Appendix A

Answers to Questions and Exercises

Chapter 1

1. A membrane is a solid or liquid barrier which separates phases, and which can be a liquid or gas mixture and controls the transport of mass, electrical charges, and energy between the separated phases.
2. Synthetic membranes are capable of passive transport only which requires an externally applied driving force, such as a concentration or pressure difference between the two phases separated by the membrane. Biological membranes are capable of the so-called active transport in which the energy needed to for the transport is generated by the membrane itself and no external driving force is required.
3. Synthetic membranes are generally prepared from solid materials such as polymers, ceramics, and metals or liquids which are not miscible, with two phases separated by the membrane.
4. The four most relevant applications of membranes are:

   a) The separation of liquid and gas molecular mixtures as in reverse osmosis or ultrafiltration and dialysis.
   b) The controlled release of certain components from a reservoir as in certain long term medical therapy.
   c) Membranes are key components in electrochemical synthesis and membrane reactors.
   d) Membranes are also key components in energy storage and conversion systems such as batteries and fuel cells.

5. The advantage of membrane processes is that membrane operations can be carried out at ambient temperature and the transported components are not exposed to heat or an aggressive chemical environment as in distillation or certain precipitation processes which is of importance for the treatment of sensitive biological components.
   The main disadvantages are the thermal and sometimes chemical instability of the membranes.

Chapter 2

1. The transport of certain components across a membrane is determined by the membrane permeability for the components, the membrane thickness, and the driving force acting on the components, that is,

   $$J_i = \frac{P_i}{\Delta z}$$

   where is J_i the flux of the component i, P_i its permeability, and Δz the thickness of the membrane.
2. The materials used for the preparation of membranes used in mass separation processes can be solid or liquid, their chemical nature can be hydrophilic or hydrophobic and they can also carry fixed positive or negative electrical charges. Their structure can be a homogeneous dense layer, or a porous symmetric structure, or an asymmetric structure with a dense or porous selective layer on one surface.
3. The geometrical configurations most often applied to commercially available membranes are:

   a) Flat sheet
   b) Hollow fibers
   c) Tubes and capillaries.
4. The most important properties of synthetic membranes are:

   a) High transport selectivity for certain components;
   b) High transport rates;
   c) Good stability in the process environment;
   d) Low production costs.
5. The membrane rejection is expressed by: $R_A = \left(1 - \frac{C_A^p}{C_A^f}\right)$, the membrane permselectivity for a mixture of two components is given by: $S_{A/B} = \frac{P_A}{P_B}$ and the separation factor is given by: $\alpha_{A/B} = \frac{x_A^p x_B^f}{x_A^f x_B^p}$
   where R is the rejection, S the permselectivity, α the separation factor, and C the concentration; the subscripts A and B refer to components and the superscripts f and p refer to feed and permeate.
6. Diffusive mass flux across a membrane is the result of a difference in the Gibbs free energy or, if a single component is considered, of the chemical potential of the component in the two phases in contact with the membrane surfaces as driving force. Convective mass flux, that is, viscous flow is the result of a pressure difference between the two phases separated by the membrane as driving force. The term *migration* refers to a transport of positive or negative charged ions and is the result of an electrical potential difference between two sides of the membrane as driving force.
7. Facilitated transport is based on a chemical interaction of the transported component with a specific fixed or mobile carrier in the membrane matrix. Counter-current coupled transport is based on a coupling of fluxes in opposite

directions. For example, a flux of cations across a cation-exchange can cause a flux of other cations in the opposite direction.

8. $\mathrm{d}G = V\mathrm{d}p - S\mathrm{d}T + \sum \left(\frac{\partial G}{\partial n_i}\right)_{p,T,n_j} \mathrm{d}n_i$
   where G is the Gibbs free energy, V is the volume, S is the entropy, T is the temperature, p is the pressure, and n is the number of the component i in the system under consideration; the subscript n_j refers to components in the system which are kept constant.
9. The partial Gibbs free energy is referred to as the *chemical potential*, that is: $\left(\frac{\partial G}{\partial n_i}\right)_{p,t,n_j} = \mu_i$.
10. $d\mu = \mathrm{R}T\ln\frac{30}{2} = 7050\ (\mathrm{kJ\ mol^{-1}})$.
11. In reversible processes the entropy production is zero and in irreversible processes the entropy production is always positive, that is: for reversible processes $\mathrm{d}S = \frac{\mathrm{d}q}{\mathrm{T}} = 0$, for irreversible processes $\mathrm{d}S = \frac{\mathrm{d}q}{\mathrm{T}} \geq 0$.
    where S is the entropy, T the temperature, and q the heat of the system under consideration.
    This dissipation function refers to the entropy production in an irreversible process and is given by: $\Psi = T\frac{\mathrm{d}s}{\mathrm{d}t}$
    where Ψ is the dissipation function and t the time.
12. The change of the chemical potential in a mixture is a function of the pressure, the entropy, and the composition of the mixture, that is, $\mathrm{d}\mu_i = V_i\mathrm{d}p + T\mathrm{d}S + \mathrm{R}T\mathrm{d}\ln a_i$.
    The change of the electrical potential of a charged component in a mixture is also a function of pressure, entropy and composition and an electrical potential. It is given by:
    $\mathrm{d}\tilde{\mu}_i = V_i\mathrm{d}p + T\mathrm{d}S + \mathrm{R}T\mathrm{d}\ln a_i + z_i F\mathrm{d}\varphi$, where μ_i and $\tilde{\mu}_i$ are the chemical and the electrochemical potential of a component i, a_i is its activity, φ is the electrical potential, and R is the gas constant.
13. Osmotic equilibrium between two solutions separated by a membrane and composed of a solvent, which can permeate the membrane and solutes which cannot permeate, is achieved when the chemical potential of the solvent is identical on both sides of the membrane. At constant temperature the osmotic equilibrium is given by:

    $\mu_l^{s1} = \mu_l^{s2}$ and $\mu_l^o + V_l p^{s1} + \mathrm{R}T\ln a_l^{s1} = \mu_l^o + V_l p^{s2} + \mathrm{R}T\ln a_l^{s2}$

    The osmotic pressure of a solution is defined in reference to the pure solvent and given at constant temperature by:
    $\pi = -\frac{\mathrm{R}T}{V_l}\ln a_l^s$. In very dilute solutions the osmotic pressure can also be expressed by the concentration of the solutes. For salt solutions the osmotic pressure is given to first approximation by:

    $\pi = \mathrm{R}T\sum g_i\left(\nu_{ic} + \nu_{ia}\right)C_i$.

    where π is the osmotic pressure, R is the gas constant, T is the temperature, g is the osmotic coefficient, ν is the stoichiometric coefficient, C is the concentration, and the subscripts i, c, and a refer to salt, cation, and anion.

14. To calculate the osmotic pressure the weight concentrations must be converted in molar concentrations as follows:

Salt ions	**Concentration (mg l^{-1})**	**MW (g mol^{-1})**	**C_s (mol m^{-3})**
Na	12 300	22.9	537.1
Mg	1500	24.31	61.7
Ca	900	40.0	22.5
K	450	39.1	11.5
HCO_3	150	61.0	2.4
Cl	21500	35.5	605.6
SO_4	2500	96.1	26.0
			$\sum$ 1266.8

$\pi = \text{gRTC}_s = 0.9 \times 8.314 \times 298.15 \times 1266.8 = 2826151(\text{Pa}) \cong 28.3$ bar.

15. The Donnan potential of the membrane and the solution is given by:

$$\varphi_{Don} = \varphi_m - \varphi_s = \frac{1}{z_c \text{F}}\left(\text{R}T\ln\frac{a_c^s}{a_c^m} + V_c\Delta\pi\right)$$

The activity of the Na^+ ions in the membrane is calculated by:
Charge density of wet membrane is: $\frac{2}{1.25} = 1.6$ meq g^{-1}
or $1.6 \times 1.15 = 1.84$ meq cm^{-3} or 1840 mol m^{-3}
The activity of the Na^+ ions in the solution is: 100 mol m^{-3}.
The osmotic pressure, that is, the swelling pressure of the membrane is: 4.31 Pa or 43.1 bar.
$\varphi_{Don} \cong 17.8$ mV

16. The Donnan equilibrium under the assumption that the activity coefficients of the Na^+ ions in the membrane and the solution are under the given boundary conditions:

$$\text{R}T\ln\frac{a_c^s}{a_c^m} + V_c\Delta\pi = -\text{R}T\ln\frac{a_a^s}{a_a^m} + V_a\Delta\pi.$$

With the given boundary conditions:

$\frac{C^m_{Cl-}}{C^s_{Cl-}}\frac{C^m_{Na+}}{C^s_{Na+}} = \exp - \frac{\Delta\pi\, V_S}{\text{R}T} \cong 1$ and
$C^m_{Na+} = C^m_{fix} + C^m_{Cl-} \cong C^m_{fix}$

where C is the concentration, V is the molar volume, p is the osmotic pressure difference between the solution and the membrane, V is the molar volume and the superscripts m and s refer to membrane and solution, and the subscripts c, a, and fix refer to cation, anion, and fixed ions of the membrane.
$C^m_{Cl-} \cong \frac{{C^s_{Cl-}}^2}{C^m_{fix}} \cong 5.4$ mol m^{-3}

17. The molar flux across a membrane is expressed by:

$$J_i \text{ (mol m}^{-2}\text{ s}^{-1})$$
$$J_m = J_i \times \text{MW (kg m}^{-2}\text{ S}^{-1})$$
$$J_v = J_i \times \text{MW} \times \rho^{-1} \text{ (m s}^{-1})$$
$$i = J_i \times z_i \times \text{F (A m}^{-2})$$

where J is the flux, M is the molecular weight, ρ is the mass density, F is the Faraday constant, i is the current density, and z is the charge number, the subscripts m and i refer to mass and a component.

18. The Fickian diffusion coefficient relates the diffusive flux of a component to a concentration gradient as driving force and the thermodynamic diffusion coefficient relates the diffusive flux of a component to an activity gradient as driving force, that is, $D_i = \text{Đ}_i\left(1 + \frac{\mathrm{d}\ln\gamma_i}{\mathrm{d}\ln C_i}\right)$.

where D is the Fickian diffusion coefficient, Đ is the thermodynamic diffusion coefficient, and γ is the activity coefficient.

19. Because of the electroneutrality, the equation is:

$$J_{\mathrm{Na}^+} = J_{\mathrm{Cl}^-} = J_{\mathrm{NaCl}}$$

Furthermore:

$$J_{Na^+} = -D_{Na^+}\frac{\mathrm{d}c_{Na^+}}{\mathrm{d}z} = J_{Cl^-} = -D_{Cl^-}\frac{\mathrm{d}c_{Cl^-}}{\mathrm{d}z} = J_{NaCl} = -D_{NaCl}\frac{\mathrm{d}c_{NaCl}}{\mathrm{d}z}$$

and $C_{\mathrm{Na}^+} = C_{\mathrm{Cl}^-} = C_{\mathrm{NaCl}}$ and thus $D_{NaCl} = \overline{D}_{Na^+} = \overline{D}_{Cl^-}$

$$D_{NaCl} = 2\frac{D_{Na^+}D_{Cl^-}}{D_{Na^+} + D_{Cl^-}}$$

The diffusion coefficients are related to their mobility by: $D_i = \frac{u_i RT}{F}$

With $u_{\mathrm{Na}}^{+} = 5.19 \times 10^{-8}$ and $u_{\mathrm{Cl}}^{-} = 7.91 \times 10^{-8}$ this gives $D_{\mathrm{Na}}^{+} = 1.33 \times 10^{-9}$ and $D_{\mathrm{Cl}}^{-} = 2.03 \times 10^{-9}$

Thus: $D_{NaCl} = 1.61 \times 10^{-9} (\mathrm{m}^2\ \mathrm{s}^{-1})$

20. The transport number of ions in solution is given by: $t_i = \frac{|z_i|J_i}{\sum_i |z_i|J_i}$

$$t_{Na^+} = \frac{u_{Na^+}}{u_{Na^+} + u_{Cl^-}} = \frac{5.19}{5.19 + 7.91} = 0.396$$
$$t_{Cl^-} = 0.604$$

a) The mean free path length λ at 25 °C and 1 bar is given by: $\lambda = \frac{\mathrm{k}T}{\pi d_{gas}^2 p\sqrt{2}}$ The Boltzmann constant k is given in Table B1 of Appendix B as $1.38 \times 10^{-23} (\mathrm{J^\circ K^{-1}})$; diameters d of O_2 and N_2can be calculated from Table B12 in Appendix B as 0.346 (nm) and 0.364 (nm), and p is the pressure.

$$\lambda_{O_2} = \frac{1.38 \times 10^{-23} \times 298}{3.14 \times \left(0.346 \times 10^{-9}\right)^2 \times 10^5 \times \sqrt{2}} = 78 \text{ (nm)}$$

$$\lambda_{N_2} = \frac{1.38 \times 10^{-23} \times 298}{3.14 \times \left(0.364 \times 10^{-9}\right)^2 \times 10^5 \times \sqrt{2}} = 70 \text{ (nm)}$$

b) The oxygen flux through a porous membrane is given by:

$$J_i = \frac{n\pi r^2 D_i^k}{\mathrm{R}T\tau}\frac{\Delta p}{\Delta z}$$

Introducing the Knudsen diffusion coefficient $D_i^k = 0.66r\sqrt{\frac{8RT}{\pi M_i}}$ and the porosity of the membrane leads to:

$$J_i = \frac{4\varepsilon r}{3}\sqrt{\frac{2RT}{\pi M_i}}\frac{\Delta p}{\mathrm{R}T\tau\Delta z}$$

Using the pore radius of the membrane deducted from the free path length of N $_2$ as $r_i = 0.25 \times 70 = 17.5$ nm, the porosity ε of the membrane as 0.5, the applied pressure difference Δp as 5 bar, the membrane thickness as 0.5 mm, and the tortuosity factor τ as 1:

$$J_{O_2} = 2.59\ (\mathrm{mol\ m^{-2}\ s^{-1}})$$
$$J_{N_2} = 2.77\ (\mathrm{mol\ m^{-2}\ s^{-1}})$$

c) The separation factor is:

$$\alpha_{N_2/O_2} = \sqrt{\frac{M_{O_2}}{M_{N_2}}} = \sqrt{\frac{32}{28}} = 1.07$$

21. Fick's diffusion coefficient relates the flux of a component to a concentration difference as driving force. The thermodynamic diffusion coefficient, the phenomenological coefficient, and the mobility coefficient relate the flux of a component to the chemical potential difference:

$$D_i = \text{Đ}_i\left(1 + \frac{\partial\gamma_i}{\partial C_i}\right) = \frac{L_i\mathrm{R}T}{C_i}\left(1 + \frac{\partial\gamma_i}{\partial C_i}\right) = m_i\mathrm{R}T\left(1 + \frac{\partial\gamma_i}{\partial C_i}\right)$$

where D_i and $\overline{D}_i$ are the Fickian and the thermodynamic diffusion coefficients, L_i and m_i are the phenomenological and the mobility coefficient, and γ_i is the activity coefficient.

22. The rejection of a porous membrane can be described under the specified boundary condition by: $R = \left[1 - 2\left(1 - \frac{a}{r}\right)^2 + \left(1 - \frac{a}{r}\right)^4\right]$
(a) $R = 0.88$, (b), $R = 0.44$, and (c) $R = 0.19$.

Chapter 3

1. The structure of symmetric membranes is uniform over the entire cross-section and there are no differences in their transport properties between the two sides of the membrane. Their structure can be porous with pore sizes of 0.05–10 μm or it can be solid. The main application of porous symmetric membranes is in processes such as microfiltration. Symmetric membranes with a solid structure are used mainly in electrodialysis and controlled release devices.
Asymmetric membranes have different structures on the top and bottom surfaces. Their mass transport properties are determined by a relatively thin

barrier layer on a highly porous support structure which has very little effect on the permselectivity and the transport properties of the membrane.

If the barrier layer and the support structure are made from the same material and in one preparation process, the membrane obtained is referred to as *integral asymmetric*. If the barrier layer and the support structure are made from different materials in two or more consecutive preparation processes, the membrane obtained is referred to as *composite membrane*. Asymmetric membranes are mainly used in pressure driven processes.

2. a) Porous polymer membranes are made (i) by pressing and sintering a fine polymer powder, (ii) by extruding and stretching a partial crystalline polymer perpendicular to the direction of extrusion, (iii) by irradiation of a thin polymer film by collimated charged particles followed by etching the film along the tracks of the collimated particles, (iv) by a phase inversion process in which a homogeneous polymer solution is converted into a two phase system consisting of a solid polymer-rich phase forming the solid membrane structure and a liquid polymer-lean phase forming the membrane pores, and (v) by UV irradiation and template leaching.
   b) Ceramic membranes are made (i) by slip casting a fine ceramic powder such as Al_2O_3 with a polymer binder and sintering at high temperature of more than 1200 °C, (ii) by a conversion of a colloidal sole into a colloidal gel and sintering at circa 800 °C.
   c) Porous glass membranes are made by template leaching using a glass mixture composed of SiO_2, Na_2O, and B_2O_3 which form a homogeneous solution at 1400 °C but separate into two phases, one is rich in SiO_2 and insoluble in strong acids, and the other is rich in BeO_3 and soluble in strong acids and can be leached out.
3. A polymer suitable as basic material must be soluble under certain conditions of temperature and composition in an appropriate solvent and must separate into a polymer-rich solid phase and a polymer-lean liquid phase under other conditions of temperature and composition. Furthermore, the two phases must be continuous.
4. Chemical properties of polymers to be considered as basic material for the preparation of membranes are their stability in strong acids or bases and oxidizing environment, their hydrophilicity or hydrophobicity, and their sorption capacity for various chemical species. Mechanical properties of polymers to be considered as basic material for the preparation of membranes are their e-modulus and tensile strength, their degree of cross-linking and crystallinity, the glass transition temperature, and their free volume.
5. The number average of polymer chains is given by:

$$\overline{M}_n = \frac{\sum_i N_i M_i}{\sum_i N_i}$$

The weight average of polymer chains is given by:

$$\overline{M}_w = \frac{\sum_i N_i M_i^2}{\sum_i N_i M_i}$$

For a polymer composed of 1 g of molecular chains having a weight of 80 000 g mol^{-1} and 1 g of polymer chains having a weight of 20 000 g mol^{-1} the number average molecular weight is: 32 000 and the weight average is 50 000.

6. The Gibbs free energy of mixing of a two component system is completely miscible over the entire range of composition and is given by:

   a) $\Delta G_m = n_1 \Delta\mu_1 + n_2 \Delta\mu_2$,
   with $\mu_i = \mu_i^o + \mathrm{R}T \ln X_i$ is $\Delta G_m = (n_1 + n_2)\,\mathrm{R}T\left(X_1 \ln X_1 + X_2 \ln X_2\right)$
   Since $X \leq 1$ is $\ln X \leq 0$ and $\Delta G_m \leq 0$.

   b) The binodal represents the equilibrium between the two separated phases in which the Gibbs free energy of mixing has reached a minimum, that is, $\Delta G_m = \text{minimum}$ and $\left(\frac{\partial \Delta G_m}{\partial X_i}\right)_{p,T,j} = 0$ and $\left(\frac{\partial^2 \Delta G_m}{\partial X_i^2}\right)_{p,T,j} = 0$
   The spinodal represents the transition of the system from a stable or metastable state to the unstable state in which the Gibbs free energy becomes positive, that is, $\Delta G_m \geqslant 0$ and $\left(\frac{\partial \Delta G_m}{\partial X_i}\right)_{p,T,j} = \text{maximum}$ and $\left(\frac{\partial^2 \Delta G_m}{\partial X_i^2}\right)_{p,T,j} = 0$
   At the critical point binodal and spinodal curves become identical and the derivatives of the Gibbs free energy is $\left(\frac{\partial \Delta G_m}{\partial X_i}\right)_{p,T,j} = 0$, $\left(\frac{\partial^2 \Delta G_m}{\partial X_i^2}\right)_{p,T,j} = 0$, and $\left(\frac{\partial^3 \Delta G_m}{\partial X_i^3}\right)_{p,T,j} = 0$

7. a) The effective diffusion path length in the barrier layer is given by:

$$Z_{\mathit{eff}} = \varepsilon Z_o + (1-\varepsilon)\,\frac{1}{2}\left(\sqrt{r^2\left(\frac{1-\varepsilon}{\varepsilon}\right) + Z_o^{\,2}} + Z_o\right)$$

   The properties of the membrane are: the barrier layer thickness is $Z_o = 0.1\ \mu\mathrm{m}$, the pore radius is $r = 0.1$ and the porosity is $\varepsilon = 0.1$.
   The effective diffusion path length is $Z_{\mathit{eff}} = 0.018$.

   b) The water flux of the composite reverse osmosis membrane with an effective diffusion path length of $Z_{\mathit{eff}} = 0.018$ and an applied pressure of 10 bar can be calculated from:

$$J_w = \frac{D_w C_w V_w}{RT}\frac{\Delta p}{Z_{\mathit{eff}}},\, J_w V_w = J_v = \frac{D_w C_w V_w^2}{RT}\frac{\Delta p}{Z_{\mathit{eff}}}$$

The water flux is:

$$\begin{aligned} J_v &= \frac{3 \times 10^{-10} \times 0.1 \times 18 \times 10^{-6} \times 10^{6}}{8.314 \times 298 \times 0.018 \times 10^{-6}} = 0.121 \times 10^{-4}\ (\mathrm{m\ s^{-1}}) \\ &= 0.043 (\mathrm{m\ h^{-1}}) \end{aligned}$$

8. The two types of liquid membrane used in practical applications are so-called supported and emulsified liquid membranes. The key components of liquid membranes are a liquid and a carrier component which has selective transport properties for certain components in a feed solution. Neither the membrane liquid nor the carrier component should be soluble in the feed solution. In supported liquid membranes the membrane liquid and the carrier are confined in the pores of a microporous membrane. Unsupported liquid membranes consist of an emulsion of a feed solution and the liquid membrane with the feed solution droplets surrounded by the membrane liquid. When the emulsion is dispersed in a stripping solution the liquid membrane separates as a thin film from the feed solution and controls the transport selectively of components from the feed to the stripping solution.
   The advantage of supported membranes is their high selectivity and the continuous operation of the separation process, and that it can be applied to liquid as well as vapor mixtures. The disadvantage is the relatively low fluxes due to the relatively long diffusion path in the liquid membrane filled pores in the support membrane. The advantage of the emulsified liquid membranes is the relatively high fluxes due to the thin membrane film surrounding the feed or stripping solution. Disadvantages are that emulsified liquid membranes cannot be applied to gas or vapor, and that the process is continuous.
9. The water flux of the microfiltration membrane is given by:

$$\begin{aligned} J_v &= \frac{\varepsilon r^2}{8\eta\tau}\frac{\Delta p}{\Delta z} = \frac{0.3 \times \left(0.2 \times 10^{-6}\right)^2 \times 1 \times 10^{5}}{8 \times 1 \times 10^{-3} \times 0.5 \times 10^{3}} = 2 \times 10^{-4}\ (\mathrm{m\ s^{-1}}) \\ &= 0.720\ (\mathrm{m\ h^{-1}}) \end{aligned}$$

10. The water flux of the ultrafiltration membrane is given by:

$$\begin{aligned} J_v &= \frac{\varepsilon r^2}{8\eta\tau}\frac{\Delta p}{\Delta z} = \frac{0.1 \times \left(0.005 \times 10^{-6}\right)^2 \times 2 \times 10^{5}}{8 \times 1 \times 10^{-3} \times 2 \times 10^{-6}} \\ &= 3.13 \times 10^{-5} (\mathrm{m\ s^{-1}}) = 0.113 (\mathrm{m\ h^{-1}}) \end{aligned}$$

11. a) The most important properties of ion-exchange membranes used in dialysis, electrodialysis, and fuel cells are:
   High permselectivity for the transport of ions of opposite charges.
   Low electrical resistance for the transport of ions.
   Low transport rates of components carrying no electrical charges.
   Low degree of swelling in solutions with electrolyte concentration.
   High mechanical and chemical stability at operating temperature and environment.

   b) High permselectivity and low electrical resistance in ion-exchange membranes can be achieved by introducing high concentrations of fixed strong acid or strong basic groups such as sulfonic acid or quaternized amine into a polymer matrix. Low swelling of the membranes and low transport of components carrying no electrical charges can be achieved by cross-linking of the polymer matrix. Good chemical and mechanical stability of ion-exchange membranes can be achieved by selecting highly cross-linked or crystalline polymers such as fluorinated carbon polymers as matrix for the ion-exchange membranes.

12. Optical microscopy has the advantage that the structural properties of membranes can be viewed at ambient temperature and pressure without any sample preparation. The disadvantage of the optical microscopy is the relatively low maximum resolution which is circa 1 μm.
    Electron microscopy has the advantage of significantly higher maximum resolution of circa 0.001 μm and providing rather clear images of all ultra- and microfiltration membranes. However, electron microscopy needs generally extensive sample preparation and can only be carried out in a high vacuum. The sample preparation and the applied vacuum can change the structure of the membrane significantly, especially when the membrane material is rather hydrophilic and contains significant amounts of absorbed water or when small pores of the membrane, that at ambient pressure are filled with water, collapse under vacuum.
    Atomic force microscopy has the advantage that an image of membrane surfaces can be obtained at ambient temperature and pressure without any sample preparation at a maximum resolution of circa 0.001 μm. However, when the surface of the membrane is quite soft the cantilever tip can damage the membrane surface, and it is often difficult to distinguish pores from surface roughness.
13. The retention of a membrane with circular pores as a function of the pore radius and the component radius can be described by the Ferry–Renkin model as:

    $$R = \left[1 - 2\left(1 - \frac{a}{r}\right)^2 + \left(1 - \frac{a}{r}\right)^4\right]$$

    The radius of the membrane pores r is 0.005 μm, the radius of spherical particles can be related to their volume by:

    $$V = \frac{4}{3}\pi r^3$$

    The volume of a component can be related to its weight by:

    $$V = \frac{W}{1.2}$$

    The weight of a component can be related to the molecular weight by:

    $$W = \frac{M}{6.022 \times 10^{23}}$$

    The radius of a component with a molecular weight of 1000 Da is:

    $$a = \sqrt[3]{\frac{3}{4\pi}\frac{1}{1.2\times 6.022\times 10^{23}}} = 0.69\times 10^{-9}\ (\mathrm{m})$$

The rejection of an ultrafiltration membrane with a pore radius of 0.01 µm for a component with a molecular weight of 1000 Da is:

$$R = \left[1 - 2\left(1 - \frac{0.69 \times 10^{-9}}{10 \times 10^{-9}}\right)^2 + \left(1 - \frac{0.69 \times 10^{-9}}{10 \times 10^{-9}}\right)^4\right] = 0.02$$

The radius of a component with a molecular weight of 100 000 Da is:

$$\mathrm{a} = 3.2 \times 10^{-9}(\mathrm{m})$$

The rejection of an ultrafiltration membrane with a pore radius of 0.01 µm for a component with a molecular weight of 100 000 Da is:

$$R = 0.76$$

The radius of a component with a molecular weight of 100 000 Da is:

$$a = 6.9 \times 10^{-9}(\mathrm{m})$$

The rejection of an ultrafiltration membrane with a pore radius of 0.01 µm for a component with a molecular weight of 1 million Da is:

$$R = 0.82$$

14. In the so-called "bubble point" pore size determination the membrane pores are filled with water which is displaced by air which will penetrate the pores under a certain applied pressure. The pressure required to replace the water in a pore by air is a function of the pore size, the applied pressure, and the interfacial tension between air and water. This relationship is described by the Laplace equation which is given by:

$$r_p = \frac{2\sigma \cos\phi}{p}$$

The surface tension between air and water is $\sigma = 72.3 \times 10^{-3}(\mathrm{N\,m^{-1}})$, the contact angle between the liquid and membrane pore wall for a hydrophilic membrane can be assumed to be $\phi = 0$ and $\cos\phi = 1$. The minimum pore size that can be determined is inversely proportional to the applied pressure. If liquid–liquid displacement is applied for the pore size determination using two liquids such as isobutanol and water, which have an interfacial tension of $1.85 \times 10^{-3}(\mathrm{N\,m^{-1}})$, the minimum pore size that can be determined is circa 1/40 that of the air–water replacement test assuming the same applied pressure in both tests.

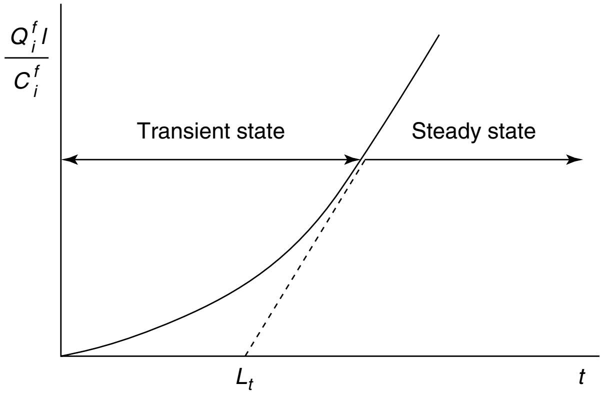
15. The minimum pore radius that can be detected in a membrane by the bubble point test with an applied pressure of 2 bar is 0.72×10^{-6} (m).
The minimum pore radius that can be detected in a membrane by replacing water by isobutanol is 1.85×10^{-8} (m).
The bubble point test is suited for determining pore sizes in microfiltration membranes that are in the range of 0.5–10 µm. The characterization ultrafiltration membranes, which have pores of circa10–100 nm in diameter using the bubble point test, would require applied test pressures up to 100 bar

which would certainly result in a compaction of the ultrafiltration membrane structure.

16. The surface porosity of a membrane with 10^{13} pores per m^2 with a pore radius of 0.05 μm is $\varepsilon = 0.079$.
17. The difference between a pore size of a membrane with a contact angle of 0 and 20° is 1–0.94, that is, ≈6%.
18. Pore size determination by air–water replacement is based on the Laplace equation which provides a relationship between the pore size, the interfacial tension between air and water, and the pore radius.

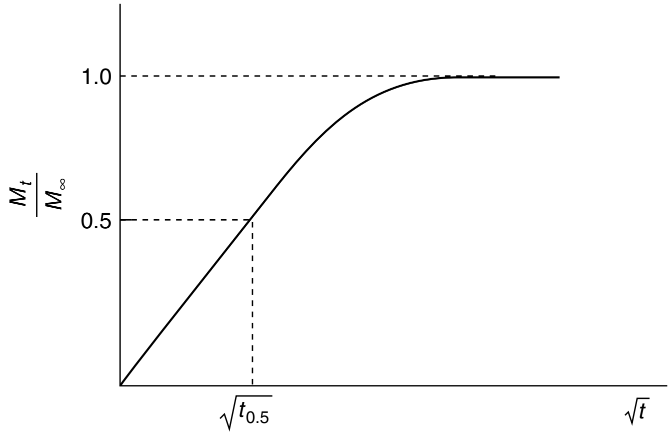
    Pore size determination by permporometry is based on the capillary condensation of a vapor in a pore, and is described by the Kelvin equation which provides a relationship between the vapor pressure of a condensable vapor in a capillary, the surface tension of the condensed vapor and the radius of the pore.

    Pore size determination by thermoporometry is based on the fusion point depression of a component in a pore, and is also described by the Kelvin equation which provides a relationship between the radius of a pore and fusion temperature change in a porous system.
19. a) The time-lag is based on measuring the total number of moles of a component transported through a membrane from a reservoir with given concentration into an empty reservoir as a function of the time. When the accumulated molar flux divided by the feed concentration is plotted versus the time the obtained curve reaches after a certain transition period a constant slope as illustrated in the following diagram:



    The extrapolation of the steady state part curve to zero-flux gives the time-lag which can be related to the diffusion coefficient of the permeating component to its diffusion coefficient in the membrane.

    In the sorption based determination of the diffusion coefficient in a polymer membrane is based on determining the mass gain of a membrane sample which is exposed to an environment of constant vapor pressure as a function of time. The ratio of the mass gained at a certain time is plotted to the mass gain at saturation is plotted versus the square root of time as illustrated in the following diagram:



The diffusion coefficient is obtained from the slope of the curve when the weight gain is 50% of the weight gained at saturation.

b) The diffusion coefficient of a component in a 300 μm thick membrane, for which the time-lag was determined experimentally to $L_t = 1.5 \times 10^5$ (s), can be calculated to a first approximation by:

$$D = \frac{l^2}{6L_t} = \frac{\left(3 \times 10^{-4}\right)^2}{6 \times 1.5 \times 10^5} = 1 \times 10^{-13}\ (\mathrm{m^2 s^{-1}})$$

c) The diffusion coefficient in a membrane which has a thickness of $l = 1 \times 10^{-5}$ (m) is obtained from the square root of the time $t_{0.5}$ required for a mass gain ratio of $M_t/M_\infty = 0.5$ according to the following relationship:

$$D = 0.049\frac{l^2}{t_{0.5}} = \frac{0.049 \times 10^{-10}}{1 \times 10^2} = 4.9 \times 10^{-14}\ (\mathrm{m^2\ s^{-1}})$$

20. The permselectivity of an ion-exchange membrane is given by:

$$\psi^m = \frac{\frac{\varphi_m}{\varphi_{sm}} + 1 - 2T^s_{cou}}{2T^s_{co}} \quad \text{for KCl is } T^s_{co} \approx T^s_{cou}$$

Thus is: $\psi^m \approx \frac{\varphi_m}{\varphi_{sm}}$, with $\varphi_m = 0.054$ and $\varphi_{sm} = 0.0592$ is: $\psi^m \approx 0.91$.

Chapter 4

1. a) The membranes used in micro- and ultrafiltration have defined permanent pores. The structure of microfiltration membranes is symmetric, that is, the pore size distribution is the same on both surfaces of the membrane and in the inner core of the membranes. Ultrafiltration membranes have an asymmetric structure with a thin barrier layer with very small permanent pores on one surface of the membrane and much larger pores and higher porosity in the core of the membrane.

Reverse osmosis membranes also have an asymmetric structure with a dense barrier layer on one surface of the membrane and a porous structure in the core of the membrane.

The membranes used in gas separation have a similar structure to those used in reverse osmosis or ultrafiltration with a dense or porous barrier layer on one surface and a porous substructure.

Dialysis membranes generally have symmetric porous structures with the same pore size distribution on both sides and in the core of the membrane.

Membranes used in electrodialysis have symmetric structure with positive or negative ions fixed on a highly swollen polymer matrix.

Membranes used in facilitated transport have generally component specific carrier components in a symmetric porous membrane. The carrier components can be fixed to the membrane matrix material or are immobilized in the liquid filled membrane pores.

b) The driving force for mass transport in micro- and ultrafiltration and in reverse osmosis and gas separation is a pressure gradient in the membrane perpendicular to the membrane surface.

The driving force for mass transport in dialysis and facilitated transport is an activity gradient of the components in the membrane perpendicular to the membrane surface.

In electrodialysis the driving force for the transport of ions across the membrane is an electrical potential gradient across the membrane.

c) In micro- and ultrafiltration the transport of mass is based on viscous flow through the membrane pores.

In reverse osmosis, gas separation, and dialysis the transport of molecular components is based on diffusion.

In electrodialysis the transport of ions is based on migration and coupled to an electric current.

2. The rejection of an ultrafiltration membrane is given by:

$$R = 1 - \frac{k^f \exp \frac{J_\nu \tau \Delta z}{{}^{m}D_i}}{k^p - 1 + \exp \frac{J_\nu \tau \Delta z}{{}^{m}D_i}}$$

a) For $J_\nu = 2 \times 10^{-6} (\mathrm{m\,s^{-1}})$ this becomes:

$$R = 1 - \frac{0.1 \exp \frac{2 \times 10^{-6} \times 2 \times 10^{-6}}{5 \times 10^{-10}}}{0.1 - 1 + \exp \frac{2 \times 10^{-6} \times 2 \times 10^{-6}}{5 \times 10^{-10}}} \approx 0.008$$

b) For $J_\nu = 5 \times 10^{-4}$ $(\mathrm{m\,s^{-1}})$ is: $R \approx 0.78$

3. a) The membranes used in nanofiltration are asymmetric in their structure with a thin skin on one surface of a highly porous substructure. The skin acts as the mass transport-controlling barrier layer of the membrane while the porous substructure has no effect on the mass transport properties of the membrane. Nanofiltration membranes have permanent pores and can

have positively or negatively charged ions fixed to the surface of the pores in the barrier layer.

Reverse osmosis membranes also have an asymmetric structure with a thin skin at the surface as mass transport controlling barrier layer. However, in reverse osmosis membranes the thin skin consists of a dense polymer layer which generally does not carry any electrical charges.

b) Mass transport in nanofiltration is based on both viscous flow through pores due to a pressure difference across the membrane and on diffusion of individual components in the pores due to an activity difference across the membrane. The transport rate of individual components depends on their exclusion from the membrane, which is a function of size of the component in relation to the size of the membrane pores and, when the membrane has fixed ions, also on the electrical charges of the components. In reverse osmosis membranes the mass transport is based only on diffusion due to a difference of the chemical potential of the components on the membrane down- and up-stream side. The transport rate of different components across the membrane is proportional to their diffusion coefficient and their concentration, which is determined by their solubility in the barrier layer polymer.

4. The retention of a nanofiltration membrane is given by:

$$R = 1 - \frac{C_i^p}{C_i^f} = 1 - \frac{J_i}{J_v C_i^f}$$

$$R \approx 0.99$$

5. a) Calculation of the volume flux J_v

$$\begin{aligned}
J_v &\approx J_w V_w = -\frac{D_w^m k_w C_w^s V_w}{RT} \frac{d\left(V_w P + RT \ln a_w\right)}{dz} \\
&\approx -\frac{D_w^m C_w^m V_w^2}{RT} \left(\frac{\Delta p - \Delta\pi}{\Delta z}\right) \\
\Delta\pi &\approx gRT2C_{NaCl}^s = 2 \times 0.92\ \mathrm{RT} \times 0.59 \times 10^3 \approx 2.7 \times 10^6\ (\mathrm{Pa}) \\
J_v &\approx \frac{6 \times 10^{-10} \times 0.1 \times 18 \times 10^{-6}}{2477} \left(\frac{3.3 \times 10^6}{0.2 \times 10^{-6}}\right) \\
&\approx 0.072 \times 10^{-4}\ (\mathrm{m\ s^{-1}}) \times 0.026\ (\mathrm{m\ h^{-1}})
\end{aligned}$$

b) Determination of J_s

$$R = 1 - \frac{J_s}{J_v C_s^f}$$

$$J_s = (1 - R) J_v C_s^F \approx 2.1 \times 10^{-4}\ (\mathrm{mol\ m^{-2}\ s^{-1}})$$

6. The rejection of a nanofiltration membrane is given by:

$$R = 1 - \frac{-{}^m D_i k_{size} k_{Don} \left(\frac{V_i {}^s\overline{C}_i}{\mathrm{R}T} \frac{\Delta p}{\Delta z} + \frac{\Delta {}^s\overline{C}_i}{\Delta z} + \frac{z_i \mathrm{F} {}^s\overline{C}_i}{\mathrm{R}T} \frac{\Delta \varphi_{Don}}{\Delta z}\right) - J_v k_{size} k_{Don} {}^s C_i^f}{J_v {}^s C_i^f}$$

The Donnan potential is given by:

$$\varphi_{Don} = \sum_i \frac{1}{z_i \mathrm{F}} \left[\mathrm{R}T \ln \frac{{}^{s}C_i}{{}^{m}C_i} \right]$$

and the Donnan exclusion is given by:

$${}^{m}C_{co} = \frac{{}^{s}C_s^2}{C_{fix}}$$

a) To calculate the succrose rejection, the Donnan potential and the Donnan must not be considered.
Thus: $R \approx 0.7$.

b) To calculate the $NaSO_4$ rejection, the Donnan potential and the Donnan exclusion must be considered.
The Donnan potential is: 0.037 (V)
The partition coefficient referring to the Donnan exclusion is: $k_{Don} = 0.05$
The ${SO_4}^2$ rejection and thus, the salt rejection is: $R \approx 0.98$

7. The free mean path length N_2 is:

$$\begin{aligned} \lambda &= \frac{\mathrm{k}T}{\pi \mathrm{d}_\mathrm{g}^2 p \sqrt{2}} \\ &= 629 \times 10^{-10} \text{ (m)} \end{aligned}$$

8. a) The gas flux of nitrogen J_g is:

$$\begin{aligned} J_\mathrm{g} &= \frac{\pi n r^2 D_\mathrm{g}^k \Delta p}{\mathrm{R}T\tau\Delta z} \quad \text{with } D_\mathrm{g}^k = 0.66r\sqrt{\frac{8RT}{\pi M_g}} \\ J_\mathrm{g} &= 5.0 \times 10^3 \text{ (mol m}^{-2}\text{ s}^{-1}) \end{aligned}$$

b) The separation factor is: $a_{\mathrm{N}_2/\mathrm{O}_2} = \sqrt{\frac{W_{\mathrm{O}_2}}{W_{\mathrm{N}_2}}} = 1.07.$

The gas flux through the membrane is: $J_i \propto \Delta_p$.

The separation factor is: $\alpha_{j,k} \propto \frac{p^f}{p^p}$.

When high gas fluxes are required a high pressure difference between the feed and the permeate is necessary. This high pressure difference can be achieved by increasing the pressure on the feed side and keeping the pressure at the permeate side at 1 bar as suggested in operation mode (i). However, the separation factor that can be achieved under these operating conditions is limited because the maximum applied pressure is limited for technical reasons to ca.100 bar.

When high separation factors are required a high ratio between the feed and the permeate is necessary. Very high pressure ratios between the feed and the permeate can easily be achieved by applying a vacuum on the permeate side and keeping the pressure on the feed side at 1 bar as described in operating mode (ii). However, under these operating conditions the maximum pressure difference between feed and permeate is 1 bar and the gas flux across the membrane is very low.

The selectivity in gas separation for two components j and k is defined as the ratios of their permeabilities: $S_{j,k} = \frac{P_j}{P_k}$

The separation factor is: $\alpha_{j,k} = S_{j,k} \frac{\left(\frac{X_j^p p^p}{p^f} - X_j^f\right)}{\left(\frac{X_k^p p^p}{p^f} - X_k^f\right)} \frac{X_k^f}{X_j^f}$. When the feed pressure is much higher than the permeate pressure the separation factor becomes identical to the selectivity, that is, $\lim\limits_{\frac{p^p}{p^f} \to 0} \alpha_{j,k} = S_{j,k}$

The enrichment factor is: $\beta_j = \frac{X_j^p}{X_j^f} = \frac{\alpha_{j,k}}{1 + \left(\alpha_{j,k} - 1\right) X_j^f}$

9. For a given selectivity the pressure ratio determines the separation factor.
10. The separation factor in pervaporation is determined by the membrane, the pressure ratio, and the thermodynamic liquid/vapor equilibrium which is given by the term $\frac{\gamma_j^l p_j^o}{\gamma_k^l p_k^l}$
11. The charge transported by 1 mol of $CaCl_2$ in electrodialysis at a given potential difference is: $2 \times F \approx 1.93 \times 10^5$ (As).
12. The transport number of an ion i describes the ratio of the electrical charges transported by this ion to the total charges transported in an electrolyte solution due to an electrical potential driving force.
13. The current use in electrodialysis is determined by the permselectivity of the ion-exchange membrane, the water transported by osmosis and electro-osmosis and by the current leakage through the manifold. However, osmotic water transport is relatively small, and the current leakage through the manifold can be avoided by a proper stack construction. Thus, the total current use is approximately given by the membrane properties and the water transport numbers of ions.
14. The transport of a component across a membrane is determined by the diffusion coefficient of the components in the membrane and their activity gradient in the membrane. Thus, the transport of a component that carries no electrical charges across a membrane that has no fixed electrical charges is given by: $J_i = -D_i^m \frac{\gamma_i^m \Delta C_i^m}{\Delta z}$

    If ions are transported across a membrane that has no fixed electrical charges the transport of anions and cations is coupled by the electroneutrality requirement and are transported with the same rate even if their individual diffusion coefficients are quite different. Their fluxes are given by:

    $$J_s + J_c + J_a = -2\left(\frac{D_a^m D_c^m \left(|z_a| + z_c\right)}{D_a^m |z_a| + D_c^m z_c}\right) \frac{\gamma_s \Delta C_s}{\Delta z} = -D_s^m \frac{\gamma_s \Delta C_s}{\Delta z}$$

    The transport of ions across a membrane that has electrical charges fixed to the membrane matrix is only possible for ions which have the opposite electrical charge, as the fixed charges of the membrane can permeate the membrane. Because of the electrodialysis requirement, a cation can only permeate a cation-exchange membrane due to an activity gradient across the membrane when the same number of charges are transported in the opposite direction. For two monovalent salt solutions separated by a cation-exchange membrane the flux of a cation from the solution with high salt concentration into the solution with lower salt concentration is given by:

$$J_{c1} = -J_{c2} = -2\left(\frac{D_{c1}^{m} D_{c2}^{m}}{D_{c1}^{m} + D_{c2}^{m}}\right)\frac{\gamma_{c1}\Delta C_{c1}}{\Delta z}$$

15. The thermodynamic efficiency of a fuel cell using H_2/O_2 as fuel is given by:

$$\eta_{th} = \frac{\Delta G_{re}}{\Delta H_{re}} = \frac{U_{re}}{U_{th}} = \frac{-237}{-285} \approx 0.83$$

The reversible cell voltage is given by: $U_{re} = \frac{\Delta G_{re}}{zF} = \frac{237}{2 \times 96500} \approx 1.23$
The cell voltage is $U_{ce} = U_{re} - IR_i$ and depends on the internal resistance of the cell.

Chapter 5

1. Advantages and disadvantages of membrane modules are:

a) The tubular membrane module can be operated at relatively high applied pressures. It provides good control of concentration polarization and is specially suited for the filtration of viscous feed solutions containing large amounts of large particles which have diameters in excess of 0.5 mm.
Its main disadvantage is the low packing density and relatively high production costs and relatively high pumping energy costs.

b) The capillary membrane module operated with the feed solution in the lumen of the capillary has a relatively high packing density and its production costs are low. Concentration polarization and membrane fouling can easily be controlled by the flow velocity of the feed in the lumen, and components accumulated and precipitated at the membrane surface can be removed by back flushing.
The main disadvantage of the capillary module is the low maximum feed pressure which is limited by the burst strength of the fibers.

c) The hollow fiber membrane module is generally operated with the feed solution on the outside of the fiber. The module provides the highest packing density and the lowest production costs of all membrane modules. It can be operated at very high applied pressures.
The main disadvantage is the poor control of concentration polarization and membrane fouling effect. Its application is limited to the separation of solutions free of dispersed particle and gas mixtures.

d) The spiral-wound membrane module provides a relatively high packing density and low production costs. It can be operated at high applied feed solution pressures of more than 10^7 Pa.

    The main disadvantage of the spiral-wound module is that feed solutions with high concentrations of dispersed particles can lead to excessive membrane fouling.
   - e) The plate-and-frame membrane module has some advantages and disadvantages in comparison to the spiral-wound module, e.g. the module can easily be disassembled and the membrane can be exchanged or cleaned mechanically. It can be equipped with different types of membranes for different applications. The main disadvantages of the plate-and-frame membrane module in comparison to the spiral-wound module are its high production costs.
2. The advantage of the rotating membrane plate module is that shear forces acting on components in a feed solution are minimized. When positive displacement pumps or hydrostatic pressure is used to provide the flow of the feed solution through the module, the only shear force acting on the feed solution constituents is due to the friction of the solutes with the membrane surface. This friction is determined by the rotation velocity of the membrane plates and can be adjusted to a value needed to control concentration polarization and membrane fouling.
3. a) The approximations that are made when the film model is applied to describe concentration polarization effects in membrane processes are:
   The velocity and the concentration profiles on the surface of the membrane are fully developed and constant over the entire surface of the membrane.
   The diffusive transport parallel to the membrane surface can be neglected.
   The solution viscosity and the diffusion coefficient are constant over the thickness of the boundary layer.
   - b) The general relationship describing concentration polarization effects in membrane filtration in devices with turbulent bulk solution flow is a function of the membrane flux, the thickness of the laminar boundary layer, the diffusion coefficient of the solutes in the laminar boundary layer, the rejection of the membrane, and the solute concentration in the bulk solution, and is given by:

$$\frac{C_s^w}{C_s^b} = \frac{\exp\frac{J_v Z_b}{D_s}}{R + (1-R)\exp\frac{J_v Z_b}{D_s}}$$

4. The concentration polarization obtained in desalination of an aqueous NaCl solution in a stirred batch cell can be calculated by:

$$\frac{C_s^w}{C_s^b} = \frac{\exp\frac{J_v Z_b}{D_s}}{R + (1-R)\exp\frac{J_v Z_b}{D_s}}$$

   Introducing the mass transfer coefficient and the Sherwood number as a function of the Reynolds and Schmidt numbers leads to:

$$k_s = \frac{D_s}{Z_b} \text{ and } N_{Sh} = k_s\frac{d_h}{D_s} = aN_{\mathrm{Re}}{}^{b}N_{Sc}{}^{c}\left(\frac{d_H}{L}\right)^{d}$$

Expressing the Sherwood, the Reynolds, and Schmidt numbers for the mass transfer in a well stirred batch cell leads to:

$$N_{Sh} = k_s \frac{D_c}{D_s}, \; N_{\mathrm{Re}} = \frac{\omega d^2}{\nu}, \; N_{Sc} = \frac{\nu}{D_s} \text{ and } k_s = \frac{D_s}{D_c} a \left(\frac{\nu}{D_s}\right)^c \left(\frac{\omega d^2}{\nu}\right)^b$$

Introducing the mass transfer coefficient with the constants $a = 0.1$, $b = 0.66$, and $c = 0.33$ into the general equation for the concentration polarization leads to:

$$\frac{C_s^w}{C_s^b} = \frac{\exp \frac{J_\upsilon D_C}{0.02 D_S \left(\frac{\nu}{D_S}\right)^{0.33} \left(\frac{\omega d^2}{\nu}\right)^{0.66}}}{R + (1 - R) \exp \frac{J_\upsilon D_C}{0.02 D_S \left(\frac{\nu}{D_S}\right)^{0.33} \left(\frac{\omega d^2}{\nu}\right)^{0.66}}}$$

Introducing the feed viscosity $\nu = 1 \times 10^{-3}$ (kg m^{-1} s^{-1}), the NaCl diffusion coefficient $D_s = 1.6 \times 10^{-9}$(m s^{-1}), the membrane salt rejection $R = 0.99$, the membrane flux $J_\nu = 1 \times 10^{-5}$ (m s^{-1}), the batch cell diameter $D_c = 0.1$ (m), the stirrer length $d = 0.09$ (m), and the stirrer circular velocity $\omega = 1800$ (rpm) gives the concentration polarization in the stirred batch cell.

$$\frac{C_s^w}{C_s^b} \approx 1.3$$

5. The concentration polarization obtained in desalination of an aqueous NaCl solution in a tubular membrane module can be calculated by the same general relationship as the one used in a stirred cell. However, now the proper relationship for the feed flow in a tube must be introduced for the Sherwood, the Reynolds, and the Schmidt numbers.
   These relationships are:

   $$K_s = \tfrac{D_S}{Z_b}, N_{sh} = K_s \tfrac{2r_t}{D_S} = a {N_{Re}}^b {N_{Sc}}^c \text{ and } N_{Re} = \tfrac{2r_t u}{\nu}, K_s = \tfrac{D_S}{2rt} a \left(\tfrac{2r_t u}{\nu}\right)^b \left(\tfrac{\nu}{D_S}\right)^c$$

   The constants are $a = 0.023$, $b = 0.8$, and $c = 0.33$. The solution and membrane properties are the viscosity $\nu = 1 \times 10^{-3}$ (kg m^{-1} s^{-1}), the NaCl diffusion coefficient $D_s = 1.6 \times 10^{-9}$ (m s^{-1}), the membrane salt rejection $R = 0.99$and the membrane flux $J_\nu = 2 \times 10^{-5}$ (m s^{-1}). The feed flow velocity in the tube is 2 (m s^{-1}) and the radius of the tube 0.005 (m). Introducing these data in the general equation describing the concentration polarization in turbulent feed flow by the film model leads to:

   $$\frac{C^w}{C^b} \approx 1.4$$

6. The entrance region in which the velocity and concentration profiles in a tubular membrane module are not fully developed is very short in turbulent flow compared with the total length of the module. In laminar flow in a tubular or capillary membrane module the entrance region in which the velocity and concentration profiles are not yet fully developed are quite long and must be taken into account for the calculation of the concentration polarization.

7. The thickness of the laminar boundary layer Z_b in a tubular membrane module, for which a concentration polarization of 1.4, a solute diffusion coefficient of 1.6×10^{-9} $(\mathrm{m\,s^{-1}})$, a membrane rejection of 0.99, and a membrane flux of 1×10^{-5} $(\mathrm{m\,s^{-1}})$ has been determined, is given by:

$$Z_b = \frac{D_s}{J_v} \ln\left(\frac{1.4R}{1 - 1.4\,(1 - R)}\right) = 5.0 \times 10^{-5}\ (\mathrm{m})$$

8. When in ultrafiltration of a macromolecular solution the concentration at the membrane surface exceeds the solubility of the solute in the solution a gel or cake layer is formed at the membrane surface and the membrane flux will no longer increase with the applied pressure due to the resistance of the gel layer.
9. The effect of the bulk solution on the gel layer limited flux in ultrafiltration of three different macromolecular feed solutions with concentrations of (a) 1.0, (b) 0.1, and (c) 0.01, $(\mathrm{kg\,m^{-3}})$ can be expressed by:

$$J_v = k_s^* \ln C_s^b$$

Thus, the fluxes for the feed solution bulk concentrations are:

a) $J_v = \mathrm{k}^*1$,
b) $J_v = \mathrm{k}^*2$,
c) $J_v = \mathrm{k}^*3$.

10. The consequences of concentration polarization in electrodialysis are twofold:

a) in the feed solution concentration polarization leads to a depletion of salt ions on the surface, and
b) in the permeate side ions are accumulated at the membrane surface.

The accumulation of ions on the permeate side has in most practical applications only little relevance. The depletion of ions on the feed membrane surface has serious consequences for the electrodialysis process. When, due to the concentration polarization, the ion concentration at the membrane feed side surface approaches zero the electrical resistance increases drastically and the current, which passes through an electrodialysis stack and determines the flux of ions, cannot further be increased by increasing the applied voltage. The current density in electrodialysis is a function of concentration polarization and, thus, a function of the laminar boundary layer. It can be described by:

$$i = -\frac{\mathrm{F} D_s}{\left(T_i^m - T_i\right)} \left(\frac{C_s^{bf} - C_s^{mf}}{\Delta z}\right)$$

The limiting current density is reached when $C_s^{mf} \rightarrow 0$.

Therefore:

$$i_{\lim} = -\frac{\mathrm{F} D_s}{\left(T_i^m - T_i\right)}\left(\frac{C_s^{bf}}{\Delta z}\right)$$

The boundary layer thickness in electrodialysis can be determined experimentally by measuring the limiting current density at various feed flow velocities.

The mass transfer coefficient is a function of the flow velocity of the feed parallel to the membrane surface and can be related to the flow velocity u by an exponential function.

$$k_s = \frac{D_s}{\Delta z} = u^b$$

The limiting current density can then be expressed as a function of the feed flow velocity parallel to the membrane surface by:

$$i_{\lim} = \frac{\mathrm{F} k_s}{\left(T_i^m - T_i^s\right)} C_s^{bf} = a C_s^{bf} u^b$$

The constants a and b can be determined from the slope of the curves obtained by a plot of log $\frac{i_{\lim}}{C_s^{bf}}$ versus the flow velocity u, and by a plot of $\frac{i_{\lim}}{C_s^{bf}}$ versus u^b.

Chapter 6

1. The true rejection of a membrane refers to the solute concentration at the feed side surface of the membrane. It includes concentration polarization effects. The observed rejection of a membrane refers to the solute concentration in the feed bulk solution. It does not consider concentration polarization effects.
2. The local permeate concentration refers to the concentration in the permeate at a certain point of the membrane and at a certain time in reference to the retentate concentration at the same point. It is defined as $C_i^p = (R-1)\,C_i^r$.
   The mixing cup permeate concentration is the concentration of permeate collected over a certain time period from a given feed solution. It is expressed as a function of the recovery rate by: $\overline{C}_i^p = \frac{C_i^f}{\Delta}\left[1-(1-\Delta)^{1-R}\right]$.
   In membrane filtration processes is $\overline{C}_i^p \leqslant C_i^p$
3. The average retentate concentration for systems operated at recovery rates of $\Delta < 0.8$ and with membranes having high salt rejection the average retentate rejection can be expressed by: $\overline{C}_i^r \cong \frac{C_i^f + C_i^r}{2} = 0.5\left(C_i^f + C_i^f\,(1-\Delta)^{-R}\right)$
4. The amount of rinse solution needed to reduce the concentration of a salt in a mixture with macromolecular components in a diafiltration process with a membrane which has a salt rejection of $R = 0.2$ from 2 to 0.1 wt% can be calculated by:

$$C_i^r = C_i^f \exp - (1-R)\,\frac{V^w}{V^f} \text{ and } V^w = \frac{1}{1-R}\ln\frac{C_i^r}{C_i^f} = 3.74$$

5. The fractional product loss in ultrafiltration is given by:

$$\delta = 1 - (1 - \Delta)^{1-R}$$

The recovery rate in a batch cell is related to the feed and retentate concentration by: $C_i^r = C_i^f\,(1 - \Delta)^{-R}$.

Thus: $\Delta = 1 - \left(\frac{C_i^r}{C_i^f}\right)^{-\frac{1}{R}} = 1 - \left(\frac{5}{0.1}\right)^{-\frac{1}{0.85}} = 0.99$

and $\delta = 1 - (1 - 0.99)^{0.15} = 0.499$

6. The protein loss during ultrafiltration is given by:

$$\delta = 1 - (1 - 0.944)^{0.2} = 0.438$$

The salt concentration is reduced during the ultrafiltration from 1 wt% to:

$$\delta = 1 - (1 - 0.944)^{0.9} = 0.925$$

The salt concentration after the ultrafiltration process is: $C_s = 1.08$

The additional product loss can be calculated by the following relationship: $C_i^r = C_i^f \exp - (1 - R)\,\frac{V^w}{V^f}$ which gives the required rinse solution V_w to reduce the salt concentration to 0.01.

Thus: $V^w = 5.2$

The additional protein loss in the diafiltration is:

$$\delta = \frac{V^p \overline{C}_i^p}{V^f\,C_i^f} = 1 - \exp - (1 - R)\,\frac{V^w}{V^f} = 0.64$$

7. The membrane flux in a reverse osmosis test with the given process parameters is given by:

$$J_v = h_p^m \left(p^f - p^p - \left(p^f - p^r\right) - k_{os} k_{con}^r \overline{C}_s^{br} + k_{os} k_{con}^p \overline{C}_s^{bp}\right)$$

The osmosis related coefficient k_{os} is: $2 \times gRT = 4954\ (\mathrm{kg\,m^2\,mol^{-1}})$

The molar salt concentration C_s^f in the feed solution which contains $30\ (\mathrm{kg\,m^{-3}})$ is:

$C_s^f = \frac{30}{58.4} \times 10^3 = 0.514 \times 10^3\ (\mathrm{mol\,m^{-3}})$(mol.wt. NaCl $= 58.4\ (\mathrm{g\,mol^{-1}})$)

The average permeate concentration is: $\overline{C}_i^p = \frac{C_i^f}{\Delta}\left[1 - (1 - \Delta)^{1-R}\right]$

The average retentate concentration is: $\overline{C}_i^r \cong 0.5 C_i^f \left(1 + \frac{R}{1-\Delta}\right)$

Thus is: $J_v = 0.84 \times 10^{-5}\ (\mathrm{m\,s^{-1}}) \approx 0.725\ (\mathrm{m\,d^{-1}})$

8. The concentration polarization in reverse osmosis is:

$$\frac{C_s^w}{C_s^b} = \frac{\exp \frac{J_v Z_b}{D_s}}{R + (1 - R) \exp \frac{J_v Z_b}{D_s}}$$

For a reverse osmosis membrane with a salt rejection in excess of $R > 0.99$ is:

$$\frac{C_s^w}{C_s^b} \approx k_p \exp J_v = \frac{C_s^w}{C_s^b} \approx k_p^* \exp \frac{Q_p}{Q_f} = k_p^* \exp \frac{2\Delta}{2 - \Delta}$$

(Using the arithmetic average values of the flux.)

9. The total energy requirement for the desalination plant is:

$$\begin{aligned}\frac{E_{tot}}{V_p} &\cong \left(\frac{1}{k_{PE}} p^f V_f - (1-\Delta)\, V_f k_{ret} p^r\right) = 110 \times 10^5\ (\mathrm{Ws\ m^{-3}})\\ &= 2.7\ (\mathrm{kWh\ m^{-3}})\end{aligned}$$

The energy required for the actual desalination process is:

$$E_s \cong V_p \left[\frac{p^f + p^r}{2} - k_{os} k_{con} \left(\frac{C_s^f}{\Delta\,(1-R)} - \frac{C_s^f}{\Delta}\right) \left(1 - (1-\Delta)^{1-R}\right)\right]$$

$E_s = 28.02 \times 10^5 (\mathrm{Ws\ m^{-3}})$, fraction of desalination energy to total applied energy $\frac{E_s}{E_{tot}} \approx 0.25$

10. With the plant operation parameters listed in the question:

a) The required membrane area is:

$$\begin{aligned}A &= \frac{\left(C^f - C^p\right) \mathrm{F}}{i_{eff}}\\ &= 930\ \left(\mathrm{m}^2\right)\end{aligned}$$

b) The process path length is given by:

$$\begin{aligned}L_{pp} &= \frac{A_{tot} Q_{cell}}{Q_{tot}}\\ &= 1.25\ [\mathrm{m}]\end{aligned}$$

c) The energy required for the desalination process is:

$$\begin{aligned}E_{des} &= \frac{iAU_{cell}}{Q_{tot}}\\ &= 1.12\ \mathrm{kWh}\end{aligned}$$