Chapter 21
Mixing and Separation

21.1 Osmosis and Osmotic Pressure

The word "osmosis" comes from the greek word for pushing and refers to the passing of a substance through a semi-permeable membrane. Applications are, e.g., cell membranes in the human body, or membranes for desalination. For the discussion of osmotic phenomena we shall assume ideal mixtures only.

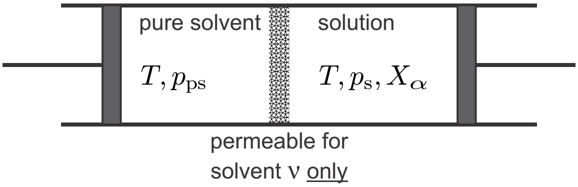

Fig. 21.1 Pressure difference at a membrane

The osmotic pressure is the pressure on the membrane due to those components of the mixture that cannot pass. Specifically, we consider a membrane which separates the pure solvent ν at pressure p_{ps} from an ideal mixture at pressure p_{s}, see Fig. 21.1. The osmotic pressure is defined as the pressure difference over the membrane in equilibrium,

$$p_{\mathrm{osm}} = p_{\mathrm{s}} - p_{\mathrm{ps}} \ . \tag{21.1}$$

The equilibrium condition for the membrane is

$$\bar{\mu}_\nu \left(T, p_{\mathrm{ps}}\right) = \bar{\mu}_\nu \left(T, p_{\mathrm{s}}, X_\alpha\right) \ . \tag{21.2}$$

For the pure solvent, the chemical potential is just the specific Gibbs free energy, and we find by Taylor expansion

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$$\bar{\mu}_\nu\left(T,p_{\mathrm{ps}}\right)=\bar{g}_\nu\left(T,p_{\mathrm{ps}}\right)=\bar{g}_\nu\left(T,p_{\mathrm{s}}\right)+\left(\frac{\partial\bar{g}_v}{\partial p}\right)_{T,p=p_{\mathrm{s}}}\left(p_{\mathrm{ps}}-p_{\mathrm{s}}\right)$$
$$+\frac{1}{2}\left(\frac{\partial^2\bar{g}_v}{\partial p^2}\right)_{T,p=p_{\mathrm{s}}}\left(p_{\mathrm{ps}}-p_{\mathrm{s}}\right)^2+\ldots \quad (21.3)$$

From now on, we assume that both, solution and solvent, are incompressible liquids. In the equation above, $\left(\frac{\partial\bar{g}_v}{\partial p}\right)_T=\bar{v}_\nu$ is the molar volume of the solvent alone which is assumed to be constant (incompressible!), so that $\left(\frac{\partial^n\bar{g}_v}{\partial p^n}\right)_T=\left(\frac{\partial^{n-1}\bar{v}_v}{\partial p^{n-1}}\right)_T=0\;\;(n\geq 2)$, and

$$\bar{\mu}_\nu\left(T,p_{\mathrm{ps}}\right)=\bar{g}_\nu\left(T,p_{\mathrm{s}}\right)-\bar{v}_\nu p_{\mathrm{osm}}\ . \quad (21.4)$$

The chemical potential of the solvent in the ideal mixture is

$$\bar{\mu}_\nu\left(T,p_{\mathrm{s}},X_\alpha\right)=\bar{g}_\nu\left(T,p_{\mathrm{s}}\right)+\bar{R}T\ln X_\nu\ , \quad (21.5)$$

and the equilibrium condition (21.2) reduces to

$$p_{\mathrm{osm}}=-\frac{\bar{R}T}{\bar{v}_\nu}\ln X_\nu\ . \quad (21.6)$$

One kilogram of seawater contains 35 g sodium chloride (NaCl, with $M_{\mathrm{NaCl}}=58.5\frac{\mathrm{g}}{\mathrm{mol}}$) and 965 g of freshwater. It has a mass density of about $1029\frac{\mathrm{kg}}{\mathrm{m}^3}$, i.e., one litre of seawater contains 36 g of NaCl and 993 g of freshwater. Since NaCl dissociates into Na^+ and Cl^- ions, the osmotic pressure of seawater at 277 K (4 °C) is

$$p_{\mathrm{osm}}^{sw}=-\frac{\bar{R}T}{M_w v_w}\ln\frac{n_w}{n_w+n_{\mathrm{Na}^+}+n_{\mathrm{Cl}^-}}$$
$$=-\frac{\bar{R}T}{M_w v_w}\ln\frac{1}{1+2\frac{M_w m_{\mathrm{NaCl}}}{m_w M_{\mathrm{NaCl}}}}=28.2\,\mathrm{bar}. \quad (21.7)$$

Recall that solutions of salt in water are not ideal mixtures, unless they are diluted, see Sec. 18.14.

21.2 Osmotic Pressure for Dilute Solutions

The osmotic pressure assumes a rather interesting form in the limit of dilute solutions, where most of the solution is solvent ν, that is $n_\nu \gg n_\alpha$ holds. Then we can expand

$$-\ln X_\nu = -\ln \frac{n_\nu}{n} = -\ln \frac{n_\nu}{n_\nu + \sum_{\alpha=1}^{\nu-1} n_\alpha} = \ln \left(1 + \sum_{\alpha=1}^{\nu-1} \frac{n_\alpha}{n_\nu} \right) \simeq \sum_{\alpha=1}^{\nu-1} \frac{n_\alpha}{n_\nu} \tag{21.8}$$

so that, when we also use that $n_\nu \bar{v}_\nu = V$ is the volume of the mixture, the osmotic pressure is

$$p_{\text{osm}} = \sum_{\alpha=1}^{\nu-1} \frac{n_\alpha \bar{R} T}{V} \; . \tag{21.9}$$

The dissolved substances in a dilute solution exert an ideal gas pressure on the membrane; the osmotic pressure is the sum of these ideal gas pressures.

21.3 Example: Pfeffer Tube

An instructive example for the strength of the osmotic forces is the Pfeffer tube (Wilhelm Pfeffer, 1845-1920), depicted in Fig. 21.2. The solvent is water. A tube is closed by a membrane that only lets the solvent ν pass, and is set vertically into a bath of solvent. Some solvent will pass the membrane, so that the solvent inside and outside the tube are at the same level. Then salt is added to the tube. This leads to an additional amount of solvent drawn from the bath into the tube; in the final equilibrium, the osmotic pressure and the hydrostatic pressure are balanced.

Since this is a system in which temperature and (environmental) pressure are controlled, the total Gibbs free energy $G = H - TS + E_{pot}$ of the system will minimize. Drawing solvent into the tube increases the entropy of the

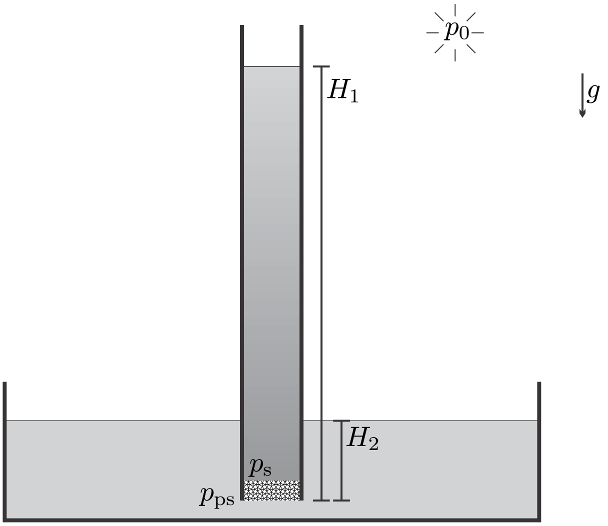

Fig. 21.2 Pfeffer tube

dissolved particles, which now have a greater volume to access, but also increases the potential energy. The final equilibrium state, a balance of height increasing entropic force and height reducing energetic force, will be calculated next under some simplifying assumptions. The goal is the computation of the height H_1 in the tube.

Directly at the membrane, the hydrostatic pressures of the solution in the tube and solvent in the bath are

$$p_{\mathrm{s}} = p_0 + \rho_{\mathrm{s}} g H_1 \quad , \quad p_{\mathrm{ps}} = p_0 + \rho_\nu g H_2 \ ,$$

and these are balanced by the osmotic pressure, so that

$$p_{\mathrm{osm}} = p_{\mathrm{s}} - p_{\mathrm{ps}} = \rho_{\mathrm{s}} g H_1 - \rho_\nu g H_2 \ .$$

With the simplified expression (21.9) we find at first.

$$\frac{\bar{R}T}{Vg} \sum_{\alpha=1}^{\nu-1} n_\alpha = \rho_{\mathrm{s}} H_1 - \rho_{\mathrm{ps}} H_2 \ .$$

$V = AH_1$ is the volume of solution in the tube of cross section A. The density of the solution is $\rho_{\mathrm{s}} = \rho_\nu + \sum_{\alpha=1}^{\nu-1} \rho_\alpha \simeq \rho_{\mathrm{ps}} + \sum_{\alpha=1}^{\nu-1} \frac{m_\alpha}{V}$, where we approximated the density of the solvent in solution, ρ_ν, by the density of the pure solvent, ρ_{ps}. After multiplication with H_1/ρ_{ps} we obtain a quadratic equation for H_1,

$$H_1^2 + H_1 \left(\frac{1}{\rho_{\mathrm{ps}} A} \sum_{\alpha=1}^{\nu-1} m_\alpha - H_2 \right) - \frac{\bar{R}T}{A \rho_{\mathrm{ps}} g} \sum_{\alpha=1}^{\nu-1} n_\alpha = 0 \ .$$

Only the positive solution for H_1 has physical meaning,

$$H_1 = \frac{1}{2} \left(H_2 - \frac{1}{\rho_{\mathrm{ps}} A} \sum_{\alpha=1}^{\nu-1} m_\alpha \right) + \sqrt{ \frac{1}{4} \left(H_2 - \frac{1}{\rho_{\mathrm{ps}} A} \sum_{\alpha=1}^{\nu-1} m_\alpha \right)^2 + \frac{\bar{R}T}{A \rho_{\mathrm{ps}} g} \sum_{\alpha=1}^{\nu-1} n_\alpha } \ .$$

As example we consider water ($\rho_{\mathrm{ps}} = 1000 \frac{\mathrm{kg}}{\mathrm{m}^3}$) in a tube of cross section $A = 1\,\mathrm{cm}^2$ in which $\sum_{\alpha=1}^{\nu-1} m_\alpha = m_{\mathrm{NaCl}} = 1\,\mathrm{g}$ of cooking salt (NaCl) is dissolved. The salt dissolves into Na^+ and Cl^- ions, and thus we have to be careful in the computation of the mole number of dissolved particles, which is (with $M_{\mathrm{NaCl}} = 58.5 \frac{\mathrm{g}}{\mathrm{mol}}$)

$$\sum_{\alpha=1}^{\nu-1} n_\alpha = n_{\mathrm{Na}^+} + n_{\mathrm{Cl}^-} = 2 \frac{m_{\mathrm{NaCl}}}{M_{\mathrm{NaCl}}} = 3.419\ 10^{-2}\,\mathrm{mol} \ .$$

When the tube is immersed into the pure solvent by $H_2 = 1\,\mathrm{cm}$, the solution in the tube will reach a height of $H_1 = 9.29\,\mathrm{m}$, which corresponds to about 1 litre of water in the tube! This shows the enormous forces that are present in osmosis, which are due to the desire of the salt to increase the entropy of mixing by making the accessible volume (i.e., the volume of the solution), as large as possible.

Due to the difference in density between salt solution and pure water, the height H_1 becomes smaller as the tube is pushed deeper into the solvent (i.e., for larger H_2), as the problems show, it might even happen that $H_2 > H_1$.

The strong desire of the salt to draw water can be used (and was widely used in the past) to cure meat: While water can pass cell membranes, salt cannot, and thus a piece of meat or fish immersed in salt will be depleted from some water. The same is true for bacteria on the meat which will die from dehydration, and thus cannot spoil the meat.

Since seawater contains more salt than the cells of the human body, drinking seawater is deadly: The seawater will draw water from the cells, which will be damaged by dehydration. In fact, after drinking seawater one will be more thirsty than before.

Another example for osmotic forces is putting sugar on strawberries, which will draw water (juice) out of the strawberries that mixes with the sugar. The opposite can be seen when raisins are put into water: the sugar inside the raisin draws water in, and the raisin swells.

21.4 Desalination in a Continuous Process

In the previous section we have seen that salt can draw water through a semipermeable membrane. In the inverse process, fresh water is obtained from saltwater, by pressing the saltwater against a semipermeable membrane, which only allows freshwater to pass, e.g., think of increasing the pressure on the saltwater column in the Pfeffer tube. We ask for the minimum work required for desalination, that is for the work required in a reversible process.

Figure 21.3 shows the general set-up for a continuous desalination plant, without specifying how desalination is taking place inside the plant, which is drawn as a grey box. A mole flow $\dot{n}_{sw}$ of salt water with salt mole fraction X_{sw} enters the plant at environmental pressure and temperature (p_0, T_0). Work $\dot{W}$ is supplied to the plant, which also exchanges heat $\dot{Q}$ with the environment. Two streams leave the plant at (p_0, T_0), a stream of freshwater $\dot{n}_{fw}$, and the brine stream $\dot{n}_b$ which contains all salt and has a salt mole fraction $X_b > X_{sw}$.

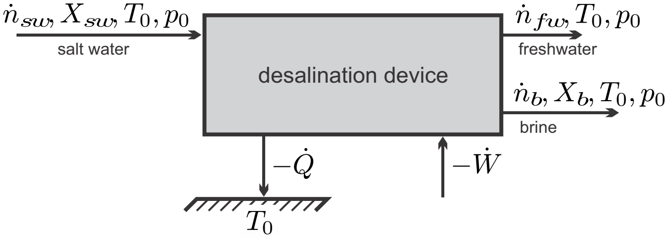

Fig. 21.3 Continuous desalination

This is a best case scenario, where the streams entering and leaving the plant are in thermal (T_0) and mechanical (p_0) equilibrium with the environment. The following calculation will assume reversible processes, and thus the actual work that a real plant requires will be larger. It is the task of the engineer to design a process that uses as little work as possible, and the calculation of the minimum work will serve as an important guideline on the quality of the actual process devised.

The overall mole balance and the mole balance for salt read

$$\dot{n}_{sw} = \dot{n}_{fw} + \dot{n}_b \quad , \quad \dot{n}_{sw} X_{sw} = \dot{n}_b X_b \; . \tag{21.10}$$

With the freshwater/seawater ratio $y = \dot{n}_{fw}/\dot{n}_{sw}$ we have

$$X_b = \frac{X_{sw}}{1-y} \; ; \tag{21.11}$$

note that y reaches its maximum $y_{\max} = 1 - X_{sw}$ for full desalination, where the brine would be pure salt ($X_b = 1$).

First and second law for the plant, which exchanges heat only at T_0, read

$$\sum_{out} \dot{n}_\alpha \bar{h}_\alpha - \sum_{in} \dot{n}_\alpha \bar{h}_\alpha = \dot{Q} - \dot{W} \quad , \quad \sum_{out} \dot{n}_\alpha \bar{s}_\alpha - \sum_{in} \dot{n}_\alpha \bar{s}_\alpha = \frac{\dot{Q}}{T_0} + \dot{S}_{gen} \; , \tag{21.12}$$

all properties are taken at environmental conditions (p_0, T_0). Elimination of $\dot{Q}$ gives

$$\dot{W} = -T_0 \dot{S}_{gen} - \Delta \dot{G}^0 \; , \tag{21.13}$$

where

$$\begin{aligned} \Delta \dot{G}^0 &= \sum_{out} \dot{n}_\alpha \left(\bar{h}_\alpha - T_0 \bar{s}_\alpha \right) - \sum_{in} \dot{n}_\alpha \left(\bar{h}_\alpha - T_0 \bar{s}_\alpha \right) \\ &= \sum_{out} \dot{n}_\alpha \bar{\mu}_\alpha \left(T_0, p_0, X_\beta \right) - \sum_{in} \dot{n}_\alpha \bar{\mu}_\alpha \left(T_0, p_0, X_\beta \right) \; . \end{aligned} \tag{21.14}$$

Since all flows are at (p_0, T_0), $\Delta \dot{G}^0$ is the difference in Gibbs free energy at environmental conditions flowing through per unit time.

According to (21.4), for reversible operation, $\dot{S}_{gen} = 0$, the work required for desalination is given by $-\Delta \dot{G}^0$. To simplify the problem we assume ideal mixtures, where $\bar{\mu}_\alpha (T_0, p_0, X_\beta) = \bar{g}_\alpha (T_0, p_0) + \bar{R} T_0 \ln X_\alpha$, and find the minimum work as

$$\dot{W}_{rev} = -\Delta \dot{G}^0 = T_0 \Delta \dot{S}_0 = \bar{R} T_0 \left[\sum_{in} \dot{n}_\alpha \ln X_\alpha - \sum_{out} \dot{n}_\alpha \ln X_\alpha \right] . \tag{21.15}$$

Inserting the proper flows and mole numbers yields at first

$$\begin{aligned} \dot{W}_{rev} = \bar{R} T_0 \big[& \dot{n}_{sw} X_{sw} \ln X_{sw} + \dot{n}_{sw} (1 - X_{sw}) \ln (1 - X_{sw}) \\ & - (\dot{n}_{fw} \ln X_{fw} + \dot{n}_b X_b \ln X_b + \dot{n}_b (1 - X_b) \ln (1 - X_b)) \big] \ ; . \end{aligned} \tag{21.16}$$

note that the freshwater outflow is unmixed, i.e., $X_{fw} = 1$. After some algebra, this finally assumes the form

$$\begin{aligned} \dot{W}_{rev} = -p_{\mathrm{osm}} \dot{V}_{fw} \Bigg[& \frac{(1-y) \ln (1-y) + (1 - X_{sw}) \ln (1 - X_{sw})}{y \ln (1 - X_{sw})} \\ & - \frac{(1 - y - X_{sw}) \ln (1 - y - X_{sw})}{y \ln (1 - X_{sw})} \Bigg] , \end{aligned} \tag{21.17}$$

where $\dot{V}_{fw} = \bar{v}_{fw} \dot{n}_{fw}$ is the volume flow of freshwater produced, and $p_{\mathrm{osm}} = -\frac{\bar{R} T}{\bar{v}_{fw}} \ln (1 - X_{sw})$ is the osmotic pressure of the incoming seawater.

The minimum work required per liter of seawater, $\dot{W}_{rev} / \dot{V}_{fw}$, depends on the salt concentration X_{sw} in the incoming seawater, and on the extraction ratio y. In the limit that only a small amount of freshwater is extracted, $y \ll 1$, the work is proportional to the osmotic pressure of the seawater,

$$\dot{W}_{rev} (y = 0) = -p_{\mathrm{osm}} \dot{V}_{fw} \ . \tag{21.18}$$

For the case of complete desalination, $y \to y_{\max} = (1 - X_{sw})$, the work required is larger,

$$\dot{W}_{rev} (y_{\max}) = -p_{\mathrm{osm}} \dot{V}_{fw} \left(1 + \frac{X_{sw} \ln X_{sw}}{(1 - X_{sw}) \ln (1 - X_{sw})} \right) = -\dot{n}_{sw} T \Delta \bar{s}_{mix} \ , \tag{21.19}$$

where $\Delta \bar{s}_{mix}$ is the entropy of mixing for mixing brine and freshwater per mole of mixture, i.e., for one mole of seawater. It should be noted that the assumption of ideal mixture will not hold for large salt content, thus this is a hypothetical value.

Figure 21.4 shows the work required as function of the freshwater ratio y. For smaller values of y the increase in work requirement is not too large, and one might consider to go to values of $y = 0.5$, or so. Note that larger values of y reduce the amount of seawater drawn for a given amount of freshwater produced, and thus the overall size of the device or plant. As y approaches the maximum value, we observe fast increase of the work requirement.

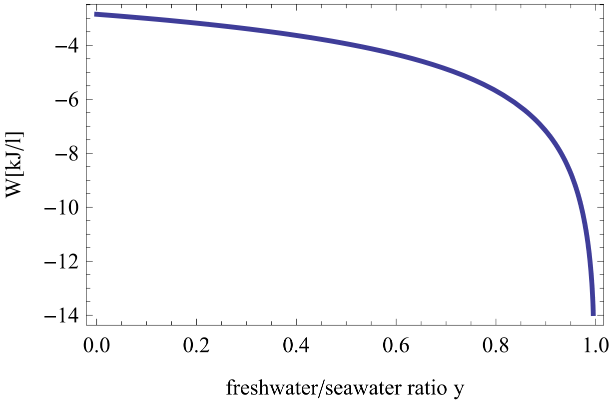

Fig. 21.4 Work required per litre of seawater over freshwater/seawater ratio y

The work requirement will be larger in actual processes, where additional work input is needed to overcome irreversible losses. For a membrane-based desalination system there are losses to friction in the pipes, the pump, in filters, and as water is pressed through the membrane, and losses due to non-uniform salt concentration: salt might accumulate in front of the membrane and this *concentration polarization* increases the local osmotic pressure and thus the work requirement. Note that less work is needed when reverse osmosis takes place at lower temperatures, where the osmotic pressure is lower. Typical values for separation work in commercial membrane desalination systems are about 10 kJ per litre of freshwater.

21.5 Reversible Mixing: Osmotic Power Generation

Rivers transport freshwater into the sea, where freshwater and saltwater mix. The difference in salt content can be used to drive osmotic power plants.

An intuitive basic set-up is to enclose saltwater in a piston-cylinder system and bring it into contact with the freshwater via a semipermeable membrane. The saltwater will draw freshwater into the cylinder to increase its entropy, the piston will be pushed and work is done. Note that, in principle, the salt inside the cylinder can draw an infinite amount of freshwater! Alternatively, one can enclose the freshwater in the cylinder and bring it into contact with the seawater via a semipermeable membrane. The saltwater will draw freshwater out of the cylinder to increase its entropy, the piston will be pulled in and work is done.

Osmotic power generation is in development, with one trial plant operating in Norway. A main bottleneck for large scale commercial application is the development of suitable membranes.

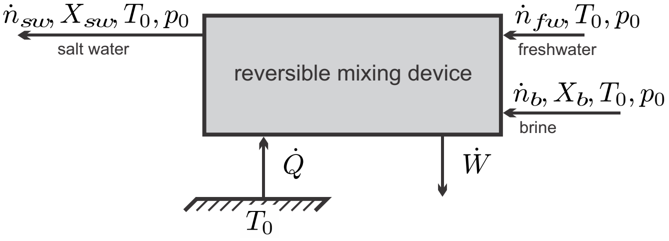

Fig. 21.5 Mole flows, work and heat for reversible mixing

The amount of work that could be obtained can be determined from inverting the continuous desalination process discussed in the previous section, see Fig. 21.5. To be able to use the same notation, we consider the reversible mixing of brine ($\dot{n}_b$, X_b) and freshwater ($\dot{n}_{fw}, X_{fw} = 1$) to saltwater ($\dot{n}_{sw}$, X_{sw}); for mixing of seawater and river water, X_b is the composition of the *seawater.*

We introduce the freshwater/brine ratio as $x = \frac{\dot{n}_{fw}}{\dot{n}_b}$, for which we have

$$1 - y = \frac{\dot{n}_{sw} - \dot{n}_{fw}}{\dot{n}_{sw}} = \frac{\dot{n}_b}{\dot{n}_b + \dot{n}_{fw}} = \frac{1}{1+x} \quad , \quad X_{sw} = \frac{X_b}{1+x} \ . \tag{21.20}$$

The work obtained by reversible mixing per litre of fresh water follows from (21.17) as (note that all signs must be inverted for the inverted process)

$$\frac{\dot{W}_{rev}}{\dot{V}_{fw}} = \frac{\bar{R}T}{\bar{v}_{fw}} \frac{1}{x} \left[(1+x) \ln (1+x) + (1 - X_b) \ln (1 - X_b) \right. \\ \left. - (1 + x - X_b) \ln (1 + x - X_b) \right] \ . \tag{21.21}$$

Here, $\dot{V}_{fw} = \bar{v}_{fw} \dot{n}_{fw}$ is the volume flow of freshwater. It is assumed that the two streams have the same temperature.

In the limit $x \to 0$, where the freshwater (fw) mixes with an infinite amount of seawater (b), the work is proportional to the osmotic pressure of the seawater, i.e.,

$$\dot{W}_{rev} = -\frac{\bar{R}T}{\bar{v}_{fw}} \dot{V}_{fw} \ln (1 - X_b) = p_{\text{osm}} \dot{V}_{fw} \ . \tag{21.22}$$

For the opposite case, where salty brine (b) mixes with a large amount of freshwater (fw), so that $x \gg 1$, the work can also be expressed with the volume flow of brine,

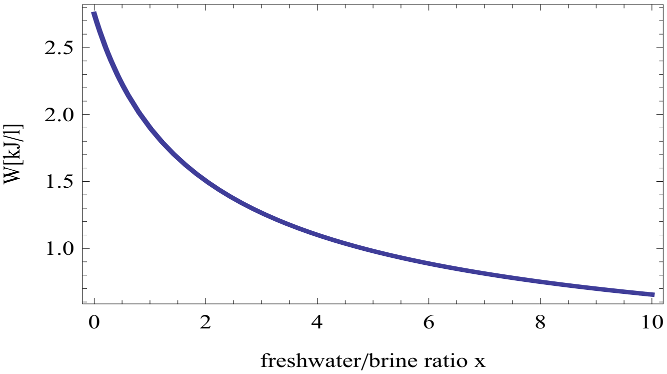

Fig. 21.6 Work produced per litre of freshwater over freshwater/saltwater ratio x

$$\dot{W}_{rev} = \dot{V}_{fw}\frac{\bar{R}T}{\bar{v}_{fw}}X_b\frac{\ln x}{x} = \dot{V}_b\frac{\bar{R}T}{\bar{v}_b}X_b\ln x \ . \tag{21.23}$$

Figure 21.6 shows the work that could be produced in the best, i.e., reversible, case per litre of freshwater for $X_b = 0.0218$ (which is the value for seawater) at $T = 5\,^\circ\mathrm{C}$. The maximum work ($2.8\frac{\mathrm{kJ}}{\mathrm{litre}}$) could be obtained by reversibly mixing the freshwater with an infinite amount of seawater (limit $x \to 0$). When even amounts of salt- and freshwater are mixed ($x = 1$), one still could produce $1.9\frac{\mathrm{kJ}}{\mathrm{litre}}$. The river Rhine, Germany's largest river, discharges in average a volume flow of $2200\frac{\mathrm{m}^3}{\mathrm{s}}$. The power potential of an osmotic power plant that uses 1/10 of the volume flow and operates at $x = 1$ is $\dot{W}_{pot} = 418\,\mathrm{MW}$. There are many rivers with large[1] or small discharge, which in principle offer a tremendous potential for regenerative energy production (driven by weather processes, i.e., the sun). Not all locations will be suitable, and a feasible technology that operates on large and small scales would be helpful.

Particular care must be taken in keeping the osmotic pressure of the incoming seawater high. Normally the freshwater discharged from a river into the ocean will mix with the local seawater, and the mixture in front of the river mouth will have a lower salt content, and therefore lower osmotic pressure, than the ocean far away. This implies that the mixture that leaves the osmotic power plant must be discharged at some distance from the origin of the saltwater entering the plant.

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[1] Amazon: $219,000\frac{\mathrm{m}^3}{\mathrm{s}}$, Congo $41,800\frac{\mathrm{m}^3}{\mathrm{s}}$, Mississippi/Missouri: $16,200\frac{\mathrm{m}^3}{\mathrm{s}}$, Mackenzie/Peace/Finlay: $9,910\frac{\mathrm{m}^3}{\mathrm{s}}$.

The Norwegian company Statkraft (www.statkraft.com) is developing a power plant based on the concept of pressure retarded osmosis, see Fig. 21.7. The process relies on the fact that seawater pressurized to a pressure p_{sw} between the environmental and the osmotic pressure of the seawater, $(p_{sw} - p_0) < p_{\text{osm}}$, draws freshwater at the environmental pressure p_0 through a semipermeable membrane. This increases the flow of pressurized brackish (lower salt content than seawater) water, which is split into two streams. The first stream runs through a turbine to produce power, while the other stream is used to pressurize the incoming seawater in a pressure exchanger. The relative amount of freshwater, i.e., x in the above calculation, depends on the pressure p_{sw}. In reversible operation, as soon as the osmotic pressure of the brackish water, which decreases due to dilution, has reached the value $(p_{sw} - p_0)$, no further freshwater is drawn in. Irreversible pressure losses in pipes and pressure exchanger will reduce the amount of power produced.

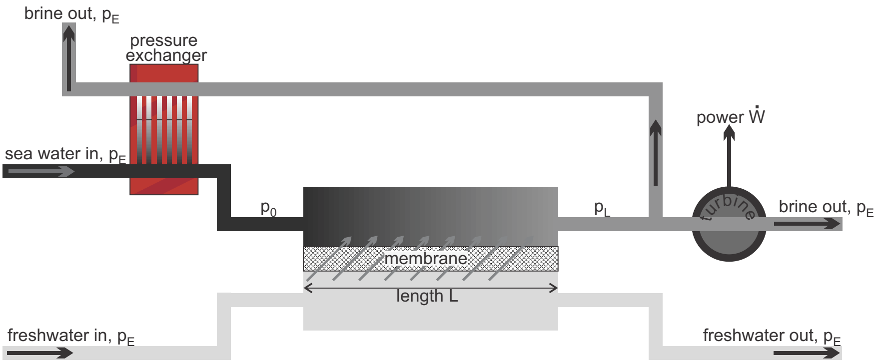

Fig. 21.7 Pressure retarded osmosis power plant (after www.statkraft.com)

21.6 Example: Desalination in Piston-Cylinder Device

A reciprocating desalination device as depicted in Fig. 21.8 operates according to the following cycle:

1-2: Intake of seawater at constant pressure p_0, until the intake valve closes at volume V_2.

2-3: Compression of seawater up to p_3, which is the pressure at which freshwater starts to pass a semipermeable membrane. The seawater can be considered as incompressible.

3-4: Further increase of pressure forces freshwater through the membrane, until a maximum pressure p_4 is reached.

4-5: The exit valve opens, and the pressure drops to p_0.

5-6: The brine is pushed out at constant pressure p_0.

6-1: Exit valve closes, inlet valve opens.

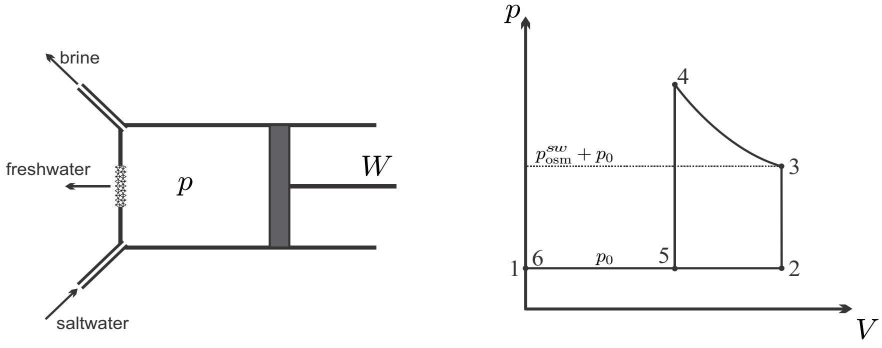

Fig. 21.8 Reciprocating desalination cycle

During the process the temperature remains constant at 15 °C.

We ask for the work to produce 1 litre of freshwater ($\rho_{H_2O}=1000\frac{\mathrm{g}}{\mathrm{litre}}$) in relation to the freshwater-seawater ratio. The local seawater has a mass density $\rho_{sw}=1030\frac{\mathrm{kg}}{\mathrm{m}^3}$, it contains 35 g sodium chloride (NaCl) and 995 g water per litre, so that $\rho_{NaCl}^{sw}=35\frac{\mathrm{g}}{\mathrm{litre}}$. Since the salt is dissociated, the mole numbers of salt and water at state 2 are

$$n_{NaCl}=2\frac{\rho_{NaCl}^{sw}}{M_{NaCl}}V_2=1.197\frac{\mathrm{mol}}{\mathrm{litre}}V_2$$

and

$$n_{H_2O}^{sw}=\frac{\rho_{sw}-\rho_{NaCl}^{sw}}{M_{H_2O}}V_2=55.28\frac{\mathrm{mol}}{\mathrm{litre}}V_2\ .$$

Thus, the mole fraction of salt in the seawater is

$$X_{sw}=\frac{n_{NaCl}}{n_{NaCl}+n_{H_2O}^{sw}}=0.021\ ,$$

and its osmotic pressure is

$$p_{osm}^{sw}=p_3-p_0=-\rho_{H_2O}R_{H_2O}T\ln\left[1-X_{sw}\right]=28.3\,\mathrm{bar}\ .$$

Next we ask for the relation between pressure and volume during the desalination in step 3-4. The volume of fresh water produced is $V_{fw}=V_2-V$ which corresponds to the mole number

$$n_{fw}=\frac{\rho_{H_2O}}{M_{H_2O}}\left(V_2-V\right)\ .$$

The mole number of water molecules remaining in the volume V is

$$n_r=n_{H_2O}^{sw}-n_{fw}=\frac{\rho_{sw}-\rho_{NaCl}^{sw}}{M_{H_2O}}V_2-\frac{\rho_{H_2O}}{M_{H_2O}}\left(V_2-V\right)=\frac{\rho_{H_2O}}{M_{H_2O}}\left(V-V_s\right)\ ,$$

where

$$V_s = \frac{\rho^{sw}_{\text{NaCl}} - \rho_{sw} + \rho_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}} V_2$$

is the volume of the salt;[2] for the given data $V_s/V_2 = 0.005$. Since all salt remains in V, the mole fraction of salt in V is

$$X_r = \frac{n_{\text{NaCl}}}{n_{\text{NaCl}} + n_r} = \left[1 + \frac{1}{2}\frac{M_{\text{NaCl}}}{M_{\text{H}_2\text{O}}}\frac{\rho_{\text{H}_2\text{O}}}{\rho^{sw}_{\text{NaCl}}}\frac{V - V_s}{V_2}\right]^{-1} = \left[1 + \frac{1}{\gamma}\frac{V - V_s}{V_2}\right]^{-1} ;$$

for the given data $\gamma = 0.02154$. Then the pressure p in the cylinder is $p(V) = p_0 + p^r_{\text{osm}}(V)$ with

$$p^r_{\text{osm}}(V) = -\rho_{\text{H}_2\text{O}} R_{\text{H}_2\text{O}} T \ln\left[1 - X_r(V)\right] .$$

The work for the cycle is

$$W = \oint p dV = \int_{V_3}^{V_4} p^r_{\text{osm}}(V)\, dV .$$

and with the abbreviations $\beta = \frac{V_{fw}}{V_2}$, $\alpha = 1 - \frac{V_s}{V_2} = 0.995$, we obtain for the work per litre of freshwater produced

$$\frac{W}{V_{fw}} = \rho_{\text{H}_20} R_{\text{H}_2\text{O}} T \frac{1}{\beta}\left[(\gamma + \alpha - \beta)\ln(\gamma + \alpha - \beta) + \alpha \ln \alpha \right.$$
$$\left. - (\alpha - \beta)\ln(\alpha - \beta) - (\gamma + \alpha)\ln(\gamma + \alpha)\right] .$$

When plotted as a function of the freshwater-seawater ratio by volume, β, the curve is very similar to the one shown in Fig. 21.4. Indeed, it is an easy, but somewhat cumbersome, exercise to show that the above agrees with (21.17).

21.7 Example: Removal of CO_2

The effect of greenhouse gases such as CO_2 on Earth's climate is widely discussed. One of the solutions to at least reduce the impact of burning carbon fuels is to remove CO_2 from the combustion product, compress it, and and store it in depleted gas or oil reservoirs below ground (CCS - *carbon capture and storage*). As an alternative, it is sometimes suggested to remove CO_2 from the atmosphere. This is a less viable alternative, since the concentration of CO_2 in the atmosphere is very low, which makes it more costly to remove it, as will be seen below.

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[2] Assuming ideal mixture. As said before, this assumption is only valid for low salt concentrations. The computation of V_s is an extrapolation, and V_s should be seen as a useful abbreviation.

In the oxy-fuel process, oxygen is separated from air, then mixed with fuel and a portion of the power plant's exhaust, then the mixture is burned to provide heat for power production. The exhaust is only CO_2 and water, which can be separated rather easily by condensation of water. Since the concentration of oxygen in the air is far higher than the concentration of CO_2 in air, the separation work for O_2 is lower in comparison.

To estimate the work requirements, we consider air as a mixture of "gas" (no need to specify the composition), and carbon dioxide or oxygen with mole fraction X and ask for the work required per mole of CO_2 or O_2 to reduce the mole fraction in the air to $\hat{X} = \alpha X$. For the computation we consider a given amount n_{air} of air at (T, p), and a fully reversible separation process. The total amount of air is

$$n_{\mathrm{air}} = n_{\mathrm{gas}} + n_{\mathrm{s}} \ ,$$

where n_{s} is the number of moles of the component to be separated (CO_2 or O_2) in the air, and n_{gas} is the number of moles of all other gases in the air.

Since all contributing gases are ideal, and since the temperature remains constant, the first law just gives that the work for separation is equal to the heat that must be removed,

$$W_{12} = Q_{12} \ .$$

The second law for the reversible process gives

$$S_2 - S_1 = \frac{Q_{12}}{T} \ ;$$

thus the separation work is

$$W_{12} = T\left(S_2 - S_1\right) \ .$$

Since total pressure and temperature remain unchanged, only the mixing contributions to entropy are relevant.

In state 1, before separation, we have n_{gas} moles of "gas" mixed with $n_{\mathrm{s}} = \frac{X}{1-X} n_{\mathrm{gas}}$ moles of CO_2 (or O_2). In state 2 we have n_{gas} moles of "gas" mixed with $\hat{n}_{\mathrm{s}} = \frac{\hat{X}}{1-\hat{X}} n_{\mathrm{gas}}$ moles of CO_2 (or O_2), and $[n_s - \hat{n}_s]$ moles of pure separated CO_2 (or O_2). The corresponding mixing contributions to entropy are

$$S_1 = -\bar{R} \sum n_\alpha \ln X_\alpha = -\bar{R}\left[n_{\mathrm{gas}} \ln\left(1 - X\right) + n_{\mathrm{s}} \ln X\right] \ ,$$
$$S_2 = -\bar{R} \sum n_\alpha \ln X_\alpha = -\bar{R}\left[n_{\mathrm{gas}} \ln\left(1 - \hat{X}\right) + \hat{n}_{\mathrm{s}} \ln \hat{X}\right] \ .$$

We obtain the work per mole of separated CO_2 (or O_2) as

$$\bar{w} = \frac{W_{12}}{n_s - \hat{n}_s} = -\bar{R}T \frac{\ln(1-\alpha X) + \frac{\alpha X}{1-\alpha X}\ln(\alpha X) - \ln(1-X) - \frac{X}{1-X}\ln X}{\frac{X}{1-X} - \frac{\alpha X}{1-\alpha X}} .$$

The absolute work is larger for smaller original mole fraction. Figure 21.9 shows $\bar{w}$ for $\alpha = \{0.9, 0.5, 0.1\}$ as function of the original mole fraction X. The figure indicates that removal from carbon rich exhaust streams, where X is larger, is cheaper.

It is worthwhile to look at some numbers: Removal of CO_2 from atmospheric air, where[3] $X_{CO_2} = 400\,\mathrm{ppm}$, requires a reversible separation work of $\{19.6,\ 20.2,\ 21.3\}\,\frac{\mathrm{kJ}}{\mathrm{mol}}$ for $\alpha = \{0.9, 0.5, 0.1\}$. On the other hand, removal of O_2 from atmospheric air, where $X_{O_2} = 0.21 = 210000\,\mathrm{ppm}$, requires a reversible separation work of approximately $\{3.99,\ 4.59,\ 5.54\}\,\frac{\mathrm{kJ}}{\mathrm{mol}}$, that is just a quarter of the work required for CO_2.

The Virgin Earth Challenge[4] asks for the removal of *one billion metric tons* of carbon dioxide per year, that is $2.273 \times 10^{10}\,\frac{\mathrm{kmol}}{\mathrm{year}}$. This would require—in form of work!— $4.5 \times 10^{14}\frac{\mathrm{kJ}}{\mathrm{year}}$ at least (in a fully reversible process), that is about 0.1 percent of the world's energy consumption of $16\,\mathrm{TW} = 5 \times 10^{17}\frac{\mathrm{kJ}}{\mathrm{year}}$, and about 0.6 percent of the world's power generation of $2.3\,\mathrm{TW} = 7.2 \times 10^{16}\frac{\mathrm{kJ}}{\mathrm{year}}$. The world's yearly emissions of CO_2 are ca. $30 \times 10^{12}\frac{\mathrm{kg}}{\mathrm{year}}$ or $6.8 \times 10^{11}\,\frac{\mathrm{kmol}}{\mathrm{year}}$. The minimum (!) work requirement for the removal of this amount directly from the atmosphere is $1.45 \times 10^{16}\frac{\mathrm{kJ}}{\mathrm{year}}$—about 2.9% of the world's energy consumption, and 20% of the world's power generation.

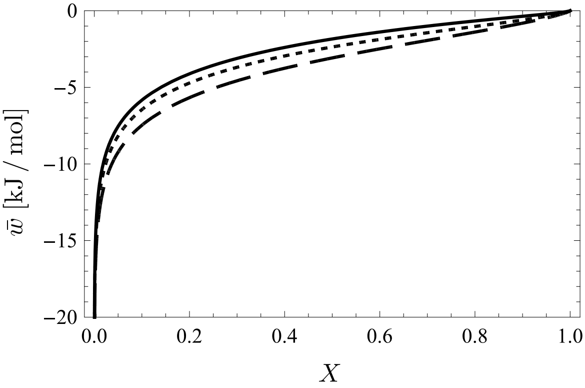

Fig. 21.9 Work $\bar{w}$ to remove 1 mole of gas from air with initial gas mole fraction X, so that remaining air has gas content αX for $\alpha = 0.9$ (continuous), $\alpha = 0.5$ (short dashes), $\alpha = 0.1$ (long dashes)

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[3] Value for January 2014. In average, the yearly increase of the CO_2 content is about 2 ppm. This is about half of the newly emitted CO_2, the remainder is absorbed into the oceans.

[4] Launched in 2007, `http://www.virginearth.com`

The reversible separation of oxygen ($X_{\mathrm{O}_2} = 0.21$) requires only about $5\frac{\mathrm{kJ}}{\mathrm{mol}}$, and thus the cost of oxygen separation is lower by approximately a factor of four. Note that one oxygen molecule is required to form one CO_2 molecule in combustion.

Obviously, additional cost occurs for compressing, pumping and storing of the removed carbon dioxide, and, most importantly, for overcoming the irreversibilities in the separation process. Thus, it might be that the separation cost is only a small part of the bill—only a careful cost analysis can show the relative importance of the various cost factors.[5]

Indeed, an important cost factor that must not be forgotten is the occurrence of *irreversible* losses in the separation process. After all, the above calculation only considers the reversible limit for separation work. The actual amount of losses will depend strongly on the process chosen for separation, and we can only make some general estimates.

It is a reasonable assumption that the work loss for separation of one mole of CO_2 (or of O_2, in the case of the oxy-fuel process) is proportional to the amount of air that must be moved through the separation plant and to the work $\bar{w}_{\mathrm{p}}(X, \alpha)$ required to move and process the incoming air in the plant.

To proceed, we need to estimate $\bar{w}_{\mathrm{p}}(X, \alpha)$. The process through the separation plant is a flow process and we can estimate the processing work as

$$\bar{w}_{\mathrm{p}} = \bar{v}_0 \Delta p \, ,$$

where $\bar{v}_0$ is the molar volume of the air at environmental conditions. The overall pressure loss Δp is associated with the actual transport and separation process; examples are the pressure difference required to press the air through a semipermeable membrane as given by Darcy's law, or the pressure difference required to transport air over larger distances, which is necessary to remove the depleted air far from the plant, so that re-circulation of depleted air is minimized. With the ideal gas law we obtain

$$\bar{w}_{\mathrm{p}} = \bar{R} T_0 \frac{\Delta p}{p_0} \, .$$

Based on the above, the work to overcome irreversible losses required per mole of gas separated can be estimated as

$$\bar{w}_{\mathrm{irr}} = \frac{n_{gas} + n_s}{n_s - \hat{n}_s} \bar{w}_{\mathrm{p}}(X, \alpha) = \frac{1 - \alpha X}{(1 - \alpha) X} \bar{R} T_0 \frac{\Delta p(X, \alpha)}{p_0} \, .$$

Due to the low CO_2 content of air, one needs to move about 550 times more air through a separation plant to remove one mole of CO_2, than one would need to remove one mole of O_2 for the oxy-fuel process. For $\alpha = 0.5$ the value for the work to overcome irreversible losses is $12990 \frac{\Delta p(X,\alpha)}{p_0} \frac{\mathrm{kJ}}{\mathrm{mol}}$ for separation

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[5] See D.W. Keith, M. Ha-Duong, J. K. Stolaroff, Climate Strategy with CO_2 Capture from the Air, Climatic Change **74**(1-3), pp. 17-45 (2006)]

of CO_2 from air, while it is only $21.26\frac{\Delta p(X,\alpha)}{p_0}\frac{\mathrm{kJ}}{\mathrm{mol}}$ for the separation of O_2 from air.

Figure 21.10 compares $\bar{w}_{\mathrm{irr}}$ for $X = 390\,\mathrm{ppm}$ (the CO_2 fraction in air in 2010) and $X = 0.21$ (the O_2 fraction in air) as function of $\alpha = \hat{X}/X$ (for small α a larger amount of CO_2 or O_2 is removed), for $\frac{\Delta p(X,\alpha)}{p_0} = 0.01$. Already for this small pressure loss, the loss to irreversible work for taking CO_2 directly from the air is about 5 times the reversible work for separation, so that the overall work would be about 6 times the reversible work! Presently, no technology exists that would even reach this value.

Obviously, the actual values for $\bar{w}_{\mathrm{irr}}$ will depend on the pressure losses $\Delta p\,(X,\alpha)$ for the actual process devised. One will expect higher pressure losses for smaller gas content X and larger extraction ratio, i.e. smaller α.

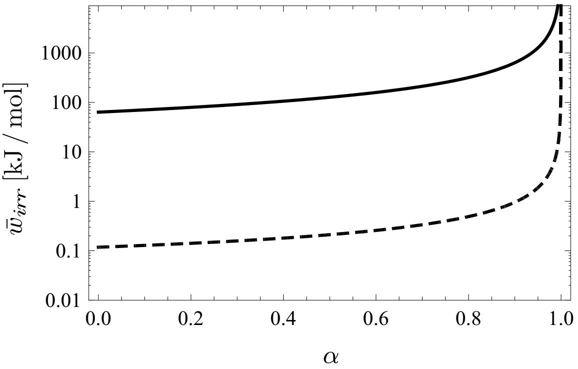


Fig. 21.10 Irreversible contribution to separation work for $X_{CO2} = 384\mathrm{ppm}$ (continuous) and $X_{CO_2} = 0.21$ (dashed) as function of $\alpha = \bar{X}/X$, for $\frac{\Delta p}{p_0} = 0.01$.

The separation processes discussed earlier in this chapter rely on membrane separation. For a membrane that allows only one component to pass, we can see from (20.39) that the pressure ratio over the membrane must be ($X_\nu^{\mathrm{II}} = 1$ for the pure separated gas)

$$\frac{p^{\mathrm{I}}}{p^{\mathrm{II}}} > \frac{1}{X_\nu^{\mathrm{I}}}\,.$$

With $X_{\mathrm{CO_2}} = 400\,\mathrm{ppm}$ this implies a pressure ratio larger than 2500, while for O_2 separation, the pressure ratio must be only above 5. Clearly, while membrane separation might be feasible for O_2, it is not at all feasible for CO_2 removal from air. Not only would the large pressure ratio require extremely sturdy membrane materials, but the creation of huge pressure ratios will lead to huge irreversible losses.

Thus, chemical processes must be considered, where the air passes over a substance A that is keen to react with the CO_2 to form A_n-CO_2 compounds.

In a subsequent step, the reaction product must be split into A and CO_2 to dispose the CO_2 and re-use the A.

Another alternative is separation by distillation as discussed in the next chapter. This requires cooling and partial liquefaction of air. All known large-scale cooling processes involve substantial irreversibilities in compressors, throttling valves, heat exchangers, also through heat leaks, and, again, the actual work required will be substantially bigger than the reversible work.

Problems

21.1. Physiological Solution for Use in Hospitals

The osmotic pressure in bodily fluids of mammals is 7.7 atm at 36 °C. Compute the amount of salt (NaCl) that must be added to 1 litre water to give a solution with the same osmotic pressure.

$M_{\mathrm{NaCl}} = 58.5 \frac{\mathrm{kg}}{\mathrm{kmol}}$. Note: NaCl dissociates in solution.

21.2. Salt Water

One kilogram of water and 80 grams of NaCl are mixed, the mixture has a temperature of 80 °C. Assume the mixture is ideal.

1. Compute the osmotic pressure of the solution.
2. Compute the entropy of mixing.
3. Compute the minimum work required for separation of salt and water.

21.3. Osmotic Equilibrium I

A semipermeable membrane which allows only water to pass, divides two containers. There is 1 litre of water in total, and 10 g of NaCl in each container. One container is kept at a pressure of 10 bar and the other at 20 bar; the temperature of both is 300 K.

1. Show that in equilibrium the pressure difference between the two containers equals the difference in osmotic pressures.
2. Set up the equation needed to determine how water is distributed between the two containers, and determine the water masses in both containers.
3. Will the equilibrium change when the temperature is lowered to 20 °C? If so, in which direction does water move, low to high pressure, or high to low?

21.4. Osmotic Equilibrium II

A semipermeable membrane which allows only water to pass, divides two containers. In thermodynamic equilibrium container A holds 400 g of water and 20 g salt, container B holds 600 g of water and 20 g of salt. Moreover, container A is kept at a pressure of 20 bar; the temperature of both is 300 K. Determine the pressure in container B.

21.5. Osmotic Equilibrium with Temperature Difference I

Two piston-cylinder systems are connected by a semipermeable membrane that allows only water to pass. Both cylinders contain water and NaCl. The left cylinder is pressurized to 15 bar and its temperature is maintained at 320 K . The right cylinder is maintained at a temperature of 325 K.

Determine the pressure that must be exerted on the right cylinder so that in chemical equilibrium the mole fraction of salt in both containers is $X_{s,L} = X_{s,R} = 0.05$.

Hint: Careful, the temperature difference affects the chemical potentials!

21.6. Osmotic Equilibrium with Temperature Difference II

Two piston-cylinder systems are connected by a semipermeable membrane that allows only water to pass. Both cylinders contain water and NaCl. The left cylinder is pressurized to 10 bar and its temperature is maintained at 300 K. The right cylinder is pressurized to 20 bar and its temperature is maintained at 305 K. The mole fraction of salt in the left container is measured as $X_{s,L} = 0.05$.

Determine the mole fraction of salt $X_{s,R}$ in the right cylinder for the case of chemical equilibrium.

Hint: Careful, the temperature difference affects the chemical potentials!

21.7. Partial Separation of a Binary Gas Mixture I

Some helium is to be separated from an equimolar mixture of argon and helium. For this, the mixture is pressurized to a pressure p_M, and then flows past a membrane, which allows only helium to pass. The helium pressure on the back of the membrane is 4 bar. Determine the pressure p_M that is necessary to remove 50% of the helium, in the best case.

21.8. Cooling Fluid

A cooling fluid consists of a mixture of water and ethylene glycol ($C_2H_6O_2$, $M = 62 \frac{\mathrm{g}}{\mathrm{mol}}$). The glycol mass fraction is $c_g = 0.3$. Assume the mixture is ideal.

1. Determine the mean molar mass of the mixture.
2. The mole volume of glycol is $\bar{v}_g = 0.056 \frac{\mathrm{m}^3}{\mathrm{kmol}}$. Compute the specific volume of the mixture, and its mole volume.
3. Determine the entropy of mixing for 1 kg of mixture.
4. What is the minimum work required for complete separation at 0 °C, per kilogram of mixture?
5. The above cooling fluid is brought into contact with a semipermeable membrane that allows only water to pass. On the other side of the membrane is a salt (NaCl) solution. In equilibrium at 300 K the cooling fluid is at pressure $p_c = 45$ bar and the salt solution is at pressure $p_s = 5$ bar. Determine the mole fraction X_s of salt in the salt solution.

21.9. Minimum Work for Reverse Osmosis

We computed the work loss in irreversible mixing as TS_{mix} . This is also the minimum work required for separation.

1. Discuss the above statement.
2. Compute the minimum work for the separation of $1\,\text{m}^3$ of salt water at 35 °C. The saltwater contains 75 g sodium chloride (NaCl, $M_{\text{NaCl}} = 58.5\frac{\text{kg}}{\text{kmol}}$) per litre and has a mass density of $1060\frac{\text{kg}}{\text{m}^3}$. Remember that NaCl dissociates into Na^+ and Cl^- ions. Note: You will get different results if you consider splitting into H_2O, Na^+, Cl^-, than if you consider splitting into H_2O and NaCl. The difference is the entropy of mixing between sodium and chlorine.

21.10. Reversible Mixing

A fabrication process produces a salty waste flow (density: $1040\frac{\text{g}}{\text{litre}}$, 50 g of salt per litre). How much work could be obtained by mixing 1 litre of seawater (density: $1025\frac{\text{g}}{\text{litre}}$, 32 g of salt per litre) with 1 litre of the waste? Assume all flows are at 8 °C.

21.11. Desalination in Piston-Cylinder Device

2 litres of saltwater are enclosed in a piston cylinder device. The saltwater is compressed up to the pressure p_2, which is the pressure at which freshwater just starts to pass a semipermeable membrane. Further increase of pressure forces freshwater through the membrane, until one litre of saltwater remains in the cylinder.

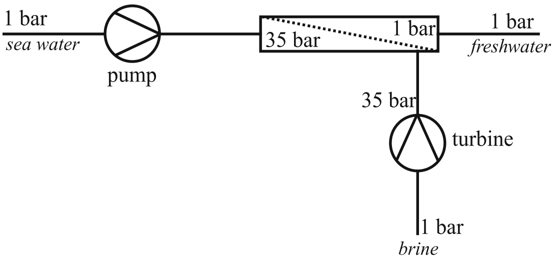
The saltwater contains 50 g sodium chloride (NaCl) per litre and has a mass density of $1040\frac{\text{kg}}{\text{m}^3}$; it can be considered as incompressible ideal mixture, the temperature remains constant at 15 °C.

Assume that the osmotic pressure can be computed from the approximation $p_{\text{osm}} = -\frac{R_W T}{v_W}\ln X_W \simeq \frac{R_W T}{v_W}(1 - X_W)$.

1. Compute the pressure p_2.
2. Find the relation between the volume remaining in the cylinder and the pressure.
3. Compute the work required for the process.

21.12. Reverse Osmosis

Consider the continuous desalination device depicted below. Fresh seawater at 15 °C, 1 bar is pumped isothermally to a pressure of 35 bar, and then flows past a semipermeable membrane, which allows only fresh water to pass. The exiting brine drives a turbine, and leaves the system at 1 bar. Assume that the temperature remains constant throughout the device, and that all processes are reversible.

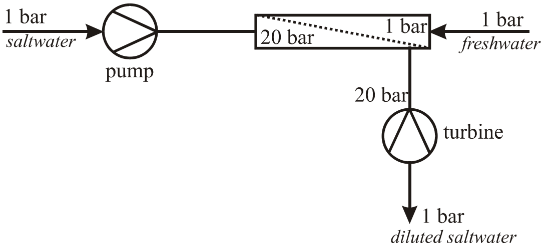


The mass densities of sea water, freshwater and brine are given as: $\rho_{sw} = 1030\frac{\text{kg}}{\text{m}^3}$, $\rho_{fw} = 1000\frac{\text{kg}}{\text{m}^3}$, $\rho_b = 1040\frac{\text{kg}}{\text{m}^3}$, and the seawater contains $35\frac{\text{g}}{\text{litre}}$ of sodium chloride ($M_{\text{NaCl}} = 58.5\frac{\text{kg}}{\text{kmol}}$).

1. Determine the volume flow of freshwater produced per volume flow of sea water.
2. Determine the work required to drive the pump, and the work that can be recovered by the turbine. Compute the net work required per litre of freshwater.
3. Assume now that pump and turbine are irreversible, with efficiencies of 85%, and determine the net work.

21.13. Osmotic Power Plant

Saltwater at 15 °C, 1 bar is pumped to a pressure of 20 bar and then flows along a semi-permeable membrane through which freshwater enters and dilutes the saltwater. The exiting solution (diluted saltwater) drives a turbine, and leaves the system at 1 bar. Assume that the temperature remains constant throughout the device, and that all processes are reversible.



The incoming saltwater contains 45 g of sodium chloride ($M_{\text{NaCl}} = 58.5\frac{\text{kg}}{\text{kmol}}$) per litre. The mass densities of saltwater and freshwater are given as: $\rho_{sw} = 1035\frac{\text{kg}}{\text{m}^3}$, $\rho_{fw} = 1000\frac{\text{kg}}{\text{m}^3}$, and there is no mixing volume.

1. Determine the osmotic pressure of the incoming saltwater.
2. The volume flow of saltwater is $1000\frac{\text{litres}}{\text{min}}$. Determine the volume flows of the freshwater drawn in, and of the diluted saltwater that enters the turbine.

3. Determine the power required to drive the pump, and the power produced by the turbine. Compute the net work produced per litre of freshwater drawn in.

21.14. Osmotic Power Plant with Irreversibilities

Saltwater at 25 °C, 1 bar is pumped to a pressure of 22 bar, and then flows along a semi- permeable membrane, through which fresh water enters and dilutes the saltwater. Due to pressure loss in the desalination system, the exiting solution (diluted saltwater) leaves the desalinator at a pressure of 19 bar. This flow drives a turbine, and leaves the system at 1 bar. Assume that the temperature remains constant throughout the device, and that pump and turbine are irreversible with isentropic efficiencies of 0.85.

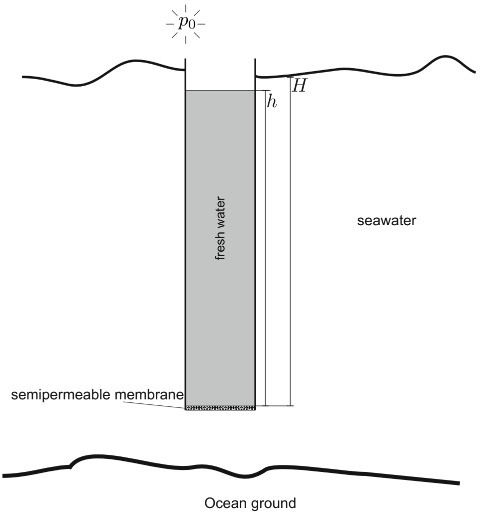
The incoming saltwater contains 42 g of sodium chloride ($M_{\mathrm{NaCl}} = 58.5\frac{\mathrm{kg}}{\mathrm{kmol}}$) per litre. The mass densities of saltwater and freshwater are given as: $\rho_{sw} = 1033\frac{\mathrm{kg}}{\mathrm{m}^3}$, $\rho_{fw} = 1000\frac{\mathrm{kg}}{\mathrm{m}^3}$, and there is no mixing volume.

1. Determine the osmotic pressure of the incoming saltwater.
2. Determine the mole fraction of water in the exiting diluted water.
3. The volume flow of saltwater is 1000 litres/minute. Determine the volume flows of the freshwater drawn in, and of the diluted saltwater that enters the turbine
4. Determine the power required to drive the pump, and the power produced by the turbine. Compute the net work produced per litre of freshwater drawn in.

21.15. Desalination I

A pipe is closed at one end with a semipermeable membrane which only allows water to pass. The pipe is pressed vertically into an ocean, see the following sketch. The temperature of the ocean is 4 °C, and the salt water contains 35 g sodium chloride (NaCl) per litre, moreover $\rho_{sw} = 1030\frac{\mathrm{kg}}{\mathrm{m}^3}$, $\rho_{fw} = 1000\frac{\mathrm{kg}}{m^3}$

1. To what height H_1 must the pipe be immersed, before fresh water passes the membrane?
2. At what height H_2 have both, sea water and fresh water, the same height, $h = H$? Explain why this is possible.
3. When $h > H_2$ one can run a water wheel with the fresh water leaving the pipe. Of course, this setup is not a perpetual motion engine. Why? (for some discussion see: Scientific American, June 1971, p. 124-125, and April 1972, p110-111). The above calculation assumed constant density of the seawater, and a homogeneous salt content. Can that be expected?



21.16. Desalination II

The solution of the previous problem assumed constant density of the seawater. Consider the same problem for the case that the salt concentration follows the barometric law, so that

$$\rho_{sw} = \rho_{fw} + \rho_{s,0} \exp\left[-\frac{gz}{2R_sT}\right] ,$$

where R_s is the gas constant for the salt (factor 2 accounts for dissociation) and $\rho_{s,0}$ is a constant specified by the density at the surface (at $z = 0$). Note that z points upwards, so that the density is larger at greater depth.

1. Discuss the salt concentration profile in the oceans. Under what circumstances would you expect the exponential and the constant profile, respectively?
2. Compute the difference $h - H$ for the exponential profile.
3. Discuss your findings.

Remark: Not all information on the web that you might find on this issue is correct (the same is true for any other topic, of course).

21.17. Desalination III

Assume that the salt concentration in a salt water lake follows the barometric law $\rho_s = \rho_{s,0} \exp\left[-\frac{gz}{2R_sT}\right]$ (salt density increasing with depth).

A pipe is closed at one end with a semipermeable membrane which only allows water to pass. The pipe is pressed vertically into the lake. The temperature of the lake is 4°C, and the salt water at the surface contains 20 g sodium chloride (NaCl) per litre. For the following, assume that the density of salt water is given by $\rho_{sw} = \rho_{fw} + \rho_s$ where $\rho_w = 1000\frac{\mathrm{kg}}{\mathrm{m}^3}$.

1. To what height H_1 must the pipe be immersed, before fresh water passes the membrane?
2. Compute the freshwater height h as a function of sea water height H.
3. Is it possible, that both, sea water and fresh water have the same height, $h = H$?

21.18. Separation
Consider a mixture of three ideal gases, say oxygen, nitrogen and carbon dioxide. Compute the minimum work required to

1. Separate the carbon dioxide from the two other gases
2. Separate all three components.

21.19. Partial Separation of a Binary Gas Mixture II
Some carbon dioxide is to be separated from a mixture of nitrogen and carbon dioxide with mole fraction $X_{CO_2} = 0.0205$. For this, the mixture is pressurized to a pressure of 50 bar, and then flows past a membrane, which allows only CO_2 to pass. The CO_2 pressure on the back of the membrane is 1 bar. Determine:

1. The mole fraction of CO_2 in the exiting mixture, in the best case.
2. The percentage of CO_2 separated from the mixture.
3. The change of the entropy of mixing.
4. The minimum separation work per mole of CO_2, when the environment temperature is $T_0 = 300\,\mathrm{K}$.

21.20. Removal of Carbon Dioxide from the Atmosphere
From http://www.virginearth.com/ (2007): *The Virgin Earth Challenge is a prize of \$25m for whoever can demonstrate to the judges' satisfaction a commercially viable design which results in the removal of anthropogenic, atmospheric greenhouse gases so as to contribute materially to the stability of Earth's climate.* From Wikipedia: *The prize will be awarded to the first scheme that is capable of removing one billion metric tons of carbon dioxide from the atmosphere per year for 10 years.*

Let's evaluate the goal thermodynamically, by computing how much work is necessary.

1. The Earth radius is 6370 km, the pressure at ground level is 1.01325 bar and the gravitational acceleration is $9.81\frac{\mathrm{m}}{\mathrm{s}^2}$. Estimate mass and mole number of Earth's atmosphere.
2. In January 2014, the mole fraction of CO_2 in the atmosphere was 397.80 ppm, up from 393.14 ppm in January 2012 (data from http://co2now.org/). The pre-industrial level was 284 ppm. Determine mole number and mass of CO_2 in the atmosphere, the amount added in the past year, and the amount added since industrialization began.
3. The yearly emissions from fossil fuels and cement production are 33.5 Gt of CO_2. Compare this number to the amount added to the atmosphere computed above. Where is the remaining CO_2 going?

4. Assume that there is a winner of the competition, the device is built, and 1 billion tons of CO_2 are removed in one year. Determine the new mole fraction of CO_2 after the year.
5. Compute the minimum work required to remove 10 billion tons from the atmosphere per year (assume $T = 290\,\mathrm{K}$ and January 2014 composition), and compare to the world energy consumption of about 16 TW, and the world generation of electric power of about 2.5 TW. Also compute the minimum work required to remove the amount added to the atmosphere per year. To simplify, consider a binary mixture of 'air molecules' and CO_2 molecules.
6. Discuss all results and also the question of irreversibilities in the processes.