Mixtures: Solutions and Colloids
- Solutions – homogeneous mixtures (a single phase)
- Colloids – heterogeneous mixtures (two or more phases)

13.1 Types of Solutions and Solubility
- **Solvent** – the substance that dissolves; usually the most abundant component of the mixture; has the same physical state as the solution
- **Solute** – the substance that is dissolved
- **Solubility (S)** – the maximum amount of solute that can be dissolved in a given amount of solvent or solution
- **Concentration** of solute – various units are used

### Intermolecular Forces in Solution
- All types of IFs in pure substances also occur in solutions (in addition, ion-dipole forces are very common)
- **Ion-dipole** forces – present in solutions of ionic compounds in polar solvents such as H₂O
  - **Hydration** (solvation)
    - The water dipoles pull the ions away from theionic crystal and surround them (typical coord. numbers 4 or 6)
    - There is a short range order around the ions consisting of H-bonded shells of water molecules

- **Dipole-dipole** forces – present in solutions of polar molecules in polar solvents such as H₂O
- **H-bonding** forces – present in solutions of O- and N-containing molecules (sugars, alcohols, amino acids, …) in protic solvents such as H₂O
- **Ion-induced dipole** forces – solutions of ionic compounds in less polar or non-polar solvents
- **Dipole-induced dipole** forces – present in solutions of polar molecules in non-polar solvents or non-polar molecules in polar solvents
- **Dispersion** forces – present in all solutions (most important for solutions of non-polar molecules in non-polar solvents)

### Example:
- Water dissolves well alcohols (ROH) with short hydrocarbon chains (R) → methanol, ethanol, …
- Strong H-bonding IFs in the solute and the solvent are replaced with strong solute-solvent H-bonding IFs
- Water does not dissolve well alcohols (ROH) with long hydrocarbon chains (R) → hexanol, …
- Strong H-bonding in water is replaced with weaker IFs between the water dipole and the large non-polar hydrocarbon chains (R) → (H-bonding with the OH part of the alcohol is a smaller fraction of the total IFs)

### Example:
What is a better solvent for diethyl ether (CH₃CH₂-O-CH₂CH₃), water or propanol (CH₃CH₂CH₂OH)?
- Both water and propanol interact with ether through H-bonding
- Propanol and ether interact well through dispersion forces (similar non-polar hydrocarbon chains)
- Water can’t interact well through dispersion forces with the hydrocarbon portion of ether
⇒ Propanol is a better solvent for ether
• Soaps – Na⁺ salts of long chain carboxylic acids
  – Long, non-polar hydrocarbon “tail” → hydrophobic
  – Small, polar-ionic carboxyl “head” → hydrophilic
  – The polar head dissolves in water; the non-polar tail dissolves in grease → washing action
• Detergents – contain surfactants (surface-active compounds) → similar to soaps

Tail

Head

Sodium stearate C_{18}H_{35}COONa

• Liquid solutions – the solvent is a liquid
  – Solid-liquid and liquid-liquid solutions
  • Some salts and polar molecular compounds dissolve well in water and short chain alcohols
  • Less polar solids dissolve well in less polar solvents like acetone, chloroform, ether, …
  • Non-polar substances dissolve best in non-polar solvents like hexane, benzene, …
  – Gas-liquid solutions
    • Non-polar gases have poor solubility in water
    • Some gases dissolve in water through chemical reactions (HCl, CO₂, SO₂, …)
• Gaseous solutions – the solvent is a gas
  – Gas-gas solutions – gases mix in all proportions

Example:
Quick cleaning of laboratory glassware:
  ➢ Cleaning a sample tube with a salt residue
    Wash with water → dissolves salt (ion-dipole forces)
    Wash with ethanol → dissolves water (H-bonding)
    Wash with acetone → dissolves ethanol (dipole-dipole, dispersion forces)
  Dry → acetone evaporates easily (low T_b)
  ➢ Cleaning a sample tube with an oily residue
    Wash with hexane → dissolves oil (dispersion forces)
    Wash with acetone → dissolves hexane (dispersion and dipole-induced dipole forces)
  Dry → acetone evaporates easily (low T_b)

13.2 Energy Changes in the Solution Process
• Solution cycle – the solution process can be divided into three steps:
  1) Separation of solute particles to make room for the solvent – endothermic (energy is needed to overcome the IFs of attraction)
  2) Separation of solvent particles to make room for the solute particles – endothermic (energy is needed to overcome the IFs of attraction)
  3) Mixing of solvent and solute particles – exothermic (solute-solvent IFs lower the energy)

\[
\Delta H_{\text{soln}} = \Delta H_{\text{solute}} + \Delta H_{\text{solvent}} + \Delta H_{\text{mix}}
\]
Solutions of Ionic Solids
- For dilute solutions of ionic solids, the solute separation has $\Delta H$ equal to the lattice enthalpy:
  \[ MX(s) \rightarrow M^+(g) + X^-(g) \quad \Delta H_{\text{lattice}} = \Delta H_{\text{solute}} > 0 \]
- The hydration of the separated solute ions is a combination of steps 2 and 3 in the solution cycle → (solvent separation + mixing)
  - Heat (enthalpy) of hydration ($\Delta H_{\text{hydr}}$) – $\Delta H$ for hydration of separated gaseous ions:
    \[ M^+(g) + X^-(g) \rightarrow M^+(aq) + X^-(aq) \quad \Delta H_{\text{hydr}} = \Delta H_{\text{solvent}} + \Delta H_{\text{mix}} \]
    \[ \Rightarrow \Delta H_{\text{soln}} = \Delta H_{\text{solute}} + \Delta H_{\text{hydr}} \]

Individual ionic heats of hydration – $\Delta H$ for the hydration of 1 mol of separated gaseous cations (or anions):
- $\Delta H_{\text{hydr}}$ of ions is always exothermic ($\Delta H_{\text{hydr}} < 0$) because the ion-dipole forces that replace some of the H-bonds in water are stronger.
- The overall heat of hydration is a sum of the heats for the cations and the anions
  - Trends in $\Delta H_{\text{hydr}}$ of ions (same as for $\Delta H_{\text{lattice}}$)
    - $\Delta H_{\text{hydr}}$ is larger (more exothermic) for ions with greater charges and smaller sizes → ions with higher charge density.
    - The charge factor is more important.

Some ionic heats of hydration in kJ/mol:
- Li$^+$(558), Be$^{2+}$(2533), F$^-$(-483)
- Na$^+$(444), Mg$^{2+}$(2003), Al$^{3+}$(-704), Cl$^-$(-340)
- K$^+$(361), Ca$^{2+}$(-1657), Br$^-$(-309)

The sign of $\Delta H_{\text{hydr}}$ is hard to predict, since both $\Delta H_{\text{lattice}}$ and $\Delta H_{\text{hydr}}$ depend on the ionic charge and size and tend to cancel each other’s effects.

Example: NaCl
- $\Delta H_{\text{lattice}} = 787$ kJ/mol
- $\Delta H_{\text{hydr}} = (-444) + (-340) = -784$ kJ/mol
- $\Delta H_{\text{soln}} = (787) + (-784) = +4$ kJ/mol

The Tendency Toward Disorder
- $\Delta H_{\text{soln}} < 0$ favors the solution process since the total energy of the system is lowered; but many ionic solids have $\Delta H_{\text{soln}} > 0$ and still dissolve readily in water.
- There is a second factor that affects the solution process and acts in addition to the enthalpy factor
  - Disorder – systems have a natural tendency to become more disordered
  - Entropy – a measure of the disorder in the system
  - Mixing leads to greater disorder and ↑ entropy

13.3 Solubility as an Equilibrium Process
- Typically solutes have limited solubility in a given solvent
  - The solution process is countered by recrystallization of the dissolved solute
  - Dynamic equilibrium – the rates of dissolution and recrystallization become equal
  - Solute (undissolved) ↔ Solute (dissolved)
  - Saturated solution – no more solute can be dissolved (can be produced by equilibrating the solution with an excess of the solute; the excess solute can be filtered out after saturation)
Molar solubility \((S)\) – the concentration of the saturated solution in \(\text{mol/L}\).
- Unsaturated solution – more solute can be dissolved
- Supersaturated solution – the concentration is higher than the solubility, \(S\) (unstable, non-equilibrium state; disturbances or addition of seed crystal lead to crystallization)

**Effect of Temperature on Solubility**
- Most solids are more soluble at higher \(T\) due to their endothermic \((+)\) \(\Delta H_{\text{soln}}\)
  - \(\Delta H_{\text{soln}}\) means that heat is absorbed during dissolution (the heat can be viewed as a reactant)

- Some solids are more soluble at higher \(T\) despite their exothermic \((-)\) \(\Delta H_{\text{soln}}\)
  - Tabulated \(\Delta H_{\text{soln}}\) values refer to the standard state (1M solution), but saturated solutions can be much more concentrated
  - At very high concentrations the hydration process is hindered so \(\Delta H_{\text{hydr}}\) becomes less negative; thus \(\Delta H_{\text{soln}}\) can change dramatically and even switch signs from \((-)\) to \((+)\)

- Gases are less soluble in water at higher \(T\) due to their exothermic \((-)\) \(\Delta H_{\text{soln}}\)
  - \(\Delta H_{\text{soln}}\) is \((-)\) since \(\Delta H_{\text{sol}} = 0\) and \(H_{\text{hydr}} < 0\)
  - Gas + Water \(\leftrightarrow\) Saturated solution + heat
  - Increasing \(T\) provides the heat needed for the reverse reaction to proceed (\(S\) ↓)

**Effect of Pressure on Solubility**
- Pressure has little effect on the solubility of solids and liquids (low compressibility)
- The molar solubility of gases \((S_{\text{gas}})\) increases with increasing their partial pressures \((P_{\text{gas}})\) over the solution (collisions with liquid surface ↑)

**Henry’s law** - \(S_{\text{gas}}\) is directly proportional to \(P_{\text{gas}}\)

\[ S_{\text{gas}} = k_{\text{H}} \times P_{\text{gas}} \]

- \(k_{\text{H}}\) – Henry’s law constant (depends on the gas, solvent and \(T\))

**Example:** What is the concentration of CO₂ in raindrops at 20°С in air that has 1.0% by volume CO₂? \([k_{\text{H}}(\text{CO}_2, 20\degree \text{C}) = 2.3 \times 10^{-2} \text{ mol/L.atm}]\)

\[ P_{\text{CO}_2} = \chi_{\text{CO}_2} \times P_{\text{tot}} = 0.010 \times 1.0 \text{ atm} = 0.010 \text{ atm} \]

\[ S_{\text{CO}_2} = k_{\text{H}} \times P_{\text{CO}_2} = 2.3 \times 10^{-2} \text{ mol/L.atm} \times 0.010 \text{ atm} \]

\[ = 2.3 \times 10^{-4} \text{ mol/L} \]

**Table 13.3: Concentration Definitions**

<table>
<thead>
<tr>
<th>Concentration Term</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molarity ((M))</td>
<td>amount (mol) of solute / volume (L) of solution</td>
</tr>
<tr>
<td>Molality ((m))</td>
<td>amount (mol) of solute / mass (kg) of solvent</td>
</tr>
<tr>
<td>Parts by mass</td>
<td>mass of solute / mass of solution</td>
</tr>
<tr>
<td>Parts by volume</td>
<td>volume of solute / volume of solution</td>
</tr>
<tr>
<td>Mole fraction ((x))</td>
<td>amount (mol) of solute / amount (mol) of solute + amount (mol) of solvent</td>
</tr>
</tbody>
</table>

**13.4 Expressing Solute Concentration**
- **Concentration** – the ratio of the quantity of solute to the quantity of solution (or solvent)

**Molarity (\(M\))** – the number of moles of solute per 1 liter of solution

\[ M = \frac{\text{mol of solute}}{\text{liters of solution}} \]

- \(M\) is affected by temperature (the solution volume changes with \(T\), so \(M\) changes too)
- The solution volume is not a sum of the solvent and solute volumes (it must be measured after mixing)

**Molality (\(m\))** – the number of moles of solute per 1 kilogram of solvent

\[ m = \frac{\text{mol of solute}}{\text{kilograms of solvent}} \]

- \(m\) is not affected by temperature (the amounts of solute and solvent don’t change with \(T\))
- The solution volume is not needed; \(m\) can be calculated from the masses of solute and solvent
• $M$ and $m$ are nearly the same for dilute aqueous solutions since 1 L of water is about 1 kg, so (liters of solution) $\approx$ (kg of solvent)

**Example:** Calculate $M$ and $m$ for a solution prepared by dissolving 2.2 g of NaOH in 55 g of water if the density of the solution is 1.1 g/mL.

\[
m = \frac{0.055 \text{ mol NaOH}}{0.055 \text{ kg water}} = 1.0 \text{ mol kg}^{-1} \approx 1.0 \text{ m (molal)}
\]

\[
M = \frac{0.055 \text{ mol NaOH}}{0.0552 \text{ L solution}} = 1.1 \text{ mol L}^{-1} \approx 1.1 \text{ M (molar)}
\]

**Parts of solute by parts of solution**

- **Mass %** – grams of solute per 100 grams of solution $\rightarrow$ % (w/w)

\[
\text{Mass\%} = \frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%
\]

- **ppm** or **ppb** – grams of solute per 1 million or 1 billion grams of solution (for trace components)

**Parts by volume**

- **Volume %** – volume of solute per 100 volumes of solution $\rightarrow$ % (v/v)

\[
\text{Volume\%} = \frac{\text{volume of solute}}{\text{volume of solution}} \times 100\%
\]

- **ppmv** or **ppbv** – volume of solute per 1 million or 1 billion volumes of solution (used for trace gases in air)

**Mole fraction** ($X$) – ratio of the # mol of solute to the total # mol (solute + solvent)

\[
X = \frac{\text{mol of solute}}{\text{mol of solute} + \text{mol of solvent}}
\]

**Example:** Calculate the $X$ of NaOH in a solution containing 2.2 g of NaOH in 55 g of water.

\[
\begin{align*}
2.2 \text{ g NaOH} & = 0.055 \text{ mol NaOH} \\
55 \text{ g H}_2\text{O} & = 3.1 \text{ mol H}_2\text{O} \\
X & = \frac{0.055 \text{ mol}}{0.055 \text{ mol} + 3.1 \text{ mol}} = 0.018
\end{align*}
\]

**Example:** What is the molality of a solution of methanol in water, if the mole fraction of methanol in it is 0.250?

Assume 1 mol of solution:

\[
\begin{align*}
n_{\text{meth}} & = 1 \text{ mol} \times 0.250 = 0.250 \text{ mol} \\
n_{\text{water}} & = 1 - 0.250 = 0.750 \text{ mol}
\end{align*}
\]

\[
0.750 \text{ mol H}_2\text{O} \times \frac{18.0 \text{ g H}_2\text{O}}{1 \text{ mol H}_2\text{O}} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 0.0135 \text{ kg H}_2\text{O}
\]

\[
m = \frac{0.250 \text{ mol methanol}}{0.0135 \text{ kg H}_2\text{O}} = 18.5 \text{ m}
\]

**Example:** A sample of water is $1.1 \times 10^{-6}$ M in chloroform (CH$_3$Cl). Express the concentration of chloroform in ppb. (Assume density of 1.0 g/mL)

\[
1.1 \times 10^{-6} \text{ M} \rightarrow 1.1 \times 10^{-6} \text{ mol CH}_3\text{Cl per 1 L solution}
\]

\[
1.1 \times 10^{-6} \text{ mol CH}_3\text{Cl} \times \frac{50.5 \text{ g CH}_3\text{Cl}}{1 \text{ mol CH}_3\text{Cl}} = 5.6 \times 10^{-5} \text{ g CH}_3\text{Cl per 1 L solution}
\]

\[
1 \text{ L} \rightarrow 1000 \text{ mL} \times \frac{1.0 \times 10^3 \text{ g}}{1 \text{ mL}} = 1.0 \times 10^6 \text{ g solution}
\]

\[
5.6 \times 10^{-5} \text{ g CH}_3\text{Cl} \times 10^9 \text{ ppb} = 56 \text{ ppb}
\]

**Example:** What is the molality of a 1.83 M NaCl solution with density of 1.070 g/mL?

Assume 1 L (10$^3$ mL) of solution:

\[
\rightarrow n_{\text{NaCl}} = 1.83 \text{ mol}
\]

\[
\text{mass of solution} = 10^3 \text{ mL} \times \frac{1.070 \text{ g}}{1 \text{ mL}} = 1070 \text{ g}
\]

\[
\text{mass of NaCl} = 1.83 \text{ mol} \times \frac{58.44 \text{ g NaCl}}{1 \text{ mol}} = 107 \text{ g}
\]

\[
\text{mass of water} = 1070 \text{ g} - 107 \text{ g} = 963 \text{ g} \approx 0.963 \text{ kg}
\]

\[
m = \frac{1.83 \text{ mol NaCl}}{0.963 \text{ kg H}_2\text{O}} = 1.90 \text{ m}
\]
Example: What is the molarity of a 1.20 m KOH solution in water having density of 1.05 g/mL?
Assume 1 kg (1000 g) of solvent (H₂O):

\[ n_{\text{KOH}} = 1.20 \text{ mol} \]

\[ \text{mass of KOH} = 1.20 \text{ mol} \times \frac{56.1 \text{ g KOH}}{1 \text{ mol}} = 67.3 \text{ g} \]

\[ \text{mass of solution} = 1000 \text{ g} + 67.3 \text{ g} = 1067 \text{ g} \]

\[ \text{volume of solution} = \frac{1067 \text{ g} \times \frac{1 \text{ mL}}{1.05 \text{ g}}}{1016 \text{ mL} = 1.02 \text{ L}} \]

\[ M = \frac{1.20 \text{ mol KOH}}{1.02 \text{ L solution}} = 1.18 \text{ M} \]

13.5 Colligative Properties of Solutions

- Colligative properties – depend on the concentration of solute particles but not on their chemical identity
  - The concentration of solute particles depends on the amount of dissolved solute as well as on its ability to dissociate to ions in solution
    - Strong electrolytes – dissociate completely (soluble salts, strong acids and bases)
    - Weak electrolytes – dissociate partially (weak acids and bases)
    - Nonelectrolytes – do not dissociate (many organic compounds)

Nonvolatile Nonelectrolyte Solutions

- No dissociation; no vapor pressure (glucose, sugar, …)

- Vapor pressure lowering (\(\Delta P\)) – the vapor pressure of the solvent over the solution (\(P_{\text{solv}}\)) is always lower than the vapor pressure over the pure solvent (\(P^o_{\text{solv}}\)) at a given temperature

Raoult’s Law – the vapor pressure of the solvent over the solution is directly proportional to the mole fraction of the solvent

- Followed strictly at all concentrations only by ideal solutions

\[ P_{\text{solv}} = X_{\text{solv}} P^o_{\text{solv}} \]

\[ X_{\text{solv}} \leq 1 \Rightarrow P_{\text{solv}} \leq P^o_{\text{solv}} \]

\[ X_{\text{solv}} = 1 - X_{\text{solute}} \Rightarrow P_{\text{solv}} = (1 - X_{\text{solute}}) P^o_{\text{solv}} \]

\[ P_{\text{solv}} = P^o_{\text{solv}} - X_{\text{solute}} P^o_{\text{solv}} \Rightarrow P_{\text{solv}} = X_{\text{solute}} P^o_{\text{solv}} \]

\[ \Delta P = X_{\text{solute}} P^o_{\text{solv}} \]

\[ \Rightarrow \text{The vapor pressure lowering is directly proportional to the mole fraction of the solute} \]

Example: The vapor pressure of water over a solution of a nonelectrolyte is 16.34 torr at 20°C. Determine the mole fraction of the solute, if the equilibrium vapor pressure of water at 20°C is 17.54 torr.

\[ P_{\text{solv}} = 16.34 \text{ torr} \quad P^o_{\text{solv}} = 17.54 \text{ torr} \]

\[ X_{\text{solute}} = ? \]

\[ X_{\text{solute}} = \frac{\Delta P}{P^o_{\text{solv}}} = \frac{(17.54 - 16.34) \text{ torr}}{17.54 \text{ torr}} = 0.0684 \]

- Most real (non-ideal) solutions behave as ideal at low concentrations (less than 0.1 m for nonelectrolytes and less than 0.01 m for electrolytes)

Boiling point elevation (\(\Delta T_b\)) and freezing point depression (\(\Delta T_f\))

- Boiling point elevation: The solution boils at a higher temperature compared to the pure solvent (the solution has lower vapor \(P\) so it needs higher \(T\) to boil)
- Freezing point depression: The solution freezes at a lower temperature compared to the pure solvent
\[
\Delta T_b = T_b - T_f > 0 \quad \Rightarrow \quad \Delta T_b = k_b m
\]
\[
\Delta T_f = T_f - T_j > 0 \quad \Rightarrow \quad \Delta T_f = k_f m
\]
\(k_b\) – boiling point elevation constant
\(k_f\) – freezing point depression constant
\(m\) – molality of solution

**Example:** What is the boiling point of a solution prepared by dissolving 12 g of glucose (MW = 180 g/mol) in 55 g of water? (For water, \(k_b = 0.512 ^\circ C/m\) and \(k_f = 1.86 ^\circ C/m\))

\[
\begin{align*}
12 \text{ g gluc} &\quad 1 \text{ mol gluc} = 0.067 \text{ mol} \quad m = \frac{0.067 \text{ mol gluc}}{0.055 \text{ kg water}} = 1.2 \text{ m} \\
180 \text{ g gluc} &\quad 1 \text{ mol gluc} = 0.067 \text{ mol} \\
\end{align*}
\]
\[\Delta T_b = 0.512 \frac{^\circ C}{m} \times 1.2 \text{ m} = 0.62^\circ C \quad T_b = 100 + 0.62 = 100.62^\circ C\]

**Osmotic pressure (\(\Pi\))**
- **Osmosis** – the flow of solvent through a semipermeable membrane from a less concentrated into a more concentrated solution
- **Semipermeable membrane** – the solute particles can’t pass through

The solvent tends to flow into the solution where the disorder is greater

\[
\Pi = MRT \quad \Pi = (n_{solute}/V_{sola})RT
\]
\(M\) – molarity of solution
\(R\) – gas constant; \(T\) – temperature in K

- \(\Pi\) is the pressure the solute would exert if it were an ideal gas occupying alone the volume of the solution
- Osmosis is essential for controlling the shape and size of biological cells and purifying blood through dialysis
- **Reverse osmosis** – reversing the flow by applying external pressure (used to purify sea water)

**Example:** What is the minimum pressure that must be applied in order to purify a 0.82 M nonelectrolyte solution by reverse osmosis at 25°C?

\[
\begin{align*}
\Pi &= \frac{MRT}{L} \cdot \frac{0.8206 \text{ mol}}{L} \times \frac{1.2 \text{ m}}{0.08206 \text{ mol} \cdot \text{K}} \times 298 \text{ K} \\
\Pi &= 20 \text{ atm}
\end{align*}
\]

→ This pressure is equivalent to a 200 meters (1/8 mile) tall water column!

**Using Colligative Properties to Find the Solute Molar Mass**
- The molar mass of the solute can be obtained by measuring one of the colligative properties of the solution, the mass of the solute and the mass of the solvent (or the volume of the solution)
  - \(\Delta P\) and \(\Delta T_s\) are not very sensitive to changes in the solute concentration (rarely used for molar mass determinations)
  - \(\Delta T_f\) is more sensitive especially when solvents with large \(k_f\) constants are used
  - \(\Pi\) is most sensitive and can be used for substances with low molar solubility such as large biomolecules
Example: The $T_f$ of camphor is 179.80°C and its $k_f$ is 39.7°C/m. When 200.0 mg of a compound (X) are added to 100.0 g of camphor, its freezing point drops to 179.29°C. What is the molar mass of X?

$\Delta T_f = k_f \cdot m \Rightarrow m = \frac{\Delta T_f}{k_f} = \frac{(179.80 - 179.29)\text{°C}}{39.7\text{°C/m}} = 0.013 \text{ mol/kg}$

$\Rightarrow$ Calc. the number of moles of X:

$m = \frac{\text{mol}(X)}{\text{kg(camphor)}} \Rightarrow 0.013 \text{ mol/kg} \times 0.1000 \text{ kg} = 0.0013 \text{ mol}$

$\Rightarrow$ Calc. the molar mass of X:

$MW = \frac{\text{grams}(X)}{\text{mol}(X)} \Rightarrow \frac{0.2000 \text{ g}}{0.0013 \text{ mol}} = 160 \text{ g/mol}$

Volatile Nonelectrolyte Solutions

- No dissociation; both solvent and solute have vapor pressures (mixtures of volatile organic compounds)
- Raoult’s law can be applied to the vapor pressures of both the solute and the solvent

$P_{\text{solv}} = X_{\text{solv}}P^\circ_{\text{solv}} \quad P_{\text{solute}} = X_{\text{solute}}P^\circ_{\text{solute}}$

$\Rightarrow$ The presence of each component lowers the vapor pressure of the other component
- The total pressure over the solution is the sum of the partial pressures of the solute and the solvent

$P_\text{tot} = P_{\text{solv}} + P_{\text{solute}} = X_{\text{solv}}P^\circ_{\text{solv}} + X_{\text{solute}}P^\circ_{\text{solute}}$

Example: The equilibrium vapor pressures of pure benzene and toluene are 95.1 and 28.4 torr, respectively at 25°C. Calculate the total pressure, partial pressures and mole fractions of benzene and toluene over a solution of 1.0 mol of benzene in 3.0 mol of toluene at 25°C.

$X_b = \frac{1.0}{1.0 + 3.0} = 0.25 \quad X_t = \frac{3.0}{1.0 + 3.0} = 0.75$

$P_b = X_bP^\circ_b = 0.25 \times 95.1 \text{torr} = 24 \text{torr}$

$P_t = X_tP^\circ_t = 0.75 \times 28.4 \text{torr} = 21 \text{torr}$

$P_\text{tot} = P_b + P_t = 24 + 21 = 45 \text{torr}$

$X_b^{\text{vap}} = \frac{P_b}{P_\text{tot}} = \frac{24}{45} = 0.53 \quad X_t^{\text{vap}} = \frac{P_t}{P_\text{tot}} = \frac{21}{45} = 0.47$

$\Rightarrow$ The mole fractions of the solute and solvent in the vapor phase are different from those in the liquid phase. The vapor phase is enriched with the more volatile component. Condensation of the vapors leads to a solution which is enriched with the more volatile component.

Electrolyte Solutions

- The solute dissociates to ions
- The number of particles in the solution is greater than the one implied by the solute concentration

$\Rightarrow$ The formulas for the colligative properties must be modified

- van’t Hoff factor ($i$) – accounts for the dissociation of the solute

$i$ is determined experimentally as a ratio of the measured colligative property versus the one expected for a nonelectrolyte

$\Delta P = i(X_{\text{solute}}P^\circ_{\text{solv}}) \quad \Delta T_b = i(k_b m)$

$\Pi = i(MRT) \quad \Delta T_f = i(k_f m)$
– For ideal solutions (very dilute solutions), the ideal value of $i$ represents the number of moles of particles to which a mole of the solute dissociates
– For real solutions, $i$ is smaller than the ideal value
– The deviation is due to clustering of cations and anions (ionic atmosphere) which reduces the “effective” concentration of particles → ($i \times \text{Conc.}$)

**Example:** Select the solution with the higher osmotic pressure: 0.1M NaCl or 0.08M CaCl$_2$

→ Calculate the effective concentrations:

→ 0.1M NaCl → $i \times M = 2 \times 0.1 = 0.2$

→ 0.08M CaCl$_2$ → $i \times M = 3 \times 0.08 = 0.24$ (higher)

⇒ 0.08M CaCl$_2$ has higher $\Pi$ ($\Pi = i \times MRT$)