SLE155 Chemistry for the Professional Sciences
Burwood and Geelong
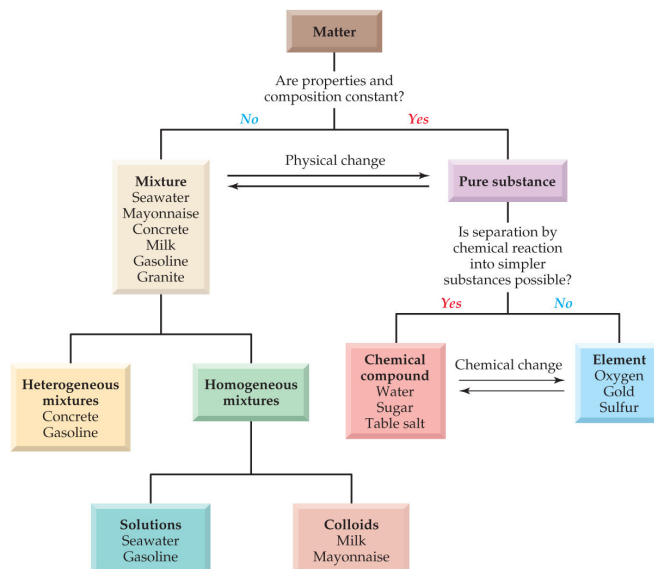
DEAKIN COLLEGE in association with DEAKIN UNIVERSITY AUSTRALIA

Class 4
Advanced Solution Chemistry

Solutions
Gaseous solutions
Liquid solutions
Quantification of solubility:
the solubility product
Colligative Properties of Solutions

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Mixtures and Solutions

Heterogeneous mixtures are those in which the mixing is not uniform so they have regions of different composition.

Homogeneous mixtures are those in which the mixing *is* uniform and have the same composition through the entire solution.

Solutions are **homogeneous mixtures** that contain particles the size of a typical ion or small molecule.

Colloids are **homogeneous mixtures** that contain particles ranging in diameter from 2 nm to 500 nm.

Mixtures and Solutions

TABLE 9.1 Some Characteristics of Solutions, Colloids, and Heterogeneous Mixtures

Type of Mixture	Particle Size	Examples	Characteristics
Solution	<2.0 nm	Air, seawater, gasoline, wine	Transparent to light; does not separate on standing; nonfilterable
Colloid	2.0–500 nm	Butter, milk, fog, pearl	Often murky or opaque to light; does not separate on standing; nonfilterable
Heterogeneous	>500 nm	Blood, paint, aerosol sprays	Murky or opaque to light; separates on standing; filterable

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The Solution Process

Solutions form when these three kinds of forces are similar.
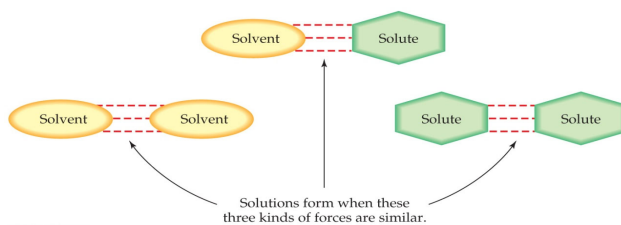
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"Like dissolves like."

In general, polar solvents dissolve polar and ionic solutes.

In general, nonpolar solvents dissolve nonpolar solutes.

"Oil and water don't mix."

The intermolecular forces between water molecules are so strong that after an oil–water mixture is shaken, the water layer re-forms, squeezing out the oil molecules.
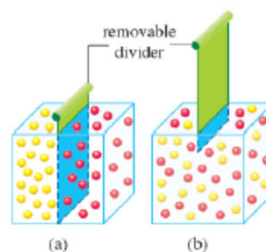
Liquid - liquid solutions
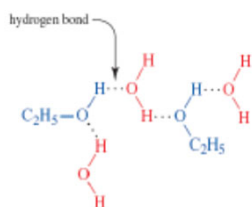
Gaseous solutions

All gases mix completely
with all other gases in all
proportions

Gases mix spontaneously
hence ΔG for mixing
process (ΔmixG) is negative

Gas liquid solutions

For a gas to dissolve in a liquid, the gas molecules must be able to disperse themselves evenly throughout the solvent.

Gas undissolved ⇌ gas dissolved

Intramolecular forces between the solvent molecules are not negligible.

Therefore the value of $\Delta_{sol}H$ (the enthalpy of solution) is also not negligible.

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Gas-Liquid solutions

The enthalpy change when a gas dissolves in solution has two contributions:

Energy is required to open 'pockets' in the solvent that can hold gas molecules. This is because attractions between solvent molecules must be overcome. Note that in the case of water, little energy is required as the structure of water already contains holes in its network.

Energy is released when gas molecules enter these pockets, due to the attraction between gas and solvent molecules.

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Temperature and Gas-Liquid solutions

Whether the overall process is endothermic (requires input of heat) or exothermic (releases heat) depends on the energy required for both contributions:

Enthalpies of solutions for gases in organic solvents are often endothermic as the energy required to open pockets is greater than the energy released by attractions between gas and solvent molecules.

Enthalpies of solutions for gases in water are often exothermic as little energy is required to open pockets.

# Temperature and Gas-Liquid solutions
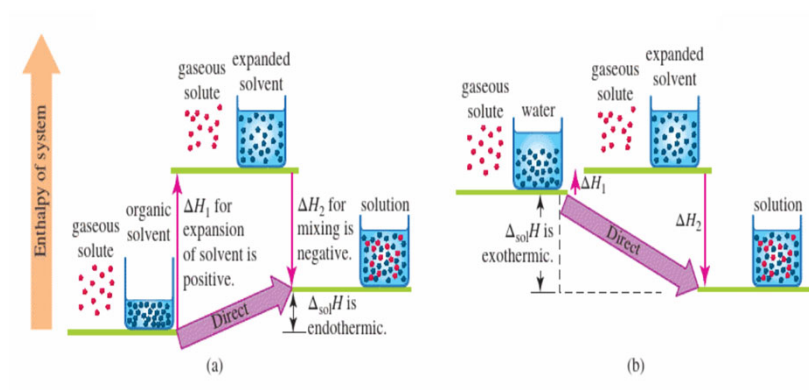
Pressure and Gas-Liquid solutions
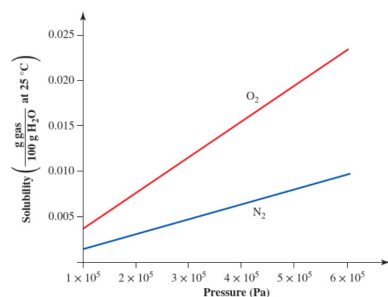
The solubility of a gas is also affected by pressure.

Gases such as nitrogen and oxygen become increasing soluble as pressure increases, as demonstrated in the graph

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Solid liquid soutions

– Solvation is when a solute molecule is surrounded by solvent molecules
– Hydration occurs when solutes become surrounded by water molecules
– Ionic compounds dissolve in water when the ion-dipole attractions overcome both ion-ion and dipole-dipole attractions

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The Solution Process

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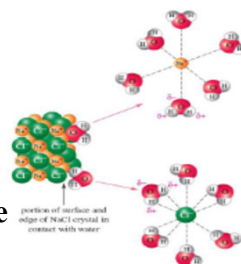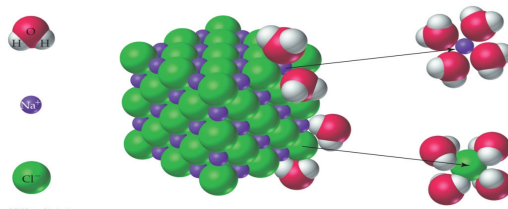
Positively charged Na$^+$ ions are attracted to the negatively polarised oxygen of water; negatively charged ions are attracted to the positively polarised hydrogens.

The forces of attraction between an ion and water molecules pull the ion away from the crystal.

Once in solution, the water molecules form a loose shell around the ions, stabilising them by electrical attraction, a phenomenon called solvation or *hydration*.

The Solution Process

The dissolution of a solute in a solvent is a physical change since the solution components retain their chemical identities.

The dissolution of a substance in a solvent has an *enthalpy change* associated with it.

Some substances dissolve exothermically, releasing heat; other substances dissolve endothermically, absorbing heat and cooling the resultant solution.

Solutions and solubility

Solution

Homogeneous mixture of two or more pure substances

It may be gaseous, liquid or solid.

Solvent

Dissolves the solute to form a solution. It is usually a liquid but can be a solid, gas or supercritical fluid.

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Solutions and solubility

Solute

Dissolved substance in solution. Most solutions that we study are liquid.

Solubility

Maximum amount of solute that dissolves completely in a given amount of solvent at a particular temperature, T.

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Solutions and solubility

Saturated solution

Solution in which no more solute will dissolve.

Dissolution

Process of dissolving a solute in a solvent to give a homogeneous solution.
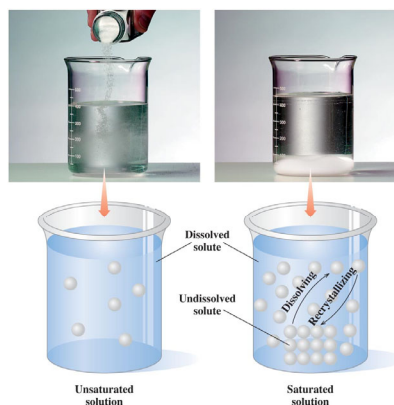

Solutions and solubility

Saturated solutions

contain the maximum amount of solute that can dissolve.

There is undissolved solute at the bottom of the container.

Dissolved solute

Undissolved solute

Dissolving

Recrystallizing

Unsaturated solution

Saturated solution

Solubility

Miscible: Mutually soluble in all proportions.

Ethanol will continue to dissolve in water no matter how much is added.

Most substances reach a solubility limit beyond which no more will dissolve in solution.

Saturated solution: Contains the maximum amount of dissolved solute at equilibrium.

A maximum of 35.8 g of NaCl will dissolve in 100 mL of water at 20 ºC. Any amount above this limit simply sinks to the bottom of the container and sits there.

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Solubility

A saturated solution is in a state of dynamic equilibrium

$$\text{Solid solute} \underset{\text{Crystallize}}{\overset{\text{Dissolve}}{\rightleftharpoons}} \text{Solution}$$
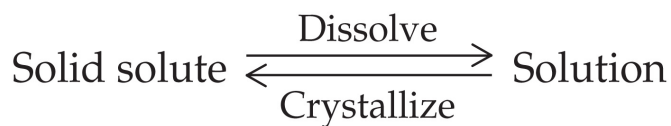
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Solubility:
The maximum amount of a substance that will dissolve in a given amount of solvent at a specified temperature.

Only 9.6 g of sodium hydrogen carbonate will dissolve in 100 mL of water at 20 °C, for instance, but 204 g of sucrose will dissolve under the same conditions.

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Quantification of solubility: solubility product

Ionic salts are generally classified as being either soluble or insoluble in water

$$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s) + NaNO_3(aq)$$
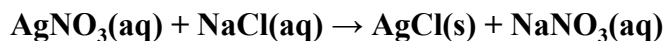
In fact, an equilibrium exists:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
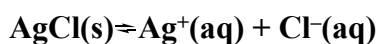
$$K_{sp} = [Ag^+][Cl^-]$$

Quantification of solubility: solubility product

The relationship between K_{sp} and solubility

Molar solubility (*s*) is the molar concentration of a salt in its saturated solution.

Molar solubility can be used to calculate K_{sp}, assuming that all of the salt that dissolves is 100% dissociated into its ions.

If the molar solubility, *s*, of AgBr is 6.9×10^{-7} mol L^{-1}
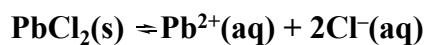then $s = [Ag^+] = [Br^-] = 6.9 \times 10^{-7}$ mol L^{-1}

and $K_{sp} = [Ag^+][Br^-] = s \times s = 4.8 \times 10^{-13}$

Note that the equilibrium constant is dimensionless

Quantification of solubility: solubility product

The common ion effect

Any ionic salt is less soluble in the presence of a common ion, an ion that is a component of the salt

$$PbCl_2(s) \rightleftharpoons Pb^{2+}(aq) + 2Cl^-(aq)$$

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

Adding $Pb(NO_3)_2(aq)$ to a saturated solution of $PbCl_2$ instantaneously increases $[Pb^{2+}]$ and therefore Q_{sp} (ionic product).

$$Q_{sp} > K_{sp}$$

$PbCl_2$ will precipitate

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Quantification of solubility: solubility product

Will a precipitate form?

K_{sp} can be used to predict whether a precipitate will form when ionic solutions are mixed by comparing with a calculated value for Q_{sp}

$Q_{sp} > K_{sp}$ a precipitate will form until $Q_{sp} = K_{sp}$

$Q_{sp} < K_{sp}$ no precipitate will form

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Measuring concentration

Molarity is the amount of solute per litre of solution.

$$\text{Molarity} = \frac{\text{number of mole of solute}}{\text{number of litre of solution}}$$

Solutions (usually) increase in volume with increasing temperature.

The molarity of a solution changes as the temperature changes.

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Measuring concentration

Molality is the amount of solute per kilogramme of solvent.

$$\text{Molality} = \frac{\text{number of mole of solute}}{\text{number of kg of solvent}}$$

Preferred method of expressing solution concentration when colligative properties are involved.

Molality is temperature **independent**.

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Measuring concentration

Mole fraction is the **amount of the component** in question **divided by the total amount of substance**, for example,

$$\text{mole fraction of solute} = \frac{\text{number of mole of solute}}{\text{total number of mole}}$$

$$x_A = \frac{n_A}{n_A + n_B + n_C}$$

Mole fraction is temperature **independent**.

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Colligative properties

Solutions prepared from **nonvolatile solutes** differ significantly in some properties from those of pure solvent.

These properties are called **colligative properties**.

**Nonvolatile solutes** are solutes that cannot evaporate from solution.

Colligative properties depend on the **number of solute particles in solution** rather than on their chemical identities.

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Colligative properties

Raoult's law

Boiling point of a solution containing a nonvolatile solute is higher than that of the pure solvent.

Boiling point of a solvent is the temperature at which the vapour pressure of the solvent is equal to the atmospheric pressure.
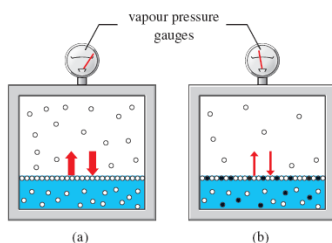
Colligative properties

Raoult's law

Raoult's law describes the relationship between vapour pressure, mole fraction of solvent and vapour pressure of solvent.

$$p_{solution} = X_{solvent}\,p^*_{solvent} \text{ (at constant } T)$$

$p_{solution}$ **is vapour pressure of the solution**

$X_{solvent}$ **is mole fraction of solvent in the solution**

$p^*_{solvent}$ **is vapour pressure of pure solvent**
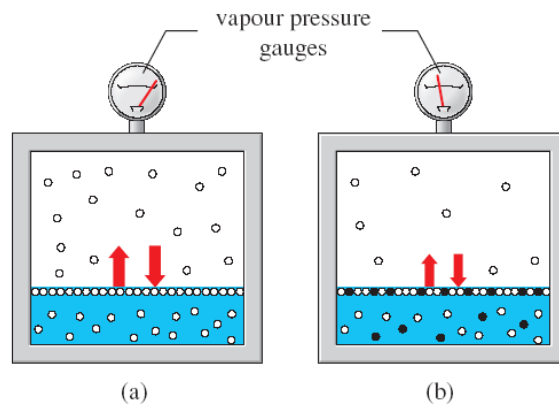
A solution that obeys Raoult's law is called an ideal solution.

16

Colligative properties

Raoult's law

A solution that obeys Raoult's law is called an ideal solution.

These solutions are generally dilute and have only small interactions between their constituent molecules.

vapour pressure gauges

(a)   (b)

Colligative properties

Vapour pressure reduction

Boiling point elevation

Freezing point depression

Osmotic pressure

Colligative properties

Vapour Pressure Lowering in Solutions

Vapour pressure depends on the equilibrium between molecules entering and leaving the liquid surface.

If some solvent molecules are replaced by solute particles, the rate of evaporation decreases.

The **vapour pressure of a solution** is **lower** than that of the **pure solvent**.

The *identity* of the solute particles is irrelevant; only their concentration matters.

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Colligative properties

Boiling Point Elevation in Solutions

The boiling point of the solution is **higher** than that of the pure solvent.

The solution must be heated to a higher temperature for its vapour pressure to reach atmospheric pressure.

Each mole of solute particles raises the boiling point of 1 kg of water by 0.51 ºC.

1 mol of glucose raises the temperature by 0.51 ºC, but 1 mol of NaCl raises it by 1.02 ºC. This is because **NaCl dissociates into two particles, glucose molecules do not.**

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Colligative properties

Freezing-Point Depression of Solutions

The freezing point of a solution is lower than that of the pure solvent.

Solute molecules are dispersed between solvent molecules, making it more difficult for solvent molecules to organise into ordered crystals.

For each mole of nonvolatile solute particles, the freezing point of 1 kg of water is lowered by 1.86 ºC.

Colligative properties

Boiling point elevation and freezing point depression
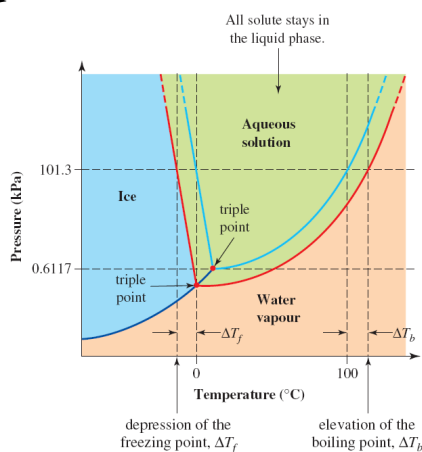
boiling point elevation ΔT_b

$\Delta T_b = K_b b$

K_b is the molal boiling point elevation constant

b is the molality of the solution

freezing point depression ΔT_f

$\Delta T_f = K_f b$

K_f is the molal freezing point depression constant

Colligative properties

At what temperature does a 10% (by mass) aqueous solution of sugar, $C_{12}H_{22}O_{11}$, boil at 1.013×10^5 Pa? K_b for water is 0.51 K mol^{-1} kg.

A 10% solution contains 10 g sugar and 90 g water:
$n(C_{12}H_{22}O_{11}) = 10$ g$/(342.296$ g $mol^{-1}) = 0.029$ mol.

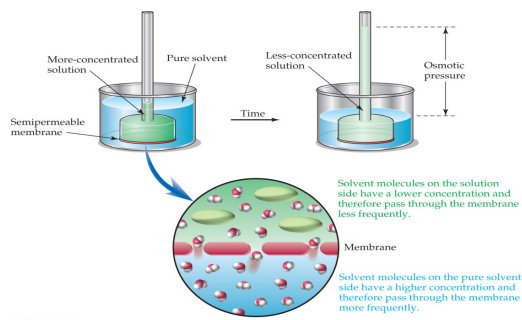Mass of water in kg: 90 g $H_2O = 0.090$ kg H_2O.

Molality: $b = 0.029$ mol$/0.090$ kg $= 0.32$ mol kg^{-1}.
Substituting into the equation for $\Delta T_{boiling}$
$\Delta T = Kb \times b = 0.51K/mol \times 0.32mol/kg = 0.16\,°C$

Therefore: $T_{boiling} = (100.00 + 0.16)°C = 100.16\ °C$.

Osmosis and Osmotic Pressure

Osmosis: The passage of a solvent through a semipermeable membrane separating two solutions of different concentration.

More-concentrated solution   Pure solvent   Less-concentrated solution   Osmotic pressure

Semipermeable membrane

Time

Solvent molecules on the solution side have a lower concentration and therefore pass through the membrane less frequently.

Membrane

Solvent molecules on the pure solvent side have a higher concentration and therefore pass through the membrane more frequently.

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Osmosis and Osmotic Pressure

As the liquid in the tube rises, its weight creates a pressure that pushes solvent back through the membrane until the rates of forward and reverse passage become equal and the liquid level stops rising.

Osmotic pressure is the amount of external pressure that must be applied to a solution to prevent the net movement of solvent molecules across a semipermeable membrane.

Colligative properties

Osmosis and osmotic pressure

A membrane keeps mixtures and solutions organised and separated.

Semipermeable membranes allow selective substances to pass through.

Dialysis occurs when a dialysing membrane allows both water and small solute particles through.

Osmosis is a net shift of only solvent through an osmotic membrane.
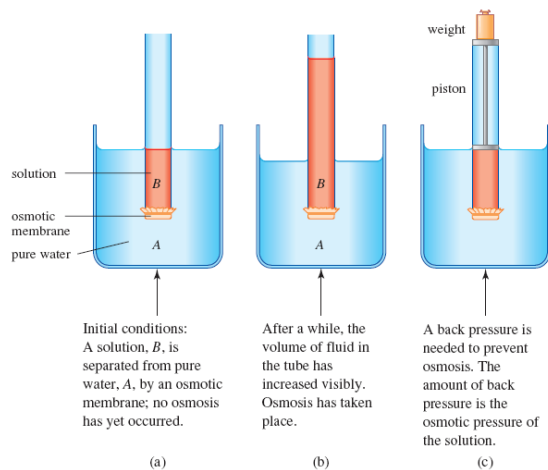
Colligative properties

Osmosis and osmotic pressure

Osmosis occurs in the *direction* of net movement of solvent **from** the more **dilute** solution (or pure solvent) **into** the more **concentrated** solution.

The pressure needed to prevent any osmotic flow when one of the liquids is a pure solvent is called the **osmotic pressure** of the solution.

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Colligative properties

Osmosis and osmotic pressure

weight

piston

solution

osmotic membrane

pure water

B   *B*

A   *A*

Initial conditions: A solution, *B*, is separated from pure water, *A*, by an osmotic membrane; no osmosis has yet occurred.

After a while, the volume of fluid in the tube has increased visibly. Osmosis has taken place.

A back pressure is needed to prevent osmosis. The amount of back pressure is the osmotic pressure of the solution.

(a)   (b)   (c)

Colligative properties

Osmosis and osmotic pressure

Cells are surrounded by an 'osmotic' membrane.
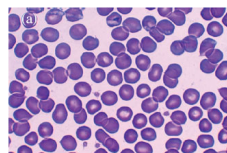A solution that has the same osmotic pressure as red blood cells is isotonic with red blood cells.
A solution that has higher salt concentration is hypertonic.
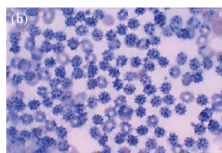A solution with a lower osmotic pressure is hypotonic.

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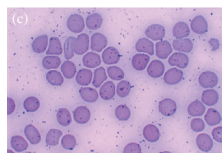

Colligative properties

Osmosis and osmotic pressure

Isotonic   Hypertonic   Hypotonic

capillary

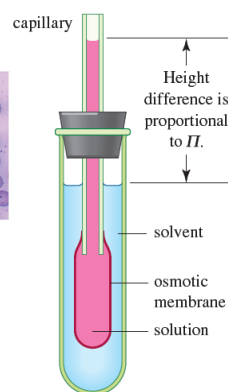Height difference is proportional to Π.
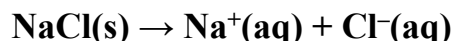
solvent

osmotic membrane

solution

Osmometer

Colligative properties

Measurement of solute dissociation

Molal freezing point depression constant for water is 1.86 K mol⁻¹ kg. It is observed that

1.00 mol kg⁻¹ NaCl freezes at about **-3.37 °C**

If NaCl(s) undergoes complete dissociation:

$$NaCl(s) \rightarrow Na^+(aq) + Cl^-(aq)$$

Solution has a total molality of *dissolved solute particles* of 2 mol kg⁻¹

Theoretically, a 1.00 mol kg⁻¹ NaCl solution should freeze at 2×(-1.86 °C) = **-3.72 °C**

NaCl does not dissociate completely.

Summary

A solution is a homogeneous mixture of two or more pure substances that can be gases, liquids or solids.

A saturated solution contains the maximum possible amount of dissolved solute at the given temperature and pressure.

All gases mix spontaneously in all proportions.

The mixing process is entropy driven.

Summary

The **solubility product**, K_{sp}, is the equilibrium constant for the dissociation of a slightly soluble salt

$$K_{sp} = [M^{b+}]^a[X^{a-}]^b$$

The **molar solubility**, s, of a salt at a specific temperature is the amount of salt dissolved in 1 L of a saturated solution at that temperature.

The **common ion effect** shows that salts are always less soluble in the presence of a common ion.

Molality, b, and **mole fraction**, X_A, are expressions for concentrations that is temperature independent.

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Summary

Colligative properties are dependent on the number of solute particles.

Raoult's law shows that the pressure above a solution is proportional to the mole fraction of the solvent. Each component in an ideal solution obeys Raoult's law.

Non-volatile solutes cause boiling point elevation and freezing point depression.

Osmosis is the passage of solvent only through a semipermeable membrane.

Osmosis results in a net shift of solvent from the side less concentrated in solute to the side more concentrated.

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