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

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Intermolecular Forces in Solution

• All types of *IF*s 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 H_2O

– **Hydration** (solvation)

• The water dipoles pull the ions away from the ionic 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

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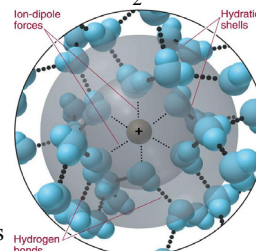
• **Dipole-dipole** forces – present in solutions of polar molecules in polar solvents such as H_2O

• **H-bonding** forces – present in solutions of O- and N-containing molecules (sugars, alcohols, amino acids, …) in protic solvents such as H_2O

• **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)

• The **"like dissolves like rule"** – substances with similar types of *IF*s dissolve in each other well

– Strong solute-solvent *IF*s lead to better solubility (lower the total energy of the system)

– The solute-solvent *IF*s created during dissolution must have comparable strength to the solute-solute and solvent-solvent *IF*s destroyed in this process

Water   Methanol   A solution of water and methanol
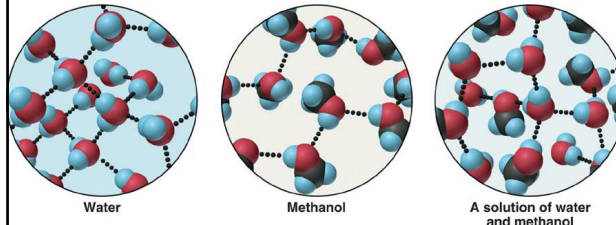
Example:

➤ Water dissolves well alcohols (ROH) with short hydrocarbon chains (R) → methanol, ethanol, …

  ➤ Strong H-bonding *IF*s in the solute and the solvent are replaced with strong solute-solvent H-bonding *IF*s

➤ Water does not dissolve well alcohols (ROH) with long hydrocarbon chains (R) → hexanol, …

  ➤ Strong H-bonding in water is replaced with weaker *IF*s 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 *IF*s)


Methanol   Water   Hexanol

Example:

What is a better solvent for diethyl ether (CH_3CH_2-O-CH_2CH_3), water or propanol ($CH_3CH_2CH_2OH$)?

➤ 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" $\rightarrow$ hydrophobic
  - Small, polar-ionic carboxyl "head" $\rightarrow$ hydrophilic
  - The polar head dissolves in water; the non-polar tail dissolves in grease $\rightarrow$ washing action
- **Detergents** – contain surfactants (surface-active compounds) $\rightarrow$ similar to soaps

Tail   **Head**


Sodium stearate $C_{18}H_{35}COONa$
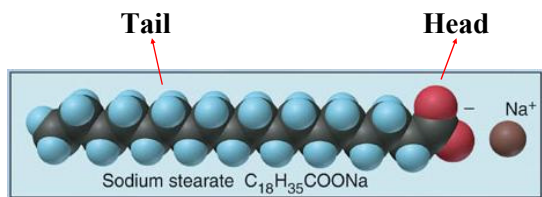
- **Liquid solutions** – the solvent is a liquid
  - Solid-liquid and liquid-liquid solutions
    - Some salts and polar molecular compounds dissolve well in water and short chain alcohols
    - Less polar solids dissolve well in less polar solvents like acetone, chloroform, ether, …
    - Non-polar 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, CO_2, SO_2, …)
- **Gaseous solutions** – the solvent is a gas
  - Gas-gas solutions – gases mix in all proportions

- **Solid solutions** – the solvent is a solid
  - Gas-solid solutions – gas molecules penetrate the crystal lattices of some metals (H_2/Pd, O_2/Cu, …)
  - Solid-solid solutions – homogeneous alloys, waxes, …

  ➤ **Substitutional** alloys – the atoms of one element take some of the positions in the lattice of another element
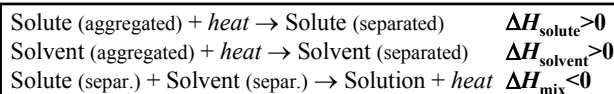 ➤ **Interstitial** alloys – the atoms of one element fit into the gaps of the lattice of another element

Brass
Zinc
Copper
Carbon steel
Carbon
Iron
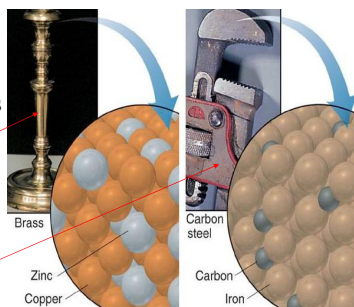
Example:
  Quick cleaning of laboratory glassware:
➤ Cleaning a sample tube with a salt residue
Wash with water $\rightarrow$ dissolves salt (ion-dipole forces)
Wash with ethanol $\rightarrow$ dissolves water (H-bonding)
Wash with acetone $\rightarrow$ dissolves ethanol (dipole-dipole, dispersion forces)
Dry $\rightarrow$ acetone evaporates easily (low T_b)
➤ Cleaning a sample tube with an oily residue
Wash with hexane $\rightarrow$ dissolves oil (dispersion forces)
Wash with acetone $\rightarrow$ dissolves hexane (dispersion and dipole-induced dipole forces)
Dry $\rightarrow$ 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 *IF*s of attraction)
  2) **Separation of solvent particles** to make room for the solute particles – endothermic (energy is needed to overcome the *IF*s of attraction)
  3) **Mixing of solvent and solute particles** – exothermic (solute-solvent *IF*s lower the energy)

Solute (aggregated) + *heat* $\rightarrow$ Solute (separated) $\Delta H_{solute} > 0$
Solvent (aggregated) + *heat* $\rightarrow$ Solvent (separated) $\Delta H_{solvent} > 0$
Solute (separ.) + Solvent (separ.) $\rightarrow$ Solution + *heat* $\Delta H_{mix} < 0$
  - **Heat of solution** (ΔH_{soln}) – the total enthalpy change during the solution cycle (can be either exothermic or endothermic)

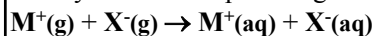$$\Delta H_{soln} = \Delta H_{solute} + \Delta H_{solvent} + \Delta H_{mix}$$
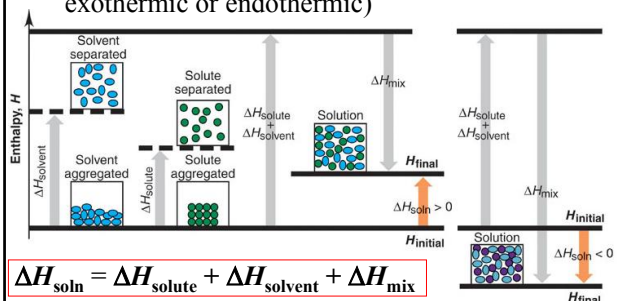
Solutions of Ionic Solids

- For dilute solutions of ionic solids, the solute separation has ΔH equal to the lattice enthalpy

$$MX(s) \rightarrow M^+(g) + X^-(g) \qquad \Delta H_{solute} = \Delta H_{lattice} > 0$$

- The **hydration** of the separated solute ions is a combination of steps 2 and 3 in the solution cycle $\rightarrow$ (solvent separation + mixing)
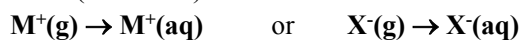 - **Heat (enthalpy) of hydration** (ΔH_{hydr}) – ΔH for hydration of separated gaseous ions

$$M^+(g) + X^-(g) \rightarrow M^+(aq) + X^-(aq)$$
$$\Delta H_{hydr} = \Delta H_{solvent} + \Delta H_{mix}$$
$$\Rightarrow \Delta H_{soln} = \Delta H_{solute} + \Delta H_{hydr}$$
$$\boxed{\Rightarrow \ \Delta H_{soln} = \Delta H_{lattice} + \Delta H_{hydr}}$$

- **Individual ionic heats of hydration** – ΔH for the hydration of 1 mol of separated gaseous cations (or anions)

$$M^+(g) \rightarrow M^+(aq) \qquad \text{or} \qquad X^-(g) \rightarrow X^-(aq)$$

  - ΔH_{hydr} of ions is always exothermic ($\Delta H_{hydr} < 0$) 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 ΔH_{hydr} of ions** (same as for $\Delta H_{lattice}$)
    - ΔH_{hydr} is larger (more exothermic) for ions with greater charges and smaller sizes $\rightarrow$ ions with higher **charge density**
    - The charge factor is more important

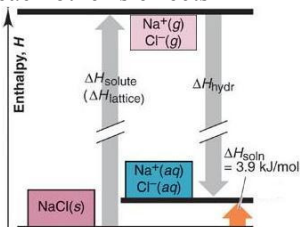| Some ionic heats of hydration in kJ/mol			
Li$^+$(-558)	Be^{2+}(-2533)		F$^-$(-483)
Na$^+$(-444)	Mg^{2+}(-2003)	Al^{3+}(-4704)	Cl$^-$(-340)
K$^+$(-361)	Ca^{2+}(-1657)		Br$^-$(-309)

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

Example: NaCl

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

The Tendency Toward Disorder

  - $\Delta H_{soln} < 0$ favors the solution process since the total energy of the system is lowered; but many ionic solids have $\Delta H_{soln} > 0$ and still dissolve readily in water
  - $\Rightarrow$ 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

$$\uparrow \textbf{Entropy} \leftrightarrow \uparrow \textbf{Disorder}$$

  - Mixing leads to greater disorder and $\uparrow$ the entropy

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- The solution process is governed by the combination of the enthalpy and entropy factors
  - Compounds with $\Delta H_{soln} < 0$ are typically soluble since both factors are favorable
  - Compounds with $\Delta H_{soln} > 0$ are soluble only if ΔH_{soln} is relatively small so the favorable entropy factor dominates
  - Compounds with $\Delta H_{soln} \gg 0$ are typically insoluble since the unfavorable enthalpy factor dominates

  Example: Benzene is insoluble in water because the solute-solvent *IF*s are weak so the (-) ΔH_{mix} is very small compared to the (+) ΔH_{solut} & ΔH_{solv}

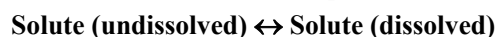$$\Rightarrow \Delta H_{soln} = \Delta H_{solute} + \Delta H_{solvent} + \Delta H_{mix} \gg 0$$

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) $\leftrightarrow$ 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 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 (+) ΔH_{soln}
  - (+) ΔH_{soln} means that heat is absorbed during dissolution (the heat can be viewed as a reactant)

Solute + Solvent + *heat* $\leftrightarrow$ Saturated solution
  - Increasing T provides the *heat* needed for the forward reaction to proceed ($S\uparrow$)

- Some **solids** are more soluble at higher T despite their exothermic (-) ΔH_{soln} (Why?)
  - Tabulated ΔH_{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 ΔH_{hydr} becomes less negative; thus ΔH_{soln} can change dramatically and even switch signs from (-) to (+)

- **Gases** are less soluble in water at higher T due to their exothermic (-) ΔH_{soln}
  - ΔH_{soln} is (-) since $\Delta H_{solute} \approx 0$ and $H_{hydr} < 0$

  Gas + Water $\leftrightarrow$ Saturated solution + *heat*
  - Increasing T provides the *heat* needed for the reverse reaction to proceed ($S\downarrow$)

Effect of Pressure on Solubility

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

- **Henry's law** - S_{gas} is directly proportional to P_{gas}
$$S_{gas} = k_H \times P_{gas}$$
  - k_H – Henry's law constant (depends on the gas, solvent and T)

Example: What is the concentration of CO_2 in rain drops at **20°C** and **1.0 atm** in air that has **1.0%** by volume CO_2? [$k_H(CO_2, 20°C) = 2.3\times10^{-2}$ mol/L.atm]

1.0% by volume $\rightarrow \chi_{CO_2} = 0.010$

$P_{CO_2} = \chi_{CO_2} P_{tot} = 0.010 \times 1.0$ atm $= 0.010$ atm

$S_{CO_2} = k_H \times P_{CO_2} = 2.3\times10^{-2}$ mol/L.atm $\times 0.010$ atm

$$= 2.3\times10^{-4} \text{ mol/L}$$

13.4 Expressing Solute Concentration

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

Table 13.5 Concentration Definitions

Concentration Term	Ratio
Molarity (M)	$\dfrac{\text{amount (mol) of solute}}{\text{volume (L) of solution}}$
Molality (m)	$\dfrac{\text{amount (mol) of solute}}{\text{mass (kg) of solvent}}$
Parts by mass	$\dfrac{\text{mass of solute}}{\text{mass of solution}}$
Parts by volume	$\dfrac{\text{volume of solute}}{\text{volume of solution}}$
Mole fraction (X)	$\dfrac{\text{amount (mol) of solute}}{\text{amount (mol) of solute + amount (mol) of solvent}}$

- **Molarity** (M) – the number of moles of solute per 1 liter of solution
  $$M = \text{(mol of solute)/(liters of solution)}$$
  - 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
  $$m = \text{(mol of solute)/(kilograms of solvent)}$$
  - 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) ≈ (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**.

$$mol\ solute = 2.2\ g\ NaOH \times \frac{1\ mol\ NaOH}{40\ g\ NaOH} = 0.055\ mol$$

$$m = \frac{0.055\ mol\ NaOH}{0.055\ kg\ water} = 1.0\ \frac{mol}{kg} \quad \rightarrow \quad \boxed{1.0\ m}\ (molal)$$

$$Volume = \frac{mass}{density} = \frac{2.2\ g + 55\ g}{1.1\ g/mL} = 52\ mL$$

$$M = \frac{0.055\ mol\ NaOH}{0.052\ L\ solution} = 1.1\ \frac{mol}{L} \quad \rightarrow \quad \boxed{1.1\ M}\ (molar)$$

- Parts of solute by parts of solution
- **Parts by mass**
  - **Mass %** – grams of solute per 100 grams of solution → % (w/w)

$$Mass\% = \frac{mass\ of\ solute}{mass\ of\ solution} \times 100\%$$

  - **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 → % (v/v)

$$Volume\% = \frac{volume\ of\ solute}{volume\ of\ solution} \times 100\%$$

- **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)

$$X = \frac{mol\ of\ solute}{mol\ of\ solute + mol\ of\ solvent}$$

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

$$2.2\ g\ \frac{1\ mol}{40\ g} = 0.055\ mol\ NaOH \quad \bigg| \quad 55\ g\ \frac{1\ mol}{18\ g} = 3.1\ mol\ H_2O$$

$$X = \frac{0.055\ mol}{0.055\ mol + 3.1\ mol} = 0.018$$

- Converting units of concentration

Example: A sample of water is **1.1×10⁻⁶ M** in chloroform (CH_3Cl). Express the concentration of chloroform in **ppb**. (Assume density of 1.0 g/mL)

$$1.1 \times 10^{-6}\ M \rightarrow 1.1 \times 10^{-6}\ mol\ CH_3Cl\ per\ 1\ L\ solution$$

$$1.1 \times 10^{-6}\ mol\ CH_3Cl \times \frac{50.5\ g\ CH_3Cl}{1\ mol\ CH_3Cl} = 5.6 \times 10^{-5}\ g\ CH_3Cl$$

$$1\ L \rightarrow 1000\ mL \times 1.0\ \frac{g}{mL} = 1.0 \times 10^{3}\ g\ solution$$

$$\frac{5.6 \times 10^{-5}\ g\ CH_3Cl}{1.0 \times 10^{3}\ g\ solution} \times 10^{9}\ ppb = 56\ ppb$$

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:

$$\rightarrow n_{meth} = 1\ mol \times 0.250 = 0.250\ mol$$

$$\rightarrow n_{water} = 1 - 0.250 = 0.750\ mol$$

$$0.750\ mol\ H_2O \times \frac{18.0\ g\ H_2O}{1\ mol\ H_2O} \times \frac{1\ kg}{10^{3}\ g} = 0.0135\ kg\ H_2O$$

$$m = \frac{0.250\ mol\ methanol}{0.0135\ kg\ H_2O} = 18.5\ m$$

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:

$$\rightarrow n_{NaCl} = 1.83\ mol$$

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

$$mass\ of\ NaCl = 1.83\ mol \times \frac{58.44\ g\ NaCl}{1\ mol} = 107\ g$$

$$mass\ of\ water = 1070\ g - 107\ g = 963\ g = 0.963\ kg$$

$$m = \frac{1.83\ mol\ NaCl}{0.963\ kg\ H_2O} = 1.90\ m$$

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 (H_2O):

$\rightarrow n_{KOH} = 1.20$ **mol**

$mass\ of\ KOH = 1.20\ mol \times \dfrac{56.1\,g\ KOH}{1\ mol} = 67.3\ g$

$mass\ of\ solution = 1000\ g + 67.3\ g = 1067\ g$

$volume\ of\ solution = 1067\ g \times \dfrac{1\,mL}{1.05\,g} = 1016\ mL = 1.02\ L$

$M = \dfrac{1.20\ mol\ KOH}{1.02\ L\ solution} = 1.18\ M$

13.5 Colligative Properties of Solutions

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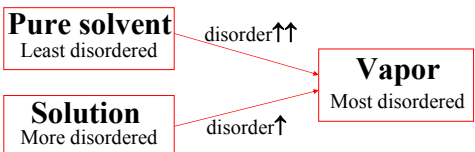 - The concentration of solute particles depends on the amount of dissolved solute as well as on its ability to dissociate to ions in solution
    - **Strong electrolytes** – dissociate completely (soluble salts, strong acids and bases)
    - **Weak electrolytes** – dissociate partially (weak acids and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

Nonvolatile Nonelectrolyte Solutions
  - No dissociation; no vapor pressure (glucose, sugar, …)
- **Vapor pressure lowering (ΔP)** – the vapor pressure of the solvent over the solution (P_{solv}) is always lower than the vapor pressure over the pure solvent (P°_{solv}) at a given temperature

Pure solvent Least disordered	disorder↑↑	
		Vapor Most disordered
Solution More disordered	disorder↑	

$\Rightarrow$ The solution has a lesser tendency to vaporize so its vapor pressure is lower

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➢**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**

$$\boxed{P_{solv} = X_{solv}P^{\circ}_{solv}}$$

$$X_{solv} \leq 1 \quad \Rightarrow \quad P_{solv} \leq P^{\circ}_{solv}$$

$$X_{solv} = 1 - X_{solute} \Rightarrow P_{solv} = (1 - X_{solute})P^{\circ}_{solv}$$

$$P_{solv} = P^{\circ}_{solv} - X_{solute}P^{\circ}_{solv} \rightarrow P^{\circ}_{solv} - P_{solv} = X_{solute}P^{\circ}_{solv}$$

$$\boxed{\Delta P = X_{solute}P^{\circ}_{solv}}$$

$\Rightarrow$ The vapor pressure lowering is directly proportional to the mole fraction of the solute

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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**.

$\rightarrow P_{solv} = 16.34$ **torr** $P^{\circ}_{solv} = 17.54$ **torr**

$\rightarrow X_{solute} = ?$
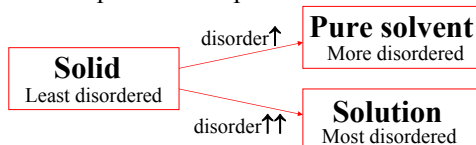
$$X_{solute} = \frac{\Delta P}{P^{o}_{solv}} = \frac{(17.54 - 16.34)\,torr}{17.54\,torr} = 0.0684$$

  - 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)
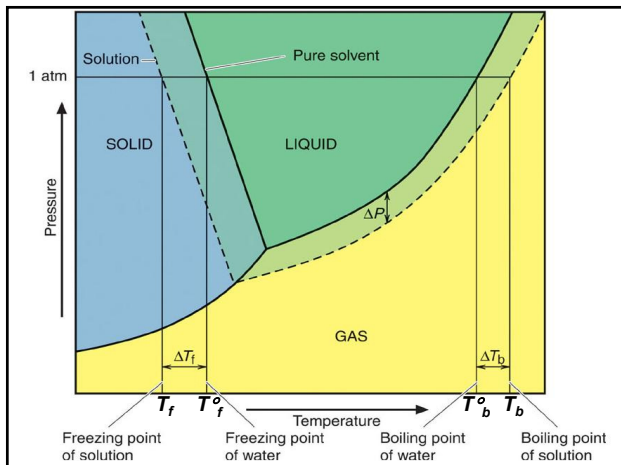

- **Boiling point elevation (ΔT_b) and freezing point depression (ΔT_f)**
  - The **solution boils at a higher temperature** compared to the pure solvent (the solution has lower vapor P so it needs higher T to boil)
  - The **solution freezes at a lower temperature** compared to the pure solvent

Solid Least disordered	disorder↑	**Pure solvent** More disordered
	disorder↑↑	**Solution** Most disordered

$\Rightarrow$ The solution has a greater tendency to melt so its melting (freezing) point is lower

$$\Delta T_b = T_b - T^\circ_b > 0 \quad \rightarrow \quad \boxed{\Delta T_b = k_b\, m}$$
$$\Delta T_f = T^\circ_f - T_f > 0 \quad \rightarrow \quad \boxed{\Delta T_f = k_f\, m}$$

$\rightarrow k_b$ – boiling point elevation constant $\rightarrow$ Depend on
$\rightarrow k_f$ – freezing point depression constant $\rightarrow$ the solvent
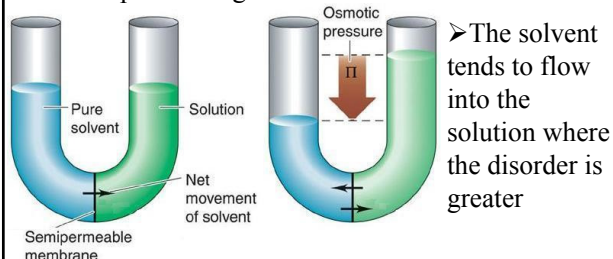$\rightarrow m$ – molality of solution

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°C/m and k_f=1.86°C/m)

$$12\ \text{g gluc}\frac{1\ \text{mol gluc}}{180\ \text{g gluc}} = 0.067\ \text{mol} \qquad m = \frac{0.067\ \text{mol gluc}}{0.055\ \text{kg water}} = 1.2\ \text{m}$$

$$\Delta T_b = 0.512\,\frac{°C}{m}\times 1.2\ \text{m} = 0.62°C \qquad T_b = 100 + 0.62 = \boxed{100.62°C}$$

- **Osmotic pressure (Π)**
  - **Osmosis** – the flow of solvent trough 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

- Π is the hydrostatic pressure necessary to stop the net flow of solvent caused by osmosis

$$\boxed{\Pi = MRT} \qquad \Pi = (n_{solute}/V_{soln})RT$$

$\rightarrow M$ – molarity of solution
$\rightarrow R$ – gas constant; T – temperature in **K**

  - The equation is the equivalent of the ideal gas law ($P = nRT/V$) applied to solutions
    - Π 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**?

$\rightarrow$ Calc. Π (the necessary pressure must be $\geq \Pi$)

$$\Pi = MRT = 0.82\,\frac{\text{mol}}{\text{L}}\times 0.08206\,\frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}\times 298\ \text{K}$$

$$\Pi = \boxed{20\ \text{atm}}$$

$\rightarrow$ 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)
  - ΔP and ΔT_b are not very sensitive to changes in the solute concentration (rarely used for molar mass determinations)
  - ΔT_f is more sensitive especially when solvents with large k_f constants are used
  - Π 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 it's k_f is 39.7**°C/m**. When **200.0 mg** of a compound (X) are added to **100.0 g** of camphor, it's freezing point drops to **179.29°C**. What is the molar mass of X?

→ **Calc. the m of X:**

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

→ **Calc. the number of moles of X:**

$$m = \frac{mol(X)}{kg(camphor)} \ \rightarrow \ 0.013\frac{mol}{kg} \times 0.1000\,kg = 0.0013\,mol$$

→ **Calc. the molar mass of X:**

$$MW = \frac{grams(X)}{mol(X)} \ \rightarrow \ \frac{0.2000\,g}{0.0013\,mol} = \boxed{160\,g/mol}$$

Example: A **3.0 g** polymer sample is dissolved in enough benzene to produce **150. mL** of solution. If the solution's osmotic pressure is **0.0119 atm** at **25°C**, what is the average MW of the polymer?

Calc. M of the solution:

$$M = \frac{\Pi}{RT} = \frac{0.0119\,atm}{0.08206\,L.atm/mol.\,K \times 298\,K} = 4.87 \times 10^{-4}\frac{mol}{L}$$

→ **Calc. the number of moles of the polymer:**

$$M = \frac{mol(pol)}{L(soln)} \rightarrow 4.87 \times 10^{-4}\frac{mol}{L} \times 0.150\,L = 7.30 \times 10^{-5}\,mol$$

→ **Calc. the molar mass of the polymer:**

$$MW = \frac{grams(polym)}{mol(polym)} \ \rightarrow \ \frac{3.0\,g}{7.30 \times 10^{-5}\,mol} = \boxed{41000\,g/mol}$$

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

$$P_{solv} = X_{solv}P°_{solv} \qquad P_{solute} = X_{solute}P°_{solute}$$

⇒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

$$P_{tot} = P_{solv} + P_{solute} = X_{solv}P°_{solv} + X_{solute}P°_{solute}$$

– The mole fractions of the solute and solvent in the vapor phase above the solution can be calculated using Dalton's law

$$P_{solv} = X_{solv}^{vap}P_{tot} \qquad\qquad P_{solute} = X_{solute}^{vap}P_{tot}$$

$$X_{solv}^{vap} = \frac{P_{solv}}{P_{tot}} \qquad\qquad X_{solute}^{vap} = \frac{P_{solute}}{P_{tot}}$$

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.

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

$$P_b = X_b P_b^o = 0.25 \times 95.1\,torr = \boxed{24\,torr}$$

$$P_t = X_t P_t^o = 0.75 \times 28.4\,torr = \boxed{21\,torr}$$

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

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

⇒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 → **distillation**

Electrolyte Solutions

– The solute dissociates to ions

– The number of particles in the solution is greater than the one implied by the solute concentration

• 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

$$\Delta P = i(X_{solute}P°_{solv}) \qquad \Delta T_b = i(k_b m)$$

$$\Pi = i(MRT) \qquad\qquad \Delta T_f = i(k_f m)$$

– 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 → ($i{\times}Conc.$)

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

→ Calculate the effective concentrations:

→ **0.1M NaCl** → $i{\times}M$ = **2×0.1 = 0.2**

→ **0.08M CaCl$_2$** → $i{\times}M$ = **3×0.08 = 0.24** (higher)

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