

Properties of Solutions

Solutions

... the components of a mixture are uniformly intermingled (the mixture is homogeneous).

TABLE 11.1 Various Types of Solutions

Example	State of Solution	State of Solute	State of Solvent
Air, natural gas	Gas	Gas	Gas
Vodka in water, antifreeze	Liquid	Liquid	Liquid
Brass	Solid	Solid	Solid
Carbonated water (soda)	Liquid	Gas	Liquid
Seawater, sugar solution	Liquid	Solid	Liquid
Hydrogen in platinum	Solid	Gas	Solid

Solution Composition

1. Molarity (M) = $\frac{\text{moles of solute}}{\text{liters of solution}}$
2. Mass (weight) percent = $\frac{\text{mass of solute}}{\text{mass of solution}} \times 100\%$
3. Mole fraction (χ_A) = $\frac{\text{moles}_A}{\text{total moles in solution}}$
4. Molality (m) = $\frac{\text{moles of solute}}{\text{kilograms of solvent}}$

Molarity

- The **molarity** of a solution is the moles of solute in a liter of solution.

$$\text{Molarity}(M) = \frac{\text{moles of solute}}{\text{liters of solution}}$$

- For example, 0.20 mol of ethylene glycol dissolved in enough water to give 2.0 L of solution has a molarity of

$$\frac{0.20 \text{ mol ethylene glycol}}{2.0 \text{ L solution}} = 0.10 \text{ M ethylene glycol}$$

Mass Percentage of Solute

- The **mass percentage** of solute is defined as:

$$\text{Mass percentage of solute} = \frac{\text{mass of solute}}{\text{mass of solution}} \cdot 100\%$$

- For example, a 3.5% sodium chloride solution contains 3.5 grams NaCl in 100.0 grams of solution.

Mole Fraction

- The **mole fraction** of a component "A" (C_A) in a solution is defined as the moles of the component substance divided by the total moles of solution (that is, moles of solute and solvent).

$$C_A = \frac{\text{moles of substance A}}{\text{total moles of solution}}$$

- For example, 1 mol ethylene glycol in 9 mol water gives a mole fraction for the ethylene glycol of $1/10 = 0.10$.

A Problem to Consider

- An aqueous solution is 0.120 *m* glucose. What are the mole fractions of each of the components?
- A 0.120 *m* solution contains 0.120 mol of glucose in 1.00 kg of water. After converting the 1.00 kg H₂O into moles, we can calculate the mole fractions.

$$1.00 \cdot 10^3 \text{ g H}_2\text{O} \cdot \frac{1 \text{ mol H}_2\text{O}}{18.0 \text{ g}} = 55.6 \text{ mol H}_2\text{O}$$

A Problem to Consider

- An aqueous solution is 0.120 *m* glucose. What are the mole fractions of each of the components?

$$C_{\text{glucose}} = \frac{0.120 \text{ mol}}{(0.120 + 55.6) \text{ mol}} = 0.00215$$

$$C_{\text{water}} = \frac{55.6 \text{ mol}}{(0.120 + 55.6) \text{ mol}} = 0.998$$

Molality

- The **molality** of a solution is the moles of solute per kilogram of solvent.

$$\text{molality}(m) = \frac{\text{moles of solute}}{\text{kilograms of solvent}}$$

- For example, 0.20 mol of ethylene glycol dissolved in 2.0×10^3 g (= 2.0 kg) of water has a molality of

$$\frac{0.20 \text{ mol ethylene glycol}}{2.0 \text{ kg solvent}} = 0.10 \text{ m ethyleneglycol}$$

A Problem to Consider

- What is the molality of a solution containing 5.67 g of glucose, C₆H₁₂O₆, dissolved in 25.2 g of water?
- First, convert the mass of glucose to moles.

$$5.67 \text{ g C}_6\text{H}_{12}\text{O}_6 \cdot \frac{1 \text{ mol C}_6\text{H}_{12}\text{O}_6}{180.2 \text{ g C}_6\text{H}_{12}\text{O}_6} = 0.0315 \text{ mol C}_6\text{H}_{12}\text{O}_6$$

- Then, divide it by the kilograms of solvent (water).

$$\text{Molality} = \frac{0.0315 \text{ mol C}_6\text{H}_{12}\text{O}_6}{25.2 \cdot 10^{-3} \text{ kg solvent}} = 1.25 \text{ m C}_6\text{H}_{12}\text{O}_6$$

Steps in Solution Formation

- Step 1 - Expanding the solute (endothermic)
- Step 2 - Expanding the solvent (endothermic)
- Step 3 - Allowing the solute and solvent to interact to form a solution (exothermic)

$$\Delta H_{\text{soln}} = \Delta H_{\text{step 1}} + \Delta H_{\text{step 2}} + \Delta H_{\text{step 3}}$$

Figure 11.1: The formation of a liquid solution can be divided into three steps: (1) expanding the solute, (2) expanding the solvent, and (3) combining the expanded solute and solvent to form the solution.

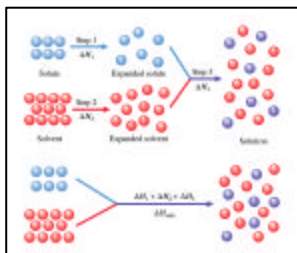


Figure 11.2: The heat of solution (a) H_{soln} has a negative sign (the process is exothermic) if step 3 releases more energy than that required by steps 1 and 2. (b) H_{soln} has a positive sign (the process is endothermic) if steps 1 and 2 require more energy than is released in step 3. (If the energy changes for steps 1 and 2 equal that for step 3, then H_{soln} is zero.)

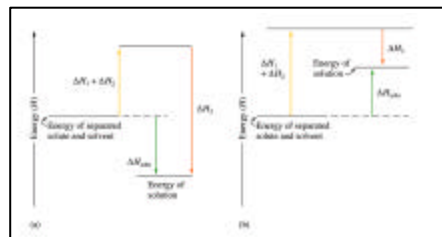
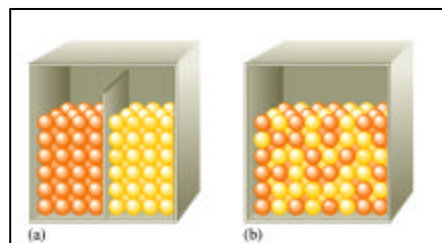


TABLE 11.3 The Energy Terms for Various Types of Solute and Solvents

	ΔH_1	ΔH_2	ΔH_3	ΔH_{soln}	Outcome
Polar solvent, polar solute	Large	Large	Large, negative	Small (+ or -)	Solution forms
Polar solvent, nonpolar solute	Small	Large	Small	Large, positive	No solution forms
Nonpolar solvent, nonpolar solute	Small	Small	Small	Small (+ or -)	Solution forms
Nonpolar solvent, polar solute	Large	Small	Small	Large, positive	No solution forms

Figure 11.3: (a) Orange and yellow spheres separated by a partition in a closed container. (b) The spheres after the partition is removed and the container has been shaken for some time.



Factors Explaining Solubility

- ! Substances also tend to mix - that is, they tend to become disordered - because of their natural random motions.
- ! For two substances to form a solution (any type), the intermolecular forces between the molecules in each substance must be similar (or weaker) than those between the molecules of the newly formed solution.

Factors Affecting Solubility

1. Structural Effects – solute and solvent have similar polarities
2. Pressure Effects – In a closed system, the amount of a gas dissolved in a gas-liquid solution is directly related to the pressure of the gas above the solution (Henry's Law)
3. Temperature Effects – difficult to predict. Some correlation between ΔH_{soln} and the variation of solubility with temperature – but best determined experimentally!

Molecular Solutions

The molecules of solute **do not** dissociate when dissolved in solvent:

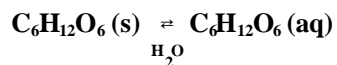
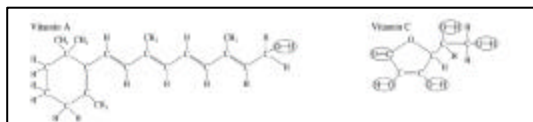
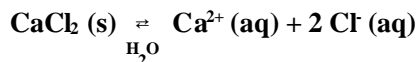


Figure 11.4: The molecular structures of (a) vitamin A (nonpolar, fat-soluble) and (b) vitamin C (polar, water-soluble). The circles in the structural formulas indicate polar bonds. Note that vitamin C contains far more polar bonds than vitamin A.



Ionic Solutions

The solute dissociates into ions in solution:



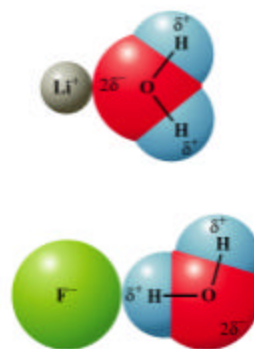
Ionic Solutions

Whether an ionic solid dissolves in water depends on the **relative magnitudes** of the **lattice energy** of the solid solute and the **hydration energy** of the solute when dissolved in water. **Ionic solutes with high lattice energies tend to be insoluble in water.**

Ionic Solutions

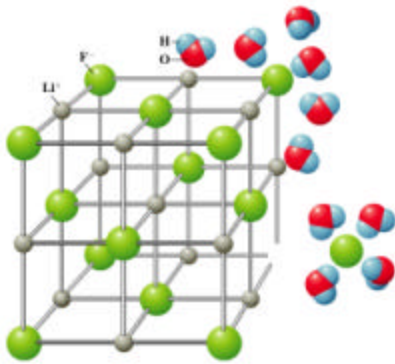
The attractive intermolecular forces most important in ionic solutions are between the charged solute ions and the polar ends of the water solvent molecules, called ion-dipole forces. **When the solvent is water, we call the energy released by this attraction “hydration energy”.**

Figure 12.7: Attraction of water molecules to ions because of the ion-dipole force.



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Figure 12.8:
The dissolving of
lithium fluoride in
water.



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Slide 12](#)

Figure 11.6:
The solubilities
of several solids
as a function of
temperature.

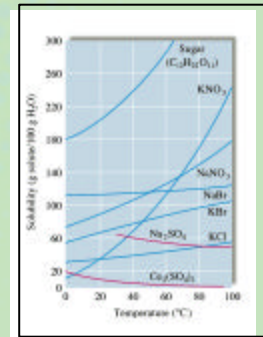


Figure 11.8: A pipe with accumulated
mineral deposits. The cross section
clearly indicates the reduction in pipe
capacity.



Henry's Law

The amount of a gas dissolved in a solution is
directly proportional to the pressure of the gas
above the solution.

$$P = kC$$

P = partial pressure of gaseous solute above
the solution

C = concentration of dissolved gas

k = a constant

Figure 11.5: (a) A gaseous solute in equilibrium with a
solution. (b) The piston is pushed in, increasing the pressure
of the gas and number of gas molecules per unit volume. This
causes an increase in the rate at which the gas enters the
solution, so the concentration of dissolved gas increases. (c)
The greater gas concentration in the solution causes an
increase in the rate of escape. A new equilibrium is reached.

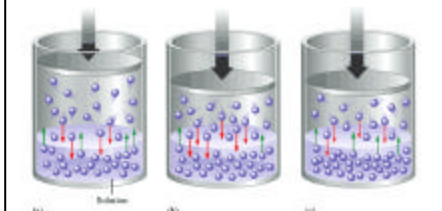
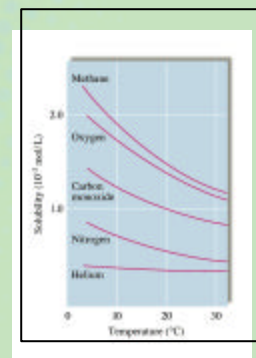


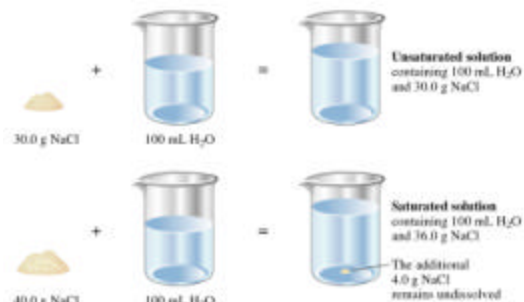
Figure 11.7:
The solubilities
of several gases
in water as a
function of
temperature at a
constant
pressure of 1
atm of gas
above the
solution.



Solubility and the Solution Process

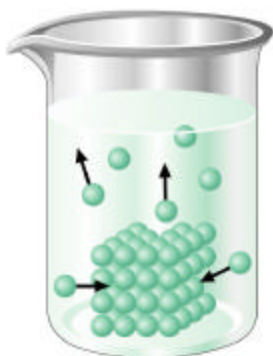
- The amount of a substance that will dissolve in a solvent is referred to as its **solubility**.
- Many factors affect solubility, such as **temperature** and, in some cases, **pressure**.
- There is a limit as to how much of a given solute will dissolve at a given temperature.
- A **saturated solution** is one holding as much solute as is allowed at a stated temperature. (see [Figure 12.3](#))

Figure 12.3: Comparison of unsaturated and saturated solutions.



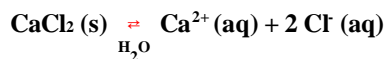
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Figure 12.2:
Solubility of
equilibrium.



Saturated Solutions

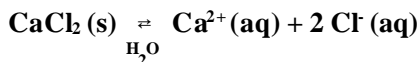
A system in **equilibrium**:



The maximum amount of calcium chloride has dissolved and the system is **saturated** with calcium and chloride ions.

For each mole of calcium chloride that dissolves, 1 mole of Ca²⁺ ions and two moles of Cl⁻ ions go into solution.

Saturated Solutions



The system is in **dynamic equilibrium** - that is, the overall concentrations of Ca²⁺ and Cl⁻ ions do not change, but solid calcium chloride is continuously dissolving into and re-forming from the ions in solution.

Solubility: Saturated Solutions

- Sometimes it is possible to obtain a **supersaturated solution**, that is, one that contains more solute than is allowed at a given temperature.
 - Supersaturated solutions are unstable - they are NOT in equilibrium.
 - If a small crystal of the solute is added to a supersaturated solution, the excess immediately crystallizes out.

Figure 12.4: Crystallization begins.
Photo courtesy of James Scherer.

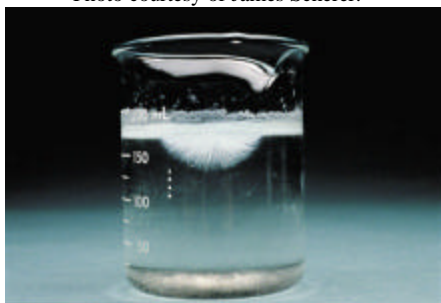


Figure 12.4: Crystal growth spreads.
Photo courtesy of James Scherer.

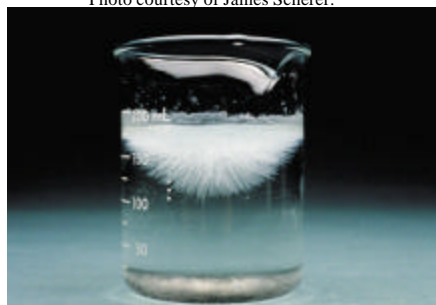
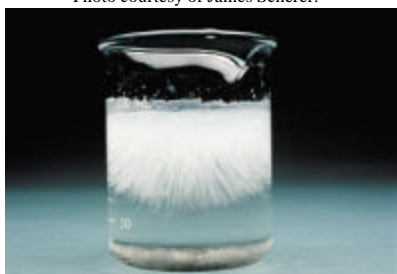


Figure 12.4: Crystal growth spreads through the solution.
Photo courtesy of James Scherer.



Vapor Pressure of Solutions

Nonvolatile solutes lower the vapor pressure of the solvent – fewer solvent molecules at the surface (escaping tendency is low) and attractive forces between solute and solvent also decrease escaping tendency of solvent molecules.

Figure 11.9: An aqueous solution and pure water in a closed environment. (a) Initial stage. (b) After a period of time, the water is transferred to the solution.

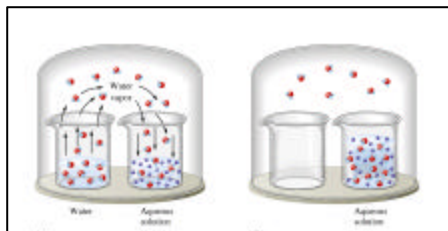
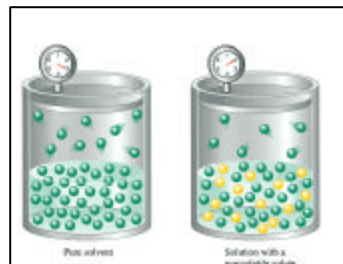


Figure 11.10: The presence of a nonvolatile solute inhibits the escape of solvent molecules from the liquid and so lowers the vapor pressure of the solvent.



Raoult's Law

The presence of a nonvolatile solute lowers the vapor pressure of a solvent.

$$P_{\text{soln}} = \chi_{\text{solvent}} P_{\text{solvent}}^{\circ}$$

P_{soln} = vapor pressure of the solution
 χ_{solvent} = mole fraction of the solvent
 $P_{\text{solvent}}^{\circ}$ = vapor pressure of the pure solvent

Figure 11.11: For a solution that obeys Raoult's law, a plot of P_{soln} versus x_{solvent} gives a straight line.

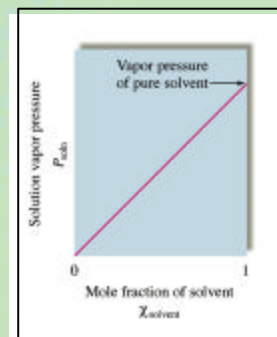
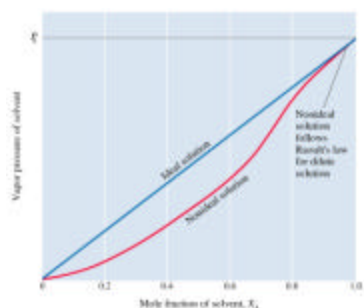


Figure 12.16: Plot of vapor pressure solutions showing Raoult's law.



Vapor Pressure of a Solution

We can relate the *change in pressure* (ΔP) of the solvent, A, to the concentration (mole fraction) of the nonvolatile solute, B:

$$\begin{aligned} \Delta P &= P_A^{\circ} - P_A = P_A^{\circ} - P_A^{\circ} X_A \\ &= P_A^{\circ} (1 - X_A) = P_A^{\circ} X_B \end{aligned}$$

Since $X_A + X_B = 1$

where P_A° = pressure of the pure solvent & P_A = pressure of the mixture, X_A is the mole fraction of the solvent and X_B is the mole fraction of the solute.

$$\Delta P = P_A^{\circ} X_B$$

Vapor Pressure of a Solution

- If a solution contains a **volatile solute**, then each component contributes to the vapor pressure of the solution.

$$P_{\text{solution}} = (P_{\text{solvent}}^{\circ})(C_{\text{solvent}}) + (P_{\text{solute}}^{\circ})(C_{\text{solute}})$$

- In other words, the vapor pressure of the solution is the sum of the partial vapor pressures of the solvent and the solute. Dalton's Law of Partial Pressures.
- Volatile compounds can be separated using fractional distillation. ([see Figure 12.17](#))

Figure 11.12: When a solution contains two volatile components, both contribute to the total vapor pressure.



Figure 11.13: Vapor pressure for a solution of two volatile liquids. (a) The behavior predicted for an ideal liquid-liquid solution by Raoult's law. (b) A solution for which P_{TOTAL} is larger than the value calculated from Raoult's law. This solution shows a positive deviation from Raoult's law. (c) A solution for which P_{TOTAL} is smaller than the value calculated from Raoult's law. This solution shows a negative deviation from Raoult's law.

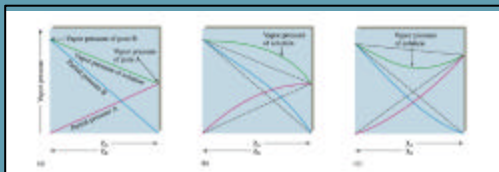


TABLE 11.4 Summary of the Behavior of Various Types of Solutions

Intermolecular Forces Between Solute (A) and Solvent (B) Particles	ΔH_{mix}	ΔT for Solution Formation	Deviation from Raoult's Law	Example
A ↔ A, B ↔ B ≡ A ↔ B	Zero	Zero	None (ideal solution)	Hexane-toluene
A ↔ A, B ↔ B < A ↔ B	Negative (exothermic)	Positive	Negative	Acetone-chloroform
A ↔ A, B ↔ B > A ↔ B	Positive (endothermic)	Negative	Positive	Ethanol-hexane

Colligative Properties

Depend only on the number, not on the identity, of the solute particles in an ideal solution.

- ▣ Boiling point elevation
- ▣ Freezing point depression
- ▣ Osmotic pressure

Boiling Point Elevation

A nonvolatile solute elevates the boiling point of the solvent.

$$\Delta T = K_b m_{\text{solute}}$$

K_b = molal boiling point elevation constant
 m = molality of the solute

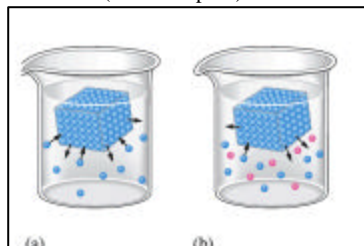
Freezing Point Depression

A nonvolatile solute depresses the freezing point of the solvent.

$$\Delta T = K_f m_{\text{solute}}$$

K_f = molal freezing point depression constant
 m = molality of the solute

Figure 11.15: (a) Ice in equilibrium with liquid water. (b) Ice in equilibrium with liquid water containing a dissolved solute (shown in pink).



The addition of antifreeze lowers the freezing point of water in a car's radiator.



Figure 11.14: Phase diagrams for pure water (red lines) and for an aqueous solution containing a nonvolatile solute (blue lines).

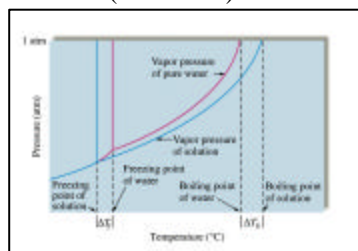


TABLE 11.5 Molal Boiling-Point Elevation Constants (K_b) and Freezing-Point Depression Constants (K_f) for Several Solvents

Solvent	Boiling Point (°C)	K_b (°C · kg/mol)	Freezing Point (°C)	K_f (°C · kg/mol)
Water (H ₂ O)	100.0	0.51	0	1.86
Carbon tetrachloride (CCl ₄)	76.5	5.03	-22.99	30.
Chloroform (CHCl ₃)	61.2	3.63	-63.5	4.70
Benzene (C ₆ H ₆)	80.1	2.53	-5.5	5.12
Carbon disulfide (CS ₂)	46.2	2.34	-111.5	3.83
Ethyl ether (C ₂ H ₅ O)	34.5	2.02	-116.2	1.79
Camphor (C ₁₀ H ₁₆ O)	208.0	5.95	179.8	40.

Osmotic Pressure

Osmosis : The flow of solvent into the solution through the semipermeable membrane.

Osmotic Pressure : The excess hydrostatic pressure on the solution compared to the pure solvent.

$$\Pi = MRT$$

Figure 11.16: A tube with a bulb on the end that is covered by a semipermeable membrane.

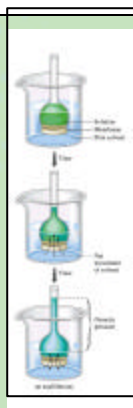


Figure 11.17: The normal flow of solvent into the solution (osmosis) can be prevented by applying an external pressure to the solution. The minimum pressure required to stop the osmosis is equal to the osmotic pressure of the solution.

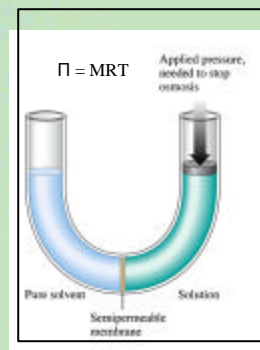


Figure 11.18: (a) A pure solvent and its solution (containing a nonvolatile solute) are separated by a semipermeable membrane through which solvent molecules (blue) can pass but solute molecules (green) cannot. The rate of solvent transfer is greater from solvent to solution than from solution to solvent. (b) The system at equilibrium, where the rate of solvent transfer is the same in both directions.

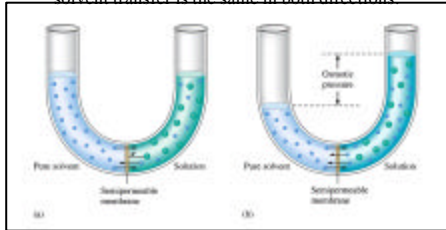
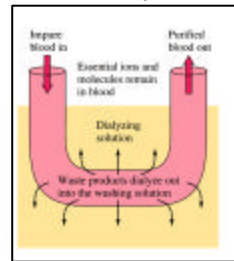


Figure 11.19: Representation of the functioning of an artificial kidney.



If the external pressure is larger than the osmotic pressure, **reverse osmosis** occurs.

One application is **desalination of seawater**.

Figure 11.20: Reverse osmosis.

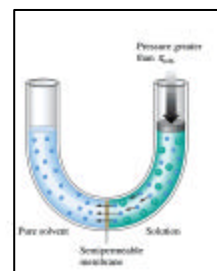
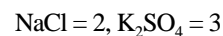


Figure 11.21: (a) Residents of Catalina Island off the coast of southern California are benefiting from a new desalination plant that can supply 132,000 gallons a day, or one-third of the island's daily needs. (b) Machinery in the desalination plant for Catalina Island.



Colligative Properties of Electrolyte Solutions

van't Hoff factor, " i ", relates to the number of ions per formula unit.



$$i = \frac{\text{moles of particles in solution}}{\text{moles of solute dissolved}}$$

$$\Delta T = i m K$$

$$p = i M R T$$

Figure 11.22: In an aqueous solution a few ions aggregate, forming ion pairs that behave as a unit.

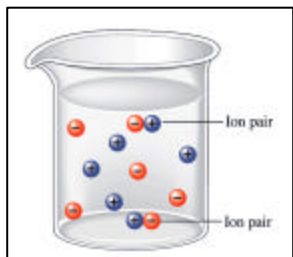


TABLE 11.6 Expected and Observed Values of the van't Hoff Factor for 0.05 *m* Solutions of Several Electrolytes

Electrolyte	<i>i</i> (expected)	<i>i</i> (observed)
NaCl	2.0	1.9
MgCl ₂	3.0	2.7
MgSO ₄	2.0	1.3
FeCl ₃	4.0	3.4
HCl	2.0	1.9
Glucose*	1.0	1.0

Colloids

Colloidal Dispersion (colloid): A suspension of tiny particles in some medium.

aerosols, foams, emulsions, sols

Coagulation: The addition of an electrolyte, causing destruction of a colloid.

Figure 11.23: The Tyndall effect.



TABLE 11.7 Types of Colloids

Examples	Dispersing Medium	Dispersed Substance	Colloid Type
Fog, aerosol sprays	Gas	Liquid	Aerosol
Smoke, airborne bacteria	Gas	Solid	Aerosol
Whipped cream, soap suds	Liquid	Gas	Foam
Milk, mayonnaise	Liquid	Liquid	Emulsion
Paint, clays, gelatin	Liquid	Solid	Sol
Marshmallow, polystyrene foam	Solid	Gas	Solid foam
Butter, cheese	Solid	Liquid	Solid emulsion
Ruby glass	Solid	Solid	Solid sol

Figure 11.24: A representation of two colloidal particles.

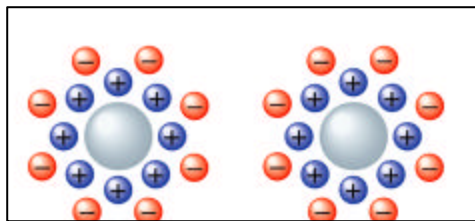


Figure 11.25: The Cottrell precipitator installed in a smokestack. The charged plates attract the colloidal particles because of their ion layers and thus remove them from the smoke.

