

13. COLLIGATIVE PROPERTIES

$$\frac{p_1^s - p_1}{p_1^s} = x_2$$

$$\Delta T_E = K_E \cdot m_2 \quad K_E = \frac{RT_{bl}^2 \cdot M_1}{\Delta_{vap} H_{m1}} \quad [\text{K} \cdot \text{kg} \cdot \text{mol}^{-1}]$$

$$-\Delta T_K = K_K \cdot m_2 \quad K_K = \frac{RT_{f1}^2 \cdot M_1}{\Delta_{fusion} H_{m1}} \quad [\text{K} \cdot \text{kg} \cdot \text{mol}^{-1}]$$

$$\pi = c_2 RT = \frac{c_w}{M_2} RT \quad \pi = i \cdot c_2 \cdot RT \quad (\text{electrolytes})$$

$$\pi = c_2 RT \cdot (1 + B \cdot c_2 + C \cdot c_2^{3/2} + D \cdot c_2^2 + \dots)$$

Vapour pressure lowering

Problem 13-01 Vapour pressure lowering

10 cm³ of glycerine was dissolved in 500 cm³ of water at the temperature of 50°C. What is the lowering of vapour pressure of the solvent above this solution? The saturated vapour pressure of water at given temperature is 12.332 kPa, water density is 0.988 g cm⁻³ and the density of glycerine 1.26 g cm⁻³.

$$[\Delta p_1 = 61.228 \text{ Pa}]$$

Problem 13-02 Vapour pressure lowering, molar mass of solute

Dissolution of 3.64 g of non-volatile substance in 400 g of chloroform ($M = 119.38 \text{ g mol}^{-1}$) at the temperature of 15°C will reduce the chloroform vapour pressure by 55 Pa. Calculate the vapour pressure above the solution and molar mass of the solute. The saturated vapour pressure of chloroform is given by Antoine equation:

| | | | |
|---|---------|---------|---------|
| $\log(p^s / \text{kPa}) = A - \frac{B}{C + (t / ^\circ\text{C})}$ | A | B | C |
| | 6.23638 | 1232.79 | 230.213 |

$$[p_1 = 16.124 \text{ Pa}; M_2 = 318.43 \text{ g mol}^{-1}]$$

Problem 13-03 Vapour pressure lowering, molar mass of solvent

The vapour pressure of pure solvent at the temperature of 40°C was determined to be 40.4 kPa. The vapour pressure above the solution formed by dissolving of 0.4 g NaCl ($M = 58.44 \text{ g mol}^{-1}$) in 650 g of the above mentioned solvent was by 121.2 Pa lower. What is the molar mass of the solvent?

$$[M_1 = 142.67 \text{ g mol}^{-1}]$$

Freezing point depression

Problem 13-04 Freezing point depression – non-electrolyte solutions

Compare the results of four cryoscopic experiments in which 0.01 mol

- (a) of bromoform ($K_K = 14.4 \text{ K kg mol}^{-1}$),
- (b) of dioxane ($K_K = 4.63 \text{ K kg mol}^{-1}$),
- (c) of cyclohexane ($K_K = 20.0 \text{ K kg mol}^{-1}$),
- (d) of camphor ($K_K = 37.7 \text{ K kg mol}^{-1}$)

was dissolved always in 400 g of benzene ($K_f = 5.12 \text{ K kg mol}^{-1}$). In which of these experiments the greatest melting point depression was achieved?

[ΔT_f is the same in all experiments]

Problem 13-05 Freezing point depression – non-electrolyte solutions

During the celebration you have hidden a bottle of wine on the balcony. In the morning you have found that it is cracked. What was the lowest temperature in the night? Wine contains about 10 wt. % of ethanol. Cryoscopic constant of water is $K_K = 1.86 \text{ K kg mol}^{-1}$.

[-4.5°C]

Problem 13-06 Freezing point depression – non-electrolyte solutions

Cryoscopic constant of water is $K_K = 1.86 \text{ K kg mol}^{-1}$. What minimum mole amount of methanol you must add to 2.6 kg of water to prevent its freezing at temperatures $t > -10^\circ\text{C}$?

[$n_2 = 14 \text{ mol}$]

Problem 13-07 Freezing point depression – non-electrolyte solutions

At which temperature will freeze 0.3 dm^3 of water ($M = 18.016 \text{ g mol}^{-1}$, density 0.9992 g cm^{-3}), to which 33 g of sucrose ($M(\text{C}_{12}\text{H}_{22}\text{O}_{11}) = 342.3 \text{ g mol}^{-1}$) was added? Enthalpy of fusion of has the value of 6009 J mol^{-1} .

[$t_{\text{fusion}} = -0.6^\circ\text{C}$, ($K_f = 1.86$, $m_2 = 0.3216 \text{ mol kg}^{-1}$)]

Problem 13-08 Freezing point depression – non-electrolyte solutions

Estimate the freezing point depression of the solution of 20.3 g of 1,3,5-trichlorobenzene in 861 g of p-dioxane against the freezing point of pure p-dioxane. Choose the appropriate data:

| | $M / (\text{g mol}^{-1})$ | $t_f / ^\circ\text{C}$ | $\Delta_{\text{fusion}}H_m$ (kJ mol^{-1}) | $t_b / ^\circ\text{C}$ | $\Delta_{\text{vap}}H_m$ (kJ mol^{-1}) |
|------------------------|---------------------------|------------------------|---|------------------------|--|
| p-dioxane | 88.1 | 11.8 | 12.46 | 101.1 | 34.2 |
| 1,3,5-trichlorobenzene | 181.4 | 63.45 | 6.5 | 208 | 42.9 |

[$\Delta T_f = -0.62 \text{ K}$ ($K_f = 4.773 \text{ K kg mol}^{-1}$)]

Problem 13-09 Freezing point depression of electrolytes and non-electrolytes solutions

Aqueous solution of 10.6 g of NaCl (on dissolving dissociates completely, $M_{\text{NaCl}} = 58 \text{ g mol}^{-1}$) in 849.8 g of water freezes at the temperature of -0.8°C . Calculate the minimum amount of ethylene glycol (not dissociating on dissolving, $M_{\text{EG}} = 62 \text{ g mol}^{-1}$) which you must dissolve in 15 kg of water to prevent the freezing at -10°C .

[$m_2 = 5 \text{ kg}$]

Problem 13-10 Freezing point depression of electrolyte solutions

What is the temperature of freezing of the solution obtained by dissolving of 7.40 g of magnesium chloride in 116.6 cm³ of water ($\rho = 0.986 \text{ g cm}^{-3}$)? Assume that magnesium chloride completely dissociates in aqueous solution. The density of water at the temperature in question is 0.986 g cm⁻³ and enthalpy of fusion at normal freezing point has the value of 6.009 kJ mol⁻¹. ($M_{\text{MgCl}_2} = 95.21 \text{ g mol}^{-1}$, $M_{\text{H}_2\text{O}} = 18.016 \text{ g mol}^{-1}$)

$$[t_f = -3.77^\circ\text{C}]$$

Problem 13-11 Freezing point depression of electrolyte solution, dissociation degree

Aqueous solution of ammonium chloride of molality 0.01 mol kg⁻¹ freezes at -0.0358°C. Find the value of the dissociation degree of NH₄Cl in this solution. Cryoscopic constant of water is 1.86 K kg mol⁻¹.

$$[\alpha = 0.925]$$

Problem 13-12 Freezing point depression of electrolyte solution, dissociation degree

0.44 g of the compound AB₂ ($M = 76 \text{ g mol}^{-1}$) was dissolved in 200 g of water. AB₂ is a weak electrolyte, in the aqueous solution of the given concentration dissociated from 80 %. At which temperature the freezing of this solution begins? Cryoscopic constant of water is 1.86 K kg mol⁻¹.

$$[-0.14^\circ\text{C}]$$

Boiling point elevation

Problem 13-13 Boiling point elevation of nonelectrolyte solution, molar mass

An addition of 1.6 g of sulphur into 500 g of carbon disulphide (ebullioscopic constant $K_E = 2.50 \text{ K kg mol}^{-1}$) resulted in elevation of boiling point of carbon disulphide by $\Delta T_b = 0.031 \text{ K}$. What is the molar mass of the dissolved sulphur?

$$[M_2 = 258.06 \text{ g mol}^{-1}]$$

Problem 13-14 Boiling point elevation and vapour pressure reduction above solution

The boiling temperature of a solution containing 4.4 g of organic substance and 1 kg of ethanol ($M_{\text{ethanol}} = 46 \text{ g mol}^{-1}$) is by 0.135°C higher than the normal boiling point of ethanol (78.3°C). The vaporization enthalpy of ethanol at normal boiling point is 38.5 kJ mol⁻¹. The organic substance in ethanol solution does not dissociate.

- (a) Determine the molar mass of the substance under study.
(b) How much lower will be the vapour pressure above the solution than the vapour pressure above pure ethanol? Saturated vapour pressure of ethanol is expressed by Antoine equation:

| | | | |
|---|--------|------|-----|
| $\log(p^s / \text{kPa}) = A - \frac{B}{C + (t / ^\circ\text{C})}$ | A | B | C |
| | 7.2335 | 1591 | 226 |

$$[(a) M_2 = 40 \text{ g mol}^{-1}; (b) \Delta p_1 = 81.09 \text{ Pa}]$$

Problem 13-15 Boiling point elevation of electrolyte solutions

1.5 mol of NaCl, 1.3 mol of Na₂SO₄, 2.0 mol of MgCl₂, and 2.0 mol of KBr were dissolved, each in 10 litres of water. Array these solutions according to the decreasing boiling temperature.

$$[\text{MgCl}_2 - \text{KBr} - \text{Na}_2\text{SO}_4 - \text{NaCl}]$$

Problem 13-16 Boiling point elevation of electrolyte solutions

1.5 mol of NaCl, 1.3 mol of Na₂SO₄, 2.0 mol of MgCl₂, and 2.0 mol of KBr were dissolved, each in 10 litres of water. Array these solutions according to the decreasing boiling temperature.

[MgCl₂ - KBr - Na₂SO₄ - NaCl]

Problem 13-17 Boiling point elevation of electrolyte solutions, dissociation degree

The boiling temperature of the solution of a weak electrolyte A₃B (concentration 0.6 mol kg⁻¹) is by 0.45° higher than the normal boiling point of pure solvent. The ebullioscopic constant of the solvent is 0.535 K kg mol⁻¹. Calculate the degree of dissociation of A₃B in this solution.

[$\alpha = 0.134$]

Problem 13-18 Boiling point elevation and freezing point elevation of non-electrolyte solutions

The cooler of your car contains 4.45 dm³ of water ($M = 18 \text{ g mol}^{-1}$) and 1 kg of ethylene glycol (C₂H₆O₂, $M = 62 \text{ g mol}^{-1}$). At what temperature the contents of your cooler (a) starts to freeze, (b) starts to boil? For the density of water take the value of 0.9986 g cm⁻³. Cryoscopic constant is $K_K = 1.86 \text{ K kg mol}^{-1}$, ebullioscopic constant is $K_f = 0.513 \text{ K kg mol}^{-1}$.

[(a) $t_{\text{freezing}} = -6.75^\circ\text{C}$; (b) $t_{\text{boiling}} = 101.86^\circ\text{C}$]

Osmotic pressure

Problem 13-19 Osmotic pressure of non-electrolyte solutions

When studying various types of haemoglobin 21.5 mg of protein was dissolved at 5°C in 1.5 cm³ of water. The osmotic pressure of this solution was found to be 3.75 torr. Determine the mean molar mass of sample under study. Assume the ideal behaviour of the solution.

[$M = 66.3 \text{ kg mol}^{-1}$]

Problem 13-20 Osmotic pressure of protein solution

A solution prepared by dissolving of 0.75 g of ribonuclease in 0.15 dm³ of NaCl solution of concentration 0.22 mol dm⁻³ exhibited osmotic pressure of 967.2 Pa, when measured against NaCl solution of the same concentration. The membrane used to measure the osmotic pressure is permeable for low molecular ions, but it is impermeable for ribonuclease molecules. Determine the molar mass of ribonuclease.

[$M_R = 12.6 \text{ kg mol}^{-1}$]

Problem 13-21 Osmotic pressure of body fluids

What is the difference between the osmotic pressure of capillary blood and of lymph at the temperature of 310 K? Concentration of low-molecular substances in both fluids is approximately the same, but the concentrations of proteins are different. Whereas their concentration in lymph is insignificant, in blood plasma it amounts to about 7 g/100 cm³. Mean molar mass of protein is 66 kg mol⁻¹.

[$\Delta\pi = 2.73 \text{ kPa}$]

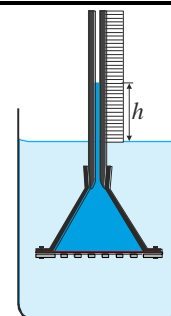
Problem 13-22 Osmotic pressure

The total concentration of dissolved particles inside the red blood cells is approximately 0.3 mol dm⁻³. Their walls are a semipermeable membrane. What would be the osmotic pressure inside the cells at the temperature of 298 K if we take them out of the blood plasma and put them in the pure water? What would happen to the cell?

[$\pi = 743.3 \text{ kPa}$, water will penetrate into the cells]

Problem 13-23 Osmotic pressure of non-electrolytes

When measuring the osmotic pressure of colloidal solution of concentration 2.2 g dm^{-3} at the temperature of 26.7°C the solution level established at a high $h = 1.3 \text{ cm}$ (see figure). The density of the solution is 984 kg m^{-3} .



- (a) Calculate the osmotic pressure.
(b) Assuming that osmotic pressure is adequately described by van'Hoff equation, calculate the molar mass of the solute.

$$[(a) \pi = 125.49 \text{ Pa}, (b) M = 43.70 \text{ kg mol}^{-1}]$$

Problem 13-24 Osmotic pressure of non-electrolyte solutions

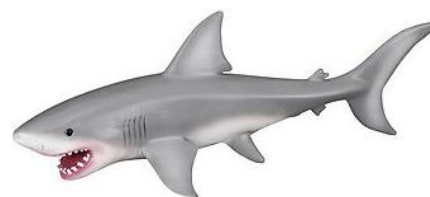
Molar mass of a polymer was determined by osmometry. At the temperature of 37.6°C the solution of the polymer in acetone climbed in the osmometric capillary up to 44 mm . The concentration of the solution was 0.616 kg m^{-3} and its density 854 kg m^{-3} . You can assume that for this case the van't Hoff equation can be used. Calculate

- (a) molar mass of the studied substance,
(b) osmotic pressure exhibited by the acetone solution of this polymer of concentration 1.79 kg m^{-3} at 42.4°C .
(c) Will be the length of 10 cm of the osmometric capillary enough for the determination of osmotic pressure of the solution of density 895 kg m^{-3} ?

$$[(a) M = 4317.4 \text{ g mol}^{-1}; (b) \pi = 1087.7 \text{ Pa}; (c) h = 12.4 \text{ cm} > \ell_{\text{capillary}}, \text{ capillary is too short}]$$

Problem 13-26 Osmoregulation

The sharks balances the osmotic pressure of the ambient sea water by retention of urea in their bodies. What should be the concentration of urea (grams per 1 dm^3) in body liquids of a shark to survive at 25°C in the sea water the osmotic pressure of approximately $2.8 \cdot 10^6 \text{ Pa}$? Assume that van't Hoff equation can be applied to the shark. Molar mass $M = 60 \text{ g mol}^{-1}$.



$$[67.77 \text{ g dm}^{-3}]$$

Problem 13-27 Osmotic pressure of non-ideal solutions

Concentration dependence of osmotic pressure of a non-uniform high-molecular substance, derived from experimental data, has the form

$$\pi = 10.92 \cdot c_w + 0.94 \cdot c_w^2$$

where π is the osmotic pressure (Pa), c_w mass concentration of the solution (kg m^{-3}).

- (a) Calculate the molar mass of the studied polymer.
(b) How high will climb the solution level in the osmometric tube if the solution concentration is 0.04 mol m^{-3} ?

$$[(a) M = 240.7 \text{ kg mol}^{-1}, (b) h = 2 \text{ cm}]$$

Problem 13-28 Osmotic pressure of electrolyte solutions

Calculate the osmotic pressure of aqueous solution of a weak electrolyte AB_2 of concentration of $0.00053 \text{ mol dm}^{-3}$ at the temperature of 16.2°C . This electrolyte is at given conditions dissociated from 80% . The solution density is 1.024 g cm^{-3} . At what high establishes the solution level in the osmometric capillary?

$$[\pi = 3.315 \text{ kPa}]$$

Problem 13-29 Osmotic pressure of electrolyte solutions

What is the value of osmotic pressure of 598.4 cm^3 of aqueous solution containing $0.88 \text{ g Ca(NO}_3)_2$? Calcium nitrate ($M = 164 \text{ g mol}^{-1}$) is a strong electrolyte, in aqueous solution completely dissociated. Assume that van't Hoff equation can be applied.

$$[\pi = 71.167 \text{ kPa}]$$