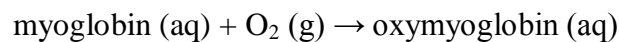


- (a) Calculate the equilibrium constant of the isomeration (standard state infinite dilution at given temperature and pressure, $c^{\text{st}} = 1 \text{ mol dm}^{-3}$) from these data: At the temperature of 48°C the initial solution contained 1.28 mol A and 0.048 mol B in 8 dm^3 , in equilibrium was left 0.72 mol A from the initial amount of A (activity coefficients: $\gamma_{\text{A}} = 0.62$; $\gamma_{\text{B}} = 1.028$).
- (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 $\gamma_{\text{A}} = 0.66$ and $\gamma_{\text{B}} = 1.05$ in this case. Which conversion degree will be larger, $\alpha_{(\text{a})}$ or $\alpha_{(\text{b})}$?
- (c) At 28°C The equilibrium mixture of isomers contains 65 mol. % of A ($\gamma_{\text{A}} = 0.58$; $\gamma_{\text{B}} = 1.12$). Calculate the standard reaction enthalpy $\Delta_{\text{r}}H^\ominus$ and entropy $\Delta_{\text{r}}S^\ominus$ of isomerization. Assume that in the temperature interval under consideration these quantities are independent of temperature.

[(a) $K_1 = 1.4$; $\alpha_{(\text{a})} = 0.4375$; (b) $\alpha_{(\text{b})} = 0.4681$; $c_{\text{A}} = 0.0851 \text{ mol dm}^{-3}$, the conversion ad (b) is larger; (c) $\Delta_{\text{r}}H^\ominus = 11950.743 \text{ J mol}^{-1}$; $\Delta_{\text{r}}S^\ominus = 40 \text{ J K}^{-1} \text{ mol}^{-1}$]

Problem 6-05 Equilibrium in liquid and gaseous phases

Standard Gibbs energy of the reaction



at the temperature of 25°C is $\Delta_{\text{r}}G_{\text{m}}^\ominus = -30 \text{ kJ mol}^{-1}$ standard state infinite dilution at given temperature and pressure, $c^{\text{st}} = 1 \text{ mol dm}^{-3}$). Henry constant of oxygen solution in water at the same conditions has the value $K_{\text{H}} = 769 \text{ bar (mol kg}^{-1}\text{)}^{-1}$. 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]