10. TRANSPORT PHENOMENA IN SOLUTIONS

$$D_i = \frac{k_B\,T}{f_i} \quad , \quad f_i = 6\,\pi \cdot \eta_o \cdot r_i$$

$$\overline{\Delta}^2 = 2\,D \cdot \tau$$

$$R = \rho \cdot \frac{\ell}{\mathcal{A}} \quad , \quad \frac{\ell}{\mathcal{A}} = C = \kappa \cdot R$$

$$\frac{I}{\mathcal{A}} = \kappa \cdot \frac{U}{\ell} = \kappa \cdot E$$

$$\kappa = (u_\mathrm{C} \cdot z_\mathrm{C} \cdot \nu_\mathrm{C} + u_\mathrm{A} \cdot z_\mathrm{A}\, \nu_\mathrm{A}) \cdot c \cdot \alpha \cdot F = \kappa_\mathrm{C} + \kappa_\mathrm{A}$$

$$\lambda = \frac{\kappa}{c} = \nu_\mathrm{A} \cdot \lambda_\mathrm{A} + \nu_\mathrm{C} \cdot \lambda_\mathrm{C} \quad , \quad \lambda_i = u_i \cdot z_i \cdot F$$

$$\lambda_e = \frac{\kappa}{z_\mathrm{C} \cdot \nu_\mathrm{C} \cdot c} = \frac{\kappa}{z_\mathrm{A} \cdot \nu_\mathrm{A} \cdot c} = (u_\mathrm{C} + u_\mathrm{A}) \cdot F$$

$$u_i = \frac{\upsilon_i}{E} \quad , \quad E = \frac{U}{\ell}$$

$$\lambda^\infty = \nu_\mathrm{C} \cdot \lambda_\mathrm{C}^\infty + \nu_\mathrm{A} \cdot \lambda_\mathrm{A}^\infty$$

$$t_\mathrm{C}^\infty = \frac{u_\mathrm{C}^\infty}{u_\mathrm{C}^\infty + u_\mathrm{A}^\infty} \quad , \quad t_i^\infty = \nu_i \cdot \frac{\lambda_i^\infty}{\lambda^\infty} \quad , \quad t_i = \nu_i \cdot \frac{\lambda_i}{\lambda} \quad , \quad \alpha = \frac{\lambda}{\lambda^\infty}$$

Problem 10-01 Mean displacement and diffusion coefficient

The diffusion coefficient of ribonuclease was found to have the value of $1.2 \cdot 10^{-6}$ cm^2 s^{-1}. Estimate how long it will take the ribonuclease molecule to pass through a porous membrane of thickness 1.8 mm. The molar mass of ribonuclease is 13.68 kg mol^{-1}.

[3.75 h]

Problem 10-02 Einstein equation, particle dimensions from diffusion coefficient

Spherical micelles of a surfactant are large particles (in comparison with the molecules of the dispersion medium) of density 1022.1 kg m^{-3}. Their diffusion coefficient at the temperature of 23.2 °C and pressure of 0.1 MPa in the dispersion medium of density 0.922 g cm^{-3} and viscosity 1.13 mPa s was found to be $4.8 \cdot 10^{-11}$ m^2 s^{-1}. Calculate

(a) the diameter of a micelle, (b) mass of one mole of micelles.

[(a) d = 8 nm; (b) M = 165 kg mol^{-1}]

Problem 10-03 Einstein equation for diffusion coefficient

Calculate the diffusion coefficient of spherical particles of a protein (density ρ = 1.228 g cm^{-3}, molar mass M = 68 kg mol^{-1}) at the temperature of 302 K and the pressure of 99.3 kPa in liquid medium of density ρ_o = 0.834 g cm^{-3} and viscosity η_o = 0.932 mPa·s.

[$D = 8.5 \cdot 10^{-11}$ m^2 s^{-1} ($r = 2.8 \cdot 10^{-9}$ m)]

Problem 10-04 Einstein equation, effective particle dimension

For the diffusion coefficient of particles having the shape of an elongated paraboloid in the liquid medium (density ρ_o = 0.934 g cm^{-3} and viscosity η_o = 0,8346 mPa s) was found the value $D = 8.6\cdot10^{-7}$ cm^2 s^{-1} at the temperature of 21 °C. Calculate

(a) friction coefficient,

(b) effective radius of a particle, i.e. the radius of a spherical particle which diffuse in the same manner as studied non-spherical particle,

(c) estimate the mass of a single particle and the mass of one mole of the these particles. The density of particles is $\rho = 1.13$ g cm^{-3}.

[(a) $f = 4.72\cdot10^{-11}$ kg s^{-1} (b) $r_{ef} = 3\cdot10^{-9}$ m, (c) $m = 1.278\cdot10^{-22}$ kg, $M = 76.96$ kg mol^{-1}]

Problem 10-05 Limiting molar conductivity, transference number

The value of limiting molar conductivity of butyric acid at the temperature of 25 °C is $3.823\cdot10^{-2}$ S m^2 mol^{-1} and the limiting molar conductivity of H$^+$ is 0.03497 S m^2 mol^{-1}. If you can assume that the mean activity coefficient equals to one, determine the limiting molar conductivity of anion $CH_3(CH_2)_2COO^-$ and the transference number of both ions at infinite dilution.

[$\lambda^\infty(C_3H_7COO^-)$ = 0.00326 S m^2 mol^{-1}, $t_{H+} = 0.9147$, $t_{A-} = 0.0853$]

Problem 10-06 Absolute velocity of ions, molar conductivity, transference numbers

Molar conductivity of NH_4Cl solution with concentration 0.01 mol dm^{-3} at the temperature of 25 °C is 0.0129 S m^2 mol^{-1}. The transference number of the cation in this solution is 0.4907. What is the absolute velocity of the chloride ion in the conductivity cell where the distance of the electrodes is 5.5 cm and the voltage between the electrodes is 7 V

[$u_A = 8.67\cdot10^{-6}$ m s^{-1}]

Problem 10-07 Conductivity, molar conductivity of sparingly soluble salts

The conductivity of saturated lead iodide solution at the temperature of 18 °C was found to be $3.742\cdot10^{-2}$ S m^{-1}, the conductivity of the water used for conductivity measurements was $1.8\cdot10^{-4}$ S m^{-1}. Calculate the solubility product of PbI_2 for the standard state of infinite dilution, c^{st} = 1 mol dm^{-3}. You can assume that activities can be replaced by relative concentrations. Limiting molar conductivities of ions are

$$\lambda^\infty(Pb^{2+}) = 0.0139 \text{ S m}^2\text{ mol}^{-1}\ ,\quad \lambda^\infty(I^-) = 0.00769 \text{ S m}^2\text{ mol}^{-1}.$$

[$K_S(PbI_2) = 8.23\cdot10^{-9}$]

Problem 10-08 Conductivity, molar conductivity of sparingly soluble salts

The resistance of the conductivity cell filled with KCl solution (molality 0.02 mol kg^{-1}) at 25 °C is 197 Ω. This solution has the conductivity of 0.2765 S m^{-1}. The resistance of the same cell filled with saturated solution of strontium sulphate was 3663 Ω. The conductivity of water used to these measurements was $1.8\cdot10^{-4}$ S m^{-1}. Use these data to determination the solubility product of strontium sulphate (standard state infinite dilution, c^{st} = 1 mol dm^{-3}) under the assumption that the activities can be replaced by relative concentrations. Limiting molar conductivities of ions are:

$$\lambda^\infty_{Sr^{2+}} = 0.0119 \text{ S m}^2\text{ mol}^{-1};\quad \lambda^\infty_{SO_4^{2-}} = 0.01596 \text{ S m}^2\text{ mol}^{-1}$$

[$K_S = 2.78\cdot10^{-7}$]

Problem 10-09 Conductivity, molar conductivity, dissociation constant

The conductivity of aqueous solution of benzoic acid with concentration 0.01 mol dm^{-3} at 21 °C was determined to be $3.004 \cdot 10^{-2}$ S m^{-1} and the conductivity of water used for the measurement was $2.4 \cdot 10^{-4}$ S m^{-1}. Assume that the activity coefficient of undissociated acid as well as the mean activity coefficient may be taken as unity. Calculate the dissociation constant of benzoic acid for the standard state of infinite dilution, $c^{st} = 1$ mol dm^{-3}. Limiting molar conductivities of ions:

$$\lambda^{\infty}(H^{+}) = 0.03497,\ \lambda^{\infty}(C_6H_5COO^{-}) = 0.00323\ \text{S m}^2\ \text{mol}^{-1}.$$

[$K = 6.6 \cdot 10^{-5}$ ($\alpha = 0.078$)]

Problem 10-10 Conductivity, molar conductivity, dissociation constant

Calculate the conductivity of the $2 \cdot 10^{-5}$ molar solution of propionic acid, the dissociation constant of which has the value of $1.32 \cdot 10^{-5}$ (standard state infinite dilution, $c^{st} = 1$ mol dm^{-3}, activity coefficients for all substances can be taken as equal to one). The conductivity of water used for the measurement was $6.6 \cdot 10^{-5}$ S m^{-1} and the limiting molar conductivities of ions have the following values:

$$\lambda^{\infty}(H^{+}) = 0.03497\ \text{S m}^2\ \text{mol}^{-1},\ \lambda^{\infty}(C_3H_7COO^{-}) = 0.00358\ \text{S m}^2\ \text{mol}^{-1}$$

[$\kappa_{solution} = 4.88 \cdot 10^{-4}$ S m^{-1}]

Problem 10-11 Conductivity, molar conductivity, dissociation constant

What amount of acetic acid (in moles) must be dissoved in 1.5 dm^3 of solution in order that its conductivity was $7.13 \cdot 10^{-3}$ S m^{-1} (conductivity of water has the value of $1.6 \cdot 10^{-4}$ S m^{-1})? Dissociation constant of the acetic acid is $1.75 \cdot 10^{-5}$ (standard state infinite dilution, $c^{st} = 1$ mol dm^{-3}, activity coefficients of all species can be taken as equal to one). Limiting molar conductivities:

$$\lambda^{\infty}(H^{+}) = 0.03497\ \text{S m}^2\ \text{mol}^{-1},\quad \lambda^{\infty}(A^{-}) = 0.00409\ \text{S m}^2\ \text{mol}^{-1}$$

[$n = 0.003$ mol ($c_0 = 0.002$ mol dm^{-3})]

Problem 10-12 Conductivity, molar conductivity, dissociation constant

420 cm^3 of ammonia at the temperature of 25 °C and pressure of 100.7 kPa was dissolved in 2 dm^3 of water (conductivity $5.3 \cdot 10^{-4}$ S m^{-1}). At these conditions the ammonia can be taken as an ideal gas. The conductivity of the resulting solution was $1.095 \cdot 10^{-2}$ S m^{-1}. Calculate the dissociation constant of ammonia in aqueous solution (standard state infinite dilution, $c^{st} = 1$ mol dm^{-3}, activity coefficients for all species can be taken as equal to one). Limiting molar conductivities:

$$\lambda^{\infty}(NH_4^{+}) = 0.00737\ \text{S m}^2\ \text{mol}^{-1},\quad \lambda^{\infty}(OH^{-}) = 0.01976\ \text{S m}^2\ \text{mol}^{-1}.$$

[$K = 1.81 \cdot 10^{-5}$ ($c_0 = 8.531 \cdot 10^{-3}$ mol dm^{-3}, $\alpha = 0.045$)]