Homogeneous mixtures (solutions) of two or more components: ideal mixtures, or $T > T_C$ for the “upward bulged” $\Delta U$, or small concentration of one of the components (the gain in entropy prevents the system from phase separation). The latter case - dilute solutions. Treatment of dilute solutions is simplified by the fact that we can neglect the interactions between the solute molecules – the solute molecules are always surrounded by the solvent molecules. As a result, we can get many useful quantitative results.

- Osmosis
- Equilibrium between different phases of dilute solutions.

**Example of a dilute solution:** When an ionic solid (e.g., KCl) is placed into water, it dissolves (“+” and “-” ions separate and move freely in the liquid). This separation of ions is driven by the entropy: though the energy of ions in the solution is higher than in an ionic solid, the entropy is much greater, so that their Gibbs free energy is lower and the solid dissolves.
Solvent and Solute Chemical Potentials

To get the quantitative results, we need the equation for the Gibbs free energy of a dilute solution in terms of the number of solvent and solute molecules ($N_A$ and $N_B$, respectively).

$$G = N_A \mu_A(T, P) + N_B \mu_B(T, P)$$

Let’s start with pure solvent:

$$G = N_A \mu_A^0(T, P) \quad \mu_A^0 = \left( \frac{\partial G}{\partial N_A} \right)_{T,P}$$

is the chemical potential of the pure solvent

Now let’s add one B molecule at fixed $T$ and $P$:

$$dG = dU + PdV - TdS$$

does not depend on $N_A$

$dU$: for short-range interactions, depends on the # of “nearest-neighbour” molecules $A$.

$PdV$: $dV$ is the volume occupied by one molecule $B$.

$TdS$: $dS = k_B \ln N_A + \text{terms independent of } N_A$ (the change in $\Omega_A$ is proportional to $N_A$)

Thus:

$$dG = f(T, P) - k_B T \ln N_A$$

adding one $B$ molecule

(for an ideal dilute solution, where all the molecules interact the same way, $f(T,P) = \mu^0(T,P)$, where $\mu^0(T,P)$ is the chemical potential of a system of pure B molecules – see Pr. 5.75)

Adding two $B$ molecules:

$$dG = 2f(T, P) - 2k_B T \ln N_A + k_B T \ln 2$$

the $B$ molecules are indistinguishable, and we have to divide the multiplicity by 2, or, in general, by $N_B$!
Solvent and Solute Chemical Potentials (cont.)

If we keep adding $B$ molecules:  
\[ dG = N_B f(T,P) - N_B k_B T \ln N_A + k_B T \ln N_B! \]
\[ \approx N_B f(T,P) - N_B k_B T \ln N_A + N_B k_B T (\ln N_B - 1) \]

\[ G = N_A \mu_A^0(T,P) + N_B f(T,P) - N_B k_B T \ln N_A + N_B k_B T (\ln N_B - 1) \]

- adding solute molecules reduces the chemical potential of the solvent (this works for all solutions, including the ideal ones)

\[ \mu_{\text{solute}} = \left( \frac{\partial G}{\partial N_A} \right)_{T,P,N_B} = \mu_{\text{solute}}^0(T,P) - k_B T \frac{N_{\text{solute}}}{N_{\text{solvent}}} \]

\[ \mu_{\text{solute}}^0(T,P) \text{ - the chem. potential of pure solvent} \]

\[ \mu_{\text{solute}} = \left( \frac{\partial G}{\partial N_B} \right)_{T,P,N_A} = f(T,P) + k_B T \ln \left( \frac{N_{\text{solute}}}{N_{\text{solvent}}} \right) \]

- and increases the chemical potential of solute

Both quantities depend on the ratio of $N_{\text{solute}} / N_{\text{solvent}} (=x)$.

\[ m_{\text{solute}} = \frac{\text{moles of solute}}{\text{kilogram of solvent}} \]

- the molality of the solute (units: molar=1 mol/kg)

Values of $\mu_{\text{solute}}^0$ - the chemical potential of the solute under the “stangard conditions” ($m_B = 1$) - are tabulated.
Osmosis

Two systems, \(A\) and \(B\), are separated by a **semi-permeable** membrane: the membrane allows free passage of **solvent** molecules, but does not allow movement of **solute** molecules.

In biological cells, a semipermeable membrane allows water to pass through it, but **not** ions (e.g., \(\text{Na}^+\), \(\text{Ca}^{++}\), \(\text{Cl}^-\)) and **not** larger molecules (e.g., hydrocarbons). Large quantities of water molecules constantly move across cell membranes by diffusion, but net movement of water into or out of cells is negligible (an amount of water equivalent to roughly 250 times the volume of the cell diffuses across the red blood cell membrane **every second**; the cell doesn't lose or gain water because equal amounts go in and out).

The chemical potential of the solvent **decreases** in the presence of the solute, but **increases** with pressure:

\[
\mu_{\text{solvent}} = \left( \frac{\partial G}{\partial N_{\text{solvent}}} \right)_{T, P, N_B} = \mu_{\text{solvent}}^0 (T, P) - k_B T \frac{N_{\text{solute}}}{N_{\text{solvent}}}
\]

If two solutions with different solute concentrations are separated by the membrane, the solvent molecules will flow from the solution with the lower solute concentration (higher \(\mu_{\text{solvent}}\)) into the solution with higher solute concentration (lower \(\mu_{\text{solvent}}\)). The process will be terminated when the pressure difference washes away the difference in \(\mu_{\text{solvent}}\). The net movement of solvent across a selectively permeable membrane driven by a difference in solute concentrations on the two sides of the membrane is called **osmosis**.

**Microscopic view:** solvent molecules are bombarding the membrane on both sides, but more frequently on the side where the solvent is more concentrated and the solute – less concentrated.
Osmotic Pressure

To reach equilibrium (i.e. to prevent the flow of solvent), some additional, **osmotic pressure** must be applied.

\[ \mu_{A,\text{solvent}} = \mu_{B,\text{solvent}} \]

\[ \mu_{\text{solvent}}(T, P_B) = \mu_{\text{solvent}}(T, P_A) - k_B T \frac{N_{\text{solute}}}{N_{\text{solvent}}} \]

For a small \( \Delta P \):

\[ \mu_{\text{solvent}}(T, P_B) = \mu_{\text{solvent}}(T, P_A) + (P_B - P_A) \frac{\partial \mu_{\text{solvent}}}{\partial P} = \frac{(P_B - P_A) \partial \mu_{\text{solvent}}}{\partial P} = k_B T \frac{N_{\text{solute}}}{N_{\text{solvent}}} \]

(\text{the net flow of solvent stops when } \Delta \mu \text{ due to } \Delta N_{\text{solute}} \text{ is compensated by } \Delta \mu \text{ due to } \Delta P)

\[ \frac{\partial \mu_{\text{solvent}}}{\partial P} = \frac{\partial}{\partial P} \left( \frac{G_{\text{solvent}}}{N_{\text{solvent}}} \right)_{T,N} = \left[ dG = -SdT + VdP + \mu dN \right] = \frac{1}{N_{\text{solvent}}} \frac{\partial G_{\text{solvent}}}{\partial P} = \frac{1}{N_{\text{solvent}}} \frac{\partial G_{\text{solvent}}}{\partial N} = \frac{V_{\text{solvent}}}{N_{\text{solvent}}} \]

**Van’t Hoff’s formula for osmotic pressure.**

\( n_{\text{solute}} \) – the number of moles of solute in volume \( V \)

The osmotic pressure is exactly the same as the pressure of an ideal gas of the same concentration as the solute (because the density dependence of).

\[ P_B - P_A = k_B T \frac{N_{\text{solute}}}{V} = \frac{n_{\text{solute}}}{V} \frac{RT}{V} \]

The membrane does not allow salt ions or sugar to pass across.

Each mole of NaCl dissociates into one mole of Na\(^+\) ions and one mole of Cl\(^-\) ions. Thus, there is no net movement of water across the membrane.

\[ 0.5M \text{ NaCl} \quad 1M \text{ glucose} \]

\[ \text{NaCl} \rightarrow \text{Na}^+ + \text{Cl}^- \]
**Examples:**

The osmotic pressure between a pure solvent and a solution of 1 mole of solute in 1 liter of solvent will be

\[
P_B - P_A = \frac{n_{solute}RT}{V} = \frac{1\text{ mol} \times 8.3\text{ J/(K} \cdot \text{mol}) \times 300\text{ K}}{1\times 10^{-3}\text{ m}^3} \approx 2.5 \times 10^6\text{ Pa} = 25\text{ bar}
\]

**Problem:** Find \(P_{\text{osmosis}}\) for a 5% solution of sugar \(C_{12}H_{22}O_{11}\) in water at \(T=17^0\text{C}\).

Molar weight of sugar: 342 g/mol. The total weight of sugar dissolved in 1 m³ of water – 50 kg. Number of moles of sugar in 1 m³ of solution:

\[
\frac{n_{solute}}{V} = \frac{50\text{ kg}}{342\text{ g/mol}} = \frac{1\text{ m}^3}{342\text{ g/mol} \times 1\text{ m}^3}
\]

\(P_{\text{osmosis}} = \frac{n_{solute}RT}{V} = \frac{50\text{ kg}}{342\text{ g/mol} \times 1\text{ m}^3} \times 8.3\text{ J/(K} \cdot \text{mol}) \times 300\text{ K} \approx 3.5 \times 10^5\text{ Pa} = 3.5\text{ bar}
\]

**Problem:** At what temperature the osmotic pressure of 2% solution of NaCl in water would be 15 bar? 75% of NaCl molecules are dissociated in the solution.

Molar weight of NaCl: 59 g/mol. The total weight of NaCl dissolved in 1 m³ of water – 20 kg. Number of moles of NaCl in 1 m³ of solution:

\[
\frac{n_{solute}}{V} = \frac{20\text{ kg}}{59\text{ g/mol}} = \frac{1\text{ m}^3}{59\text{ g/mol} \times 1\text{ m}^3}
\]

\[
T = \frac{P_{\text{osmosis}}V}{(1 + \alpha)n_{solute}R} = \frac{15 \times 10^5\text{ Pa} \times 59\text{ g/mol} \times 1\text{ m}^3}{(1 + 0.75) \times 20\text{ kg} \times 8.3\text{ J/(K} \cdot \text{mol})} = 303\text{ K}
\]
Osmotic Pressure in Biological Cells

The cell membrane being semi-permeable, makes osmosis one important phenomenon that must be taken into account by all living organisms.

In a typical biological cell, there are ~ 200 H2O molecules per each solute molecule (a reasonably dilute solution). Volume occupied by 1 mole of water - 18 cm³ /mol, thus

\[
\frac{n_{solute}}{V} = \left( \frac{1}{200} \right) \left( \frac{10^6 \text{ g/m}^3}{18 \text{ g/mol}} \right) = 278 \text{ mol/m}^3
\]

\[
P_B - P_A = \frac{n_{solute}RT}{V} = 278 \text{ mol/m}^3 \times 8.3 \text{ J/mol} \cdot \text{K} \times 300 \text{ K} = 6.9 \times 10^5 \text{ N/m}^2 \approx 7 \text{ bar}
\]

If we put a cell into pure water, it will absorb water by osmosis until the pressure inside exceed the pressure outside by ~ 7 bar!!!.

**Plant cells** have a rigid cell wall made of cellulose. This wall prevents the cell from bursting due to osmosis. The osmotic pressure for many plants can be as high as 20 bar, it helps to lift water in the trunks of tall trees (e.g., eucalyptus).

**Animal cells** do not have strong cell wall, that’s why animal organisms need to carefully control the osmotic pressure to protect a cell from shrinking and bursting. Typically, these mechanisms are efficient only over a narrow pressure range. For that reason many organisms are specialized to a certain environment, like fresh water or salt water. More complex organisms have developed a skin, which roughly blocks the penetration of liquids from the outside to the inner part of the body.
Osmosis and Red Blood Cells

The fluids flowing in the inner part of an organism like the blood plasma must have a concentration of solutes that are within a very narrow range. The Figure below shows what happens to the red blood cells immersed in solutions of varying molality.

**Isotonic** - the cells were diluted in serum. Blood serum is isotonic with respect to the cytoplasm, and red cells in that solution assume the shape of a biconcave disk.

**Hypotonic** - the cells in serum were diluted in water: at 200 milliosmols (mOs), the cells are visibly swollen and have lost their biconcave shape, and at 100 mOs, most have swollen so much that they have *ruptured*, leaving the red blood cell ghosts.

**Hypertonic** - A concentrated solution of NaCl was mixed with the cells and serum to increase osmolarity: at 400 mOs and especially at 500 mOs, water has flowed out of the cells, causing them to collapse and assume the spiky appearance.

Washing out salts from the organism results in over inflation and bursting the cells.

Dehydration results in shrinking of cells.
Reverse Osmosis

*Reverse osmosis* – a water flow through a semipermeable membrane from higher to lower concentrations. Normal osmosis cannot be used for water treatment, because the water is moving from less contaminated volume into more contaminated volume. We're interested in *reversing* the direction. Osmosis can be reversed if sufficient pressure ($P > P_{osmosis}$) is applied to the membrane from the concentrated side of the membrane. In this process the semipermeable membrane essentially acts as a filter for the water to pass through, and in fact reverse osmosis is sometimes called "ultrafiltration." The reverse osmosis is used to obtain potable water from sea water.
Equilibrium btw Different Phases of Dilute Solutions

By considering the equilibrium between two phases of a dilute solution, we can quantify shifts of the boiling and freezing points as a function of the solute concentration.

In equilibrium, the chemical potentials of solvent (as well as of solute) are the same in both phases. For pure solvent in phases I and II:

$$\mu_{0,I}(T_0, P_0) = \mu_{0,II}(T_0, P_0)$$

this equation determines the shape of the coexistence curve on the $P,T$ plane.

For coexistence of two phases of dilute solution (we consider only solvent):

$$\mu_{0,I}(T, P) - k_B T \left( \frac{N_B}{N_A} \right)_I = \mu_{0,II}(T, P) - k_B T \left( \frac{N_B}{N_A} \right)_{II}$$

$$\mu_{0,I}(T_0, P_0) + (P - P_0) \frac{\partial \mu_{0,I}}{\partial P} + (T - T_0) \frac{\partial \mu_{0,I}}{\partial T} - k_B T \left( \frac{N_B}{N_A} \right)_I = \mu_{0,II}(T_0, P_0) + (P - P_0) \frac{\partial \mu_{0,II}}{\partial P} + (T - T_0) \frac{\partial \mu_{0,II}}{\partial T} - k_B T \left( \frac{N_B}{N_A} \right)_{II}$$

By expanding $\mu_{0,I}$ and $\mu_{0,II}$ near $T_0, P_0$:

$$\frac{\partial \mu_0}{\partial P} = v_{\text{solvent}}$$

$$\frac{\partial \mu_{0,II}}{\partial T} = -s_{\text{solvent}}$$

where $v_{\text{solvent}}$ and $s_{\text{solvent}}$ are the volume and entropy per one molecule of solvent, respectively.
Equilibrium btw Different Phases of Dilute Solutions (cont.)

\[ \Delta T = k_B \left( \frac{N_B}{N_A} \right)_I - \left( \frac{N_B}{N_A} \right)_{II} \]

\[ s_{II} - s_I = \frac{q}{T} \]

\( q \) is the latent heat of transferring one molecule of solvent from phase I to phase II

\[ (v_I - v_{II}) \Delta P + \frac{q}{T} \Delta T = k_B T \left( \frac{N_B}{N_A} \right)_I - \left( \frac{N_B}{N_A} \right)_{II} \]

**I – liquid, II - gas**

\( v_1 \ll v_2, \quad q = L_{\text{vap}} > 0, \quad [N_B/N_A]_1 > [N_B/N_A]_2 \)

Typically, when we evaporate the solution, the concentration of a solute in vapor is less than in liquid, and the coexistence line shifts to the right: the **boiling point of the solvent is raised by the presence of the solute.**

**I – solid, II - liquid**

\( v_1 < v_2, \quad q = L_{\text{melt}} > 0, \quad [N_B/N_A]_1 < [N_B/N_A]_2 \)

Typically, when we freeze the solution, the concentration of a solute in solid is less than in liquid, and the coexistence line shifts to the left: the **freezing point of the solvent is lowered by the presence of the solute.**

In both cases, the entropy of mixing increases the stability of the liquid and makes the \( T \) range where the liquid exists broader.
Example: adding of ethylene glycol (antifreeze) in automobile cooling system protects against freezing by lowering the freezing point and permits a higher operating temperature by raising the boiling point.

Illustration of the shift of the freezing point in terms of the chemical potential (again, the assumption is that the concentration of the solute in ice is negligible in comparison to that in the solution).
Vapor Pressure for a Dilute Solution

Let’s consider a dilute solution at its boiling point, when liquid I is in equilibrium with gas II.

Simplifications: let’s assume that the solute does not evaporate at all: $N_B(II) = 0$ (this is a good approximation e.g., for salt dissolved in water), for liquid it is negligibly small, $v_I = 0$:

$$ (v_I - v_{II}) \Delta P + \frac{q}{T} \Delta T = k_B T \left[ \left( \frac{N_B}{N_A} \right)_I - \left( \frac{N_B}{N_A} \right)_{II} \right] $$

$$ -v_{gas} \Delta P + \frac{q}{T} \Delta T = k_B T \left( \frac{N_B}{N_A} \right)_{liq} $$

The volume per particle for the gas phase $v_{gas} \approx k_B T/P_0$, $\Delta T = 0$ (we are looking for a change in the saturated vapor pressure at $T = const$)

$$ -(P - P_0) \frac{k_B T}{P_0} = k_B T \left( \frac{N_B}{N_A} \right)_{liq} $$

the pressure difference between the saturated vapor above the surfaces of liquid pure solvent ($P_0 = P_{pure\ solvent}$) and liquid dilute solution ($P = P_{solution}$)

**Raoult’s law: the pressure of saturated vapor decreases with increasing solute concentration.** Presence of a solute reduces the number of solvent molecules at the surface of the liquid, and the solvent molecules escape into the vapor less frequently.
Example:

1 kg of seawater contains 35g of NaCl, which is approx. 1.2 moles (no ion dissociation?). The shift of the vapor pressure of seawater in comparison with the saturated vapor pressure above the surface of pure water is insignificant:

\[
\frac{P_{\text{solution}} - P_{\text{pure solvent}}}{P_{\text{pure solvent}}} = \left( \frac{N_{\text{solute}}}{N_{\text{solvent}}} \right)_{\text{liquid}} = -\frac{1.2 \text{ mol/kg}}{(1\text{ kg}/18\text{ g} \cdot \text{mol}^{-1})} = -0.022
\]
Boiling and Freezing Temperatures of a Dilute Solution

The difference in the values of the boiling temperature of liquid pure solvent \(T_{\text{pure solvent}} = T_0\) and liquid dilute solution \(T_{\text{solution}}\):

\[
-v_{\text{gas}} \Delta P + \frac{q}{T} \Delta T = k_B T \left( \frac{N_B}{N_A} \right)_{\text{liq}} \rightarrow (T - T_0) \frac{q}{T_0} = k_B T_0 \left( \frac{N_B}{N_A} \right)_{\text{liq}}
\]

\[q = \frac{L_{vap}}{N_A}\] where \(L_{vap}\) is the latent heat of vaporization:

Dissolving a solute in a solvent increases the boiling temperature of the solution:

\[
T_{\text{boil}} - T_{\text{boil,0}} = \frac{N_{\text{solute}} k_B T_0^2}{L_{vap}} = \frac{n_{\text{solute}} RT_0^2}{L_{vap}}
\]

Similarly, for the freezing temperature, if the solid phase is pure solvent:

\[
T_{\text{freezing}} - T_{\text{freezing,0}} = -\frac{N_{\text{solute}} k_B T_0^2}{L_{\text{melt}}} = -\frac{n_{\text{solute}} RT_0^2}{L_{\text{melt}}}
\]

- presence of a solute decreases the freezing temperature

The shift of the freezing point is usually greater than the shift of the boiling point because \(L_{vap} > L_{melt}\)
Example: seawater

1 kg of seawater contains 35g of NaCl, which is approx. 1.2 moles. Therefore, the **boiling temperature** of seawater at normal pressure is increased in comparison with the boiling temperature of pure water ($T_0=373$ K) by:

$$ (T - T_0)_{boil} = \frac{n_{solute} R T_0^2}{L_{vap}} = \frac{(1.2 \text{ mol})(8.3 \text{ J/mol} \cdot \text{K})(373 \text{ K})^2}{2260 \text{ kJ/kg}} \approx 0.6 \text{ K} $$

Note that the shift of the **freezing temperature** of seawater towards lower temperatures is greater:

$$ (T - T_0)_{freezing} = -\frac{n_{solute} R T_0^2}{L_{melt}} = -\frac{(1.2 \text{ mol})(8.3 \text{ J/mol} \cdot \text{K})(273 \text{ K})^2}{333 \text{ kJ/kg}} \approx -2.2 \text{ K} $$