12. MEMBRANE EQUILIBRIA

$$(c_C)_I^{z_A} \cdot (c_A)_I^{z_C} = (c_C)_{II}^{z_A} \cdot (c_A)_{II}^{z_C} \qquad (z_C > 0,\ z_A > 0)$$

$$\mu_C^{\ominus}(p_I) + \boldsymbol{R}T \ln (a_C)_I + z_C \cdot \boldsymbol{F} \cdot \varphi_I = \mu_C^{\ominus}(p_{II}) + \boldsymbol{R}T \ln (a_C)_{II} + z_C \cdot \boldsymbol{F} \cdot \varphi_{II}$$

$$\mu_A^{\ominus}(p_I) + \boldsymbol{R}T \ln (a_A)_I - z_A \cdot \boldsymbol{F} \cdot \varphi_I = \mu_A^{\ominus}(p_{II}) + \boldsymbol{R}T \ln (a_A)_{II} - z_A \cdot \boldsymbol{F} \cdot \varphi_{II}$$

$$E = \varphi_{II} - \varphi_I = \frac{\boldsymbol{R}T}{z_C \boldsymbol{F}} \ln \frac{(c_C)_I}{(c_C)_{II}} = \frac{\boldsymbol{R}T}{z_A \boldsymbol{F}} \ln \frac{(c_A)_{II}}{(c_A)_I}$$

$Na^+R^- + H_2O = R^- + H^+ + NaOH \qquad (c_{Na^+} \cdot c_{OH^-})_I = (c_{Na^+} \cdot c_{OH^-})_{II}$

$(c_{OH^-})_I = K_w/(c_{H^+})_I$

$P^+Cl^- + H_2O = P^+ + OH^- + HCl \qquad (c_{H^+} \cdot c_{Cl^-})_I = (c_{H^+} \cdot c_{Cl^-})_{II}$

Problem 12-01 Membrane equilibria

Aqueous solution of a polyelectrolyte $P^{18+}(Br^-)_{18}$ in concentration 0.003 mol dm^{-3}, which is in solution completely dissociated, contains also NaBr in concentration 0.02 mol dm^{-3}. Part of this low-molecular electrolyte must be removed. The solution was separated by a semipermeable membrane (non-permeable for ions P^{18+}) from the compartment of the same volume filled with pure water. What amount of NaBr (in per cents of initially present amount) will pass over into the compartment initially containing pure water?

[78.723 %]

Problem 12-02 Membrane equilibria

The vessel is divided in two compartment of the same volume. The barrier is a membrane non-permeable for high molecular ions. One compartment (A) is filled with 0.01 molar CsCl solution, the other (B) contains the same volume of 0.01 molar CsCl solution in which some amount of high molecular chloride RCl is dissolved. Determine the concentration of RCl, needed to expel 75 % of CsCl from the compartment B to A. Both electrolytes are completely dissociated.

[c_{RCl} = 0.012 mol dm^{-3}]

Problem 12-03 Membrane equilibria

Left compartment of the dialysis cell was filled with an aqueous solution of the sodium salt of protein (molar mass 63 kg mol^{-1}), the concentration of which was 75.6 g dm^{-3}. At pH = 7.4 the protein molecule carries six charges, $(Na^+)_6P^{6-}$. Into this solution was then added sodium chloride in such amount that its concentration was 0.18 mol dm^{-3}. The right compartment was filled with pure water. Both compartments are of the same volume and they are separated by a semipermeable membrane which lets pass the low-molecular species, but not the protein. Calculate the equilibrium concentrations of all ions in both compartments.

[$(c_{Na^+})_{Left}$ = 95.435 mmol dm^{-3}; $(c_{Cl^-})_{Left}$ = 88.235 mmol dm^{-3}; $(c_{Na^+})_{Right}$ = $(c_{Cl^-})_{Right}$ = 91.765 mmol dm^{-3}]

Problem 12-04 Membrane equilibria, Donnan potential

Aqueous solution of a polyelectrolyte NaP (c_1 = 0.015 mol dm^{-3}) and low-molecular electrolyte NaBr (c_2 = 0.005 mol dm^{-3}) is separated from the compartment of the same volume filled with pure water by a semipermeable membrane. Both electrolytes are completely dissociated. At the temperature of 28 °C

(a) Calculate how many per cent of NaBr passes from the solution into water.

(b) Calculate how many per cent of NaBr would pass from the compartment containing NaBr and NaP, in case that the initial concentration is ten-times greater than in case (a).

(c) Calculate the value of Donnan potential for both cases.

[(a) 80 % (x_a = 0.004 mol dm^{-3}) , (b) 96.875 % (x_b = 4.84375·10^{-3} mol dm^{-3});
(c) $E_{(a)}$ = 0.036 V, $E_{(b)}$ = 0.089 V]

Problem 12-05 Membrane equilibria, Donnan potential

A membrane permeable for ions Ca^{2+} and Cl^-, but not for high-molecular ions R^+, separates the inner compartment of the dialysis cell at the beginning containing the polyelectrolyte RCl in concentration c_1 and $CaCl_2$ in concentration $(c_2)_0$ = 200 mmol dm^{-3}, from the outer compartment containing only calcium chloride solution in concentration $(c_3)_0$ = 300 mmol dm^{-3}. In equilibrium, established at the temperature of 27 °C, the concentration of Ca^{2+} in the inner compartment was found to be 230 mmol dm^{-3}. (a) What is the concentration of RCl in the inner compartment? (b) Calculate the equilibrium Donnan potential.

[(a) c_1 = 125 mmol dm^{-3} ; (b) E = 2.07 mV]

Problem 12-06 Membrane equilibria, Donnan potential

At pH = 7.3 a protein carries charge −5. You have an aqueous solution containing 3 mmol dm^{-3} of potassium salt of this protein and at the same time potassium chloride in concentration 0.12 mol dm^{-3}. Both salts are completely dissociated at these conditions. At the temperature of 27 °C you need to reduce the amount of potassium ions in this solution. Calculate

(a) What should be the volume of pure water which you must take to dialysis of 0.1 dm^3 of your protein solution in order that the concentration of K^+ ions in equilibrium dropped to 0.02 mol dm^{-3}.

(b) The Donnan potential in equilibrium.

[(a) V = 1.15 dm^3; (b) E = 17.9 mV]

Problem 12-07 Membrane equilibria, Donnan potential

To 0.1 dm^3 of the solution of pepsin $(Cu^{2+})_{10}\,P^{20-}$ of concentration 4·10^{-5} mol dm^{-3}, such amount of solid $CuSO_4$ was added, that the resulting concentration of the sulphate ions was 5·10^{-3} mol dm^{-3}. This solution was then dialyzed at 32 °C against 0.4 dm^3 of pure water. Calculate the equilibrium concentrations of Cu^{2+} and SO_4^{2-} ions in the pepsin solution and the Donnan potential. All electrolytes are completely dissociated.

[$c_{Cu^{2+}}$ = 1.25·10^{-3} mol dm^{-3}; $c_{SO_4^{2-}}$ = 8.55·10^{-4} mol dm^{-3}; E = –2.522 mV]

Problem 12-08 Membrane hydrolysis

An aqueous solution of a polyelectrolyte $(Na^+)_2R^{2-}$ was dialyzed against pure water. Polyelectrolyte is completely dissociated. Measurement of pH has shown the value of 5.366 for equilibrium solution. Calculate

(a) pH in the compartment initially containing only pure water,

(b) the initial concentration of the polyelectrolyte.

Ionic product of water is for the standard state of infinite dilution, c^{st} = 1 mol dm^{-3}, is $K_w = 10^{-14}$.

[(a) pH = 8.634 ; (b) 0.004 mol dm^{-3}]

Problem 12-09 Membrane hydrolysis, Donnan potential

Aqueous solution of a polyelectrolyte M_zR (M^+ is univalent low-molecular cation, R^{z-} a high-molecular anion) of concentration 0.0065 mol dm^{-3} was separated by a semipermeable membrane from the same volume of pure water. The membrane is permeable for M^+, non-permeable for R^{z-}. In equilibrium established at the temperature of 39.8 °C the pH in the right compartment containing initially pure water was 8.5. In the aqueous solution the polyelectrolyte is completely dissociated. Calculate

(a) the charge *z* of the high-molecular anion,

(b) pH of the polyelectrolyte solution in equilibrium,

(c) the membrane potential in equilibrium.

The ionic product of water at given temperature is $K_w = 3.795 \cdot 10^{-14}$ (standard state c^{st} = 1 mol dm^{-3}).

[a) $z = 7$; (b) pH = 4.92; E = 222.2 mV]

Problem 12-10 Membrane hydrolysis, Donnan potential

The solution of ferrous salt $(Fe^{2+})_6P^{12-}$ of concentration $2 \cdot 10^{-4}$ mol dm^{-3} is at the temperature of 36 °C in the left compartment of the dialysis cell, separated from the same volume of pure water in the right compartment by a semipermeable membrane. The membrane is not permeable for high-molecular ions P^{12-}.

Calculate

(a) pH in both compartments in equilibrium

(b) Donnan potential

The ionic product of water at given temperature is $K_w = 2.255 \cdot 10^{-14}$ (standard state c^{st} = 1 mol dm^{-3}).

[pH_{Left} = 5.982 ; pH_{Right} = 7.664; E = 103.1 mV]