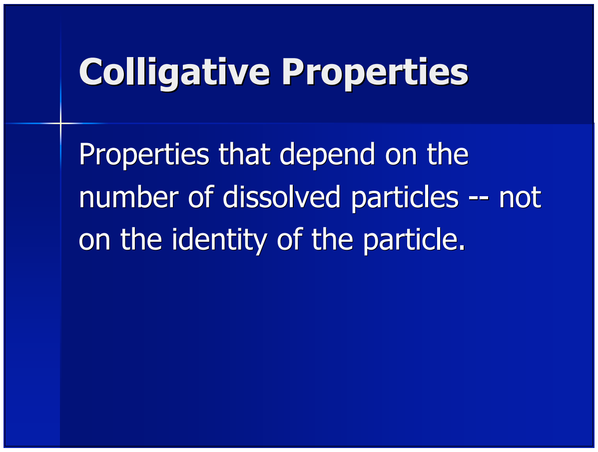
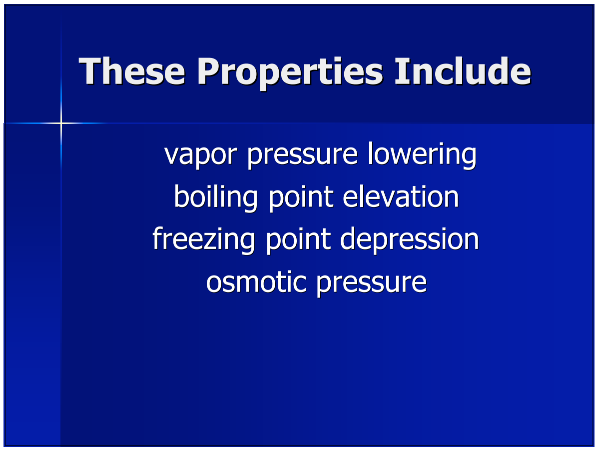
PROPERTIES OF SOLUTIONS



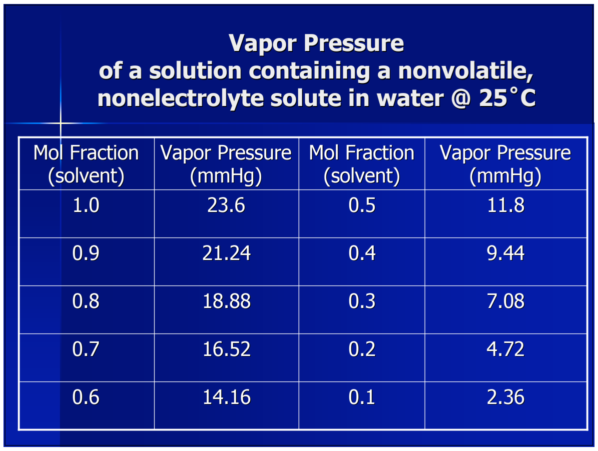
Colligative Properties

Properties that depend on the number of dissolved particles -- not on the identity of the particle.



These Properties Include

vapor pressure lowering
boiling point elevation
freezing point depression
osmotic pressure



Vapor Pressure of a solution containing a nonvolatile, nonelectrolyte solute in water @ 25˚C

Mol Fraction (solvent)	Vapor Pressure (mmHg)	Mol Fraction (solvent)	Vapor Pressure (mmHg)
1.0	23.6	0.5	11.8
0.9	21.24	0.4	9.44
0.8	18.88	0.3	7.08
0.7	16.52	0.2	4.72
0.6	14.16	0.1	2.36

Vapor Pressure Lowering

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

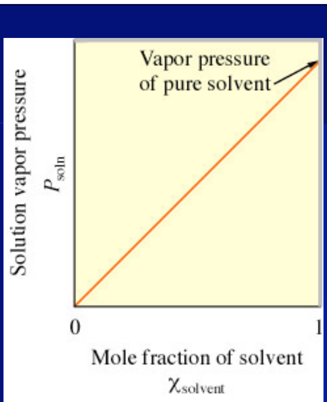
$\boxed{P_{solution} = (X_{solvent})(P^o_{solvent})}$

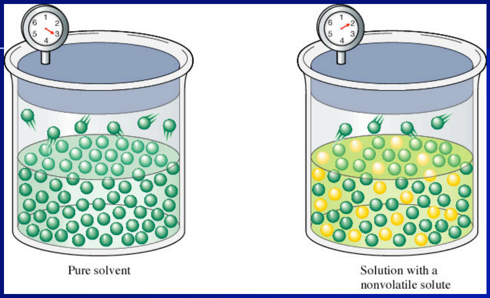
$P_{solution}$ = observed vapor pressure of the solvent in the solution

$X_{solvent}$ = mole fraction of solvent

$P^o_{solvent}$ = vapor pressure of the pure solvent

FOR AN IDEAL SOLUTION!





The vapor pressure of a solution is directly proportional to the mole fraction of solvent present.

Calculate the expected vapor pressure at 25 °C for a solution prepared by dissolving 97.4 g of common table sugar (sucrose, MM = 342) in 453 mL of water.

Calculate the expected vapor pressure at 25 °C for a solution prepared by dissolving 97.4 g of common table sugar (sucrose, MM = 342 $\mathrm{g\ mol^{-1}}$) in 453 mL of water.

We will use Raoult's law in the form

$$P_{soln} = \chi_{H_2O} P^{\circ}_{H_2O}$$

We need to determine the mol fraction of water

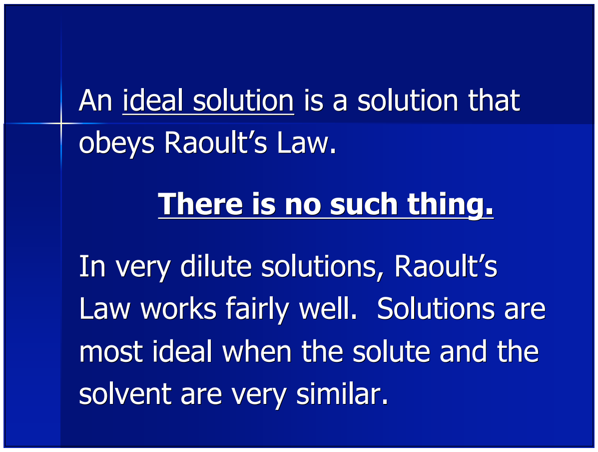
97.4 g (1 mol/342 g $\mathrm{mol^{-1}}$) = 0.285 mol sucrose
453 mL (1 g/1 mL) (1 mol/18 g $\mathrm{mol^{-1}}$) = 25.2 mol H_2O

χ_{H_2O} = 25.2 mol/(25.2 mol + .285 mol) = .989
The vapor pressure of water at 25 ˚C is 23.76 mm Hg (Appendix C in Brown & LeMay).

P_{soln} = .989 (23.76 mm) = 23.5 mm of Hg

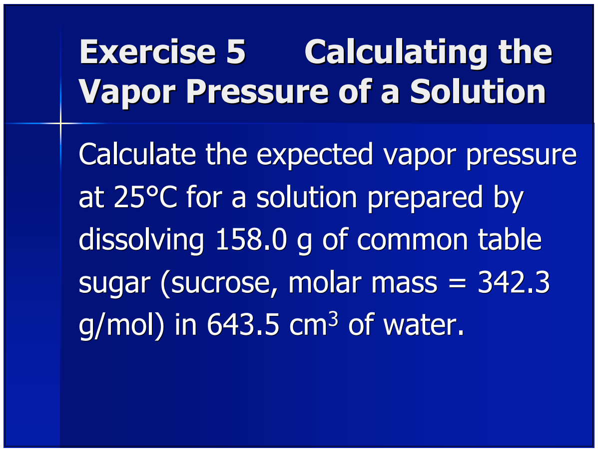
If the solute ionizes, the number of ions affects vapor pressure.

The moles of solute must be multiplied by the number of ions the given solute breaks into.

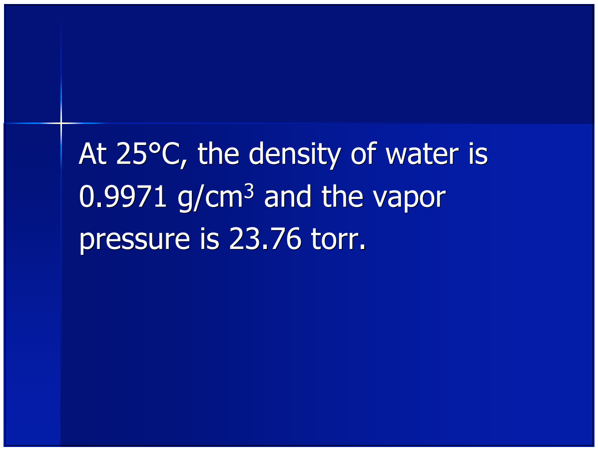

An ideal solution is a solution that obeys Raoult's Law.

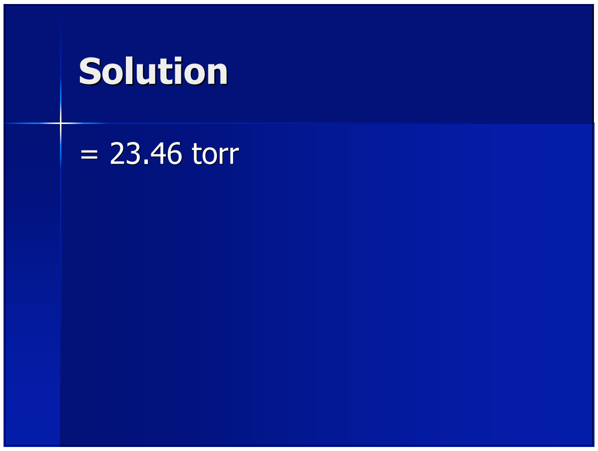
There is no such thing.

In very dilute solutions, Raoult's Law works fairly well. Solutions are most ideal when the solute and the solvent are very similar.

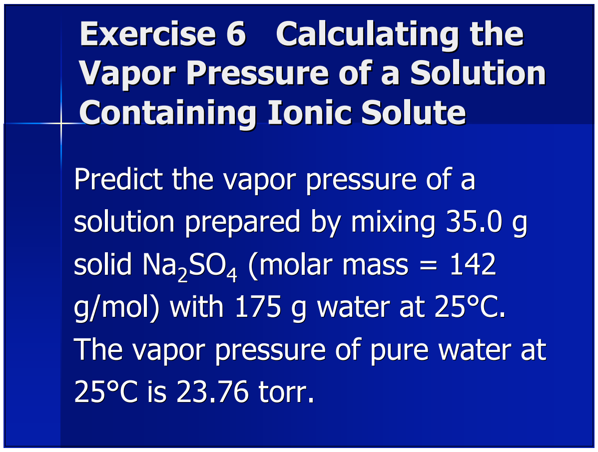

Exercise 5 Calculating the Vapor Pressure of a Solution

Calculate the expected vapor pressure at 25°C for a solution prepared by dissolving 158.0 g of common table sugar (sucrose, molar mass = 342.3 g/mol) in 643.5 cm^3 of water.


At 25°C, the density of water is 0.9971 g/cm^3 and the vapor pressure is 23.76 torr.

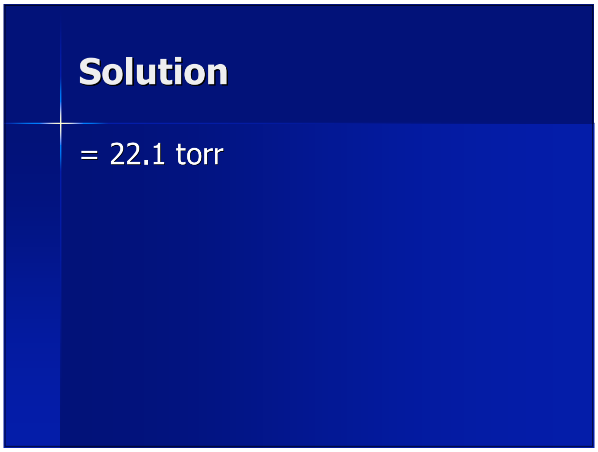

Solution

= 23.46 torr



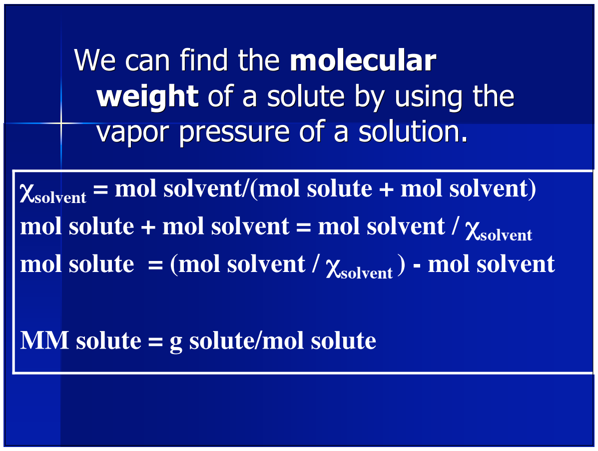
Exercise 6 Calculating the Vapor Pressure of a Solution Containing Ionic Solute

Predict the vapor pressure of a solution prepared by mixing 35.0 g solid Na_2SO_4 (molar mass = 142 g/mol) with 175 g water at 25°C. The vapor pressure of pure water at 25°C is 23.76 torr.



Solution

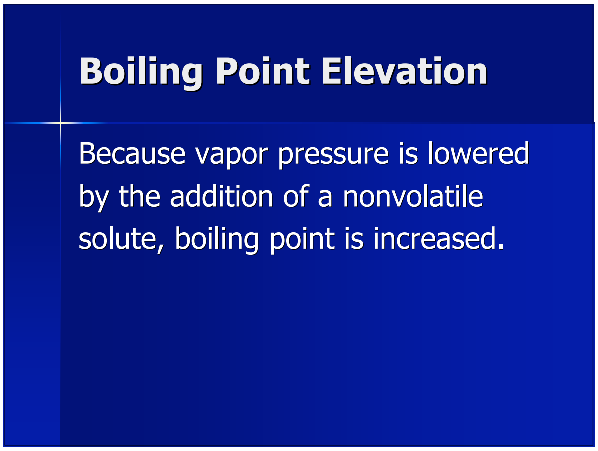
= 22.1 torr



We can find the **molecular weight** of a solute by using the vapor pressure of a solution.

$\chi_{solvent}$ = mol solvent/(mol solute + mol solvent)
mol solute + mol solvent = mol solvent / $\chi_{solvent}$
mol solute = (mol solvent / $\chi_{solvent}$) - mol solvent

MM solute = g solute/mol solute



Boiling Point Elevation

Because vapor pressure is lowered by the addition of a nonvolatile solute, boiling point is increased.

$$\boxed{\Delta T = K_b \times m_{solute} \times i}$$

K_b = molal boiling point elevation constant (for water = 0.51 ˚C/m)
i = van't Hoff factor
m = concentration in molality
ΔT = change in temperature

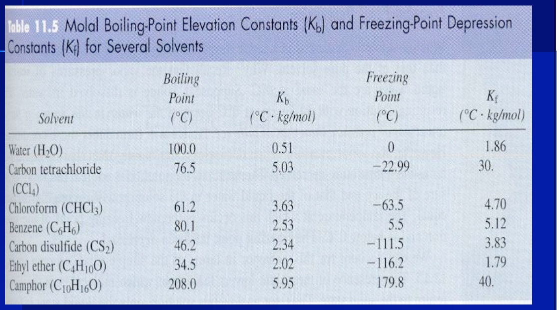


Table 11.5 Molal Boiling-Point Elevation Constants (K_b) and Freezing-Point Depression Constants (K_f) for Several Solvents

Solvent	*Boiling Point (°C)*	K_b *(°C · kg/mol)*	*Freezing Point (°C)*	K_f *(°C · kg/mol)*
Water (H_2O)	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_6H_6)	80.1	2.53	5.5	5.12
Carbon disulfide (CS_2)	46.2	2.34	−111.5	3.83
Ethyl ether ($C_4H_{10}O$)	34.5	2.02	−116.2	1.79
Camphor ($C_{10}H_{16}O$)	208.0	5.95	179.8	40.

Freezing Point Depression

Freezing is the temperature at which the vapor pressure of the solid and the liquid are equal. If the vapor pressure of the liquid is lowered, the freezing point decreases. This is why NaCl and $CaCl_2$ are used on icy roads and sidewalks.

A solution does not have a sharply defined freezing point.

Useful for separation purposes in fractional crystallization.

$$\boxed{\Delta T = K_f \times m_{solute} \times i}$$

K_f = molal freezing point depression constant (for water = 1.86 °C/m)

Add 6 qts. of antifreeze to 12 qts. cooling system in order to lower the FP to -34°F and raise the BP to +226° F.

Solute concentration must be low (0.10*m*).

Disadvantage--compound must be nonvolatile and stable at the boiling point.

Still used widely.

Remember that you are looking for grams/mole!

Example

Calculate the freezing point and boiling point of a solution of 100. g ethylene glycol ($C_2H_6O_2$) in 900. g of water.

Exercise 8 Calculating the Molar Mass by Boiling-Point Elevation

A solution was prepared by dissolving 18.00 g glucose in 150.0 g water. The resulting solution was found to have a boiling point of 100.34°C.

Calculate the molar mass of glucose.

Glucose is a molecular solid that is present as individual molecules in solution.

Solution

= 180 g/mol

Exercise 9 Freezing-Point Depression

What mass of ethylene glycol ($C_2H_6O_2$, molar mass = 62.1 g/mol), the main component of antifreeze, must be added to 10.0 L water to produce a solution for use in a car's radiator that freezes at -10.0°F (-23.3°C)? Assume the density of water is exactly 1 g/mL.

Solution

= 7.76 X 10^3 g (or 7.76 kg)

Exercise 10 Determining Molar Mass by Freezing-Point Depression

A chemist is trying to identify a human hormone, which controls metabolism, by determining its molar mass.

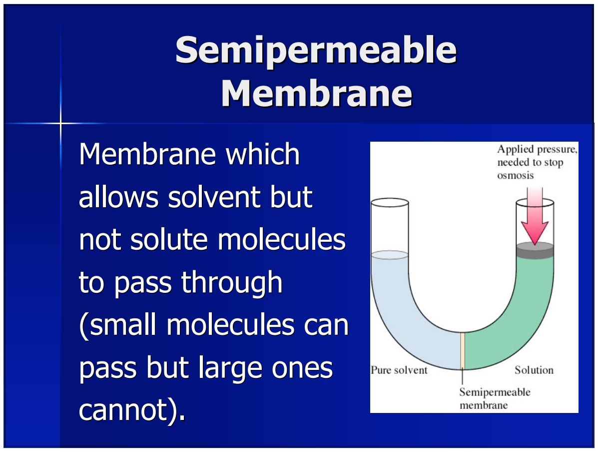
A sample weighing 0.546 g was dissolved in 15.0 g benzene, and the freezing-point depression was determined to be 0.240° C.

Calculate the molar mass of the hormone.

Solution

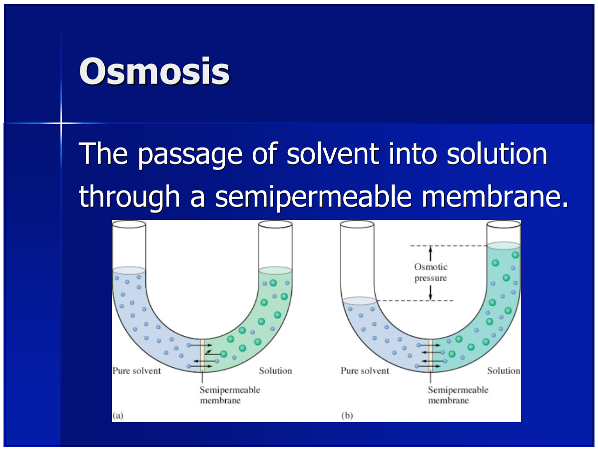
= 776 g/mol

OSMOTIC PRESSURE



Semipermeable Membrane

Membrane which allows solvent but not solute molecules to pass through (small molecules can pass but large ones cannot).



Osmosis

The passage of solvent into solution through a semipermeable membrane.

Osmosis occurs when solvent molecules move through a semipermeable membrane from a region of lower solute concentration to a region of higher solute concentration. It is driven by the need nature has to establish an equilibrium.

Osmotic Pressure-(π)

The pressure that must be applied to a solution to prevent the net movement of water from solvent to solution (osmosis).

The osmotic pressure of a solution is proportional to the number of solute particles in a given volume of solution, that is, to the molarity.

The equation is similar to the ideal gas law since both relate the pressure of a system to its concentration and temperature.

$$\boxed{\pi = MRTi \text{ or } \pi = \frac{nRT}{V} \times i}$$

π = osmotic pressure in atm
M = molarity of the solution
R = 0.08206 L-atm/K-mol
T = temperature in Kelvin
i = van't Hoff factor

The use of osmotic pressure calculations for determining the molecular mass of an unknown substance is more accurate than the use of freezing point depression or boiling point elevation data because a small concentration of solute produces a relatively large osmotic pressure.

Ideal for measuring molar masses of large molecules of biological importance.

Example

The concentration of hemoglobin in blood is roughly 15g/100mL of solution.

Assume that a solution contains 15g of hemoglobin dissolved in water to make 100 mL of solution and that the osmotic pressure of this solution is found to be 0.050 atm at 25°C.

What is the molecular mass of hemoglobin?

(The osmotic pressure of a 1 m solution at 25°C is 24.45 atm.)

[illegible]

[illegible]

Exercise 11 Determining Molar Mass from Osmotic Pressure

To determine the molar mass of a certain protein, 1.00×10^{-3} g of it was dissolved in enough water to make 1.00 mL of solution.

The osmotic pressure of this solution was found to be 1.12 torr at 25.0°C.

Calculate the molar mass of the protein.

Solution

= 1.66 X 10^4 g/mol

Exercise 12 Isotonic Solutions

What concentration of sodium chloride in water is needed to produce an aqueous solution isotonic with blood (B = 7.70 atm at 25°C)?

Solution

= 0.158 *M*

Exercise 13

Osmotic Pressure

The observed osmotic pressure for a 0.10 *M* solution of $Fe(NH_4)^2(SO_4)^2$ at 25°C is 10.8 atm.

Compare the expected and experimental values for *i*.

Solution

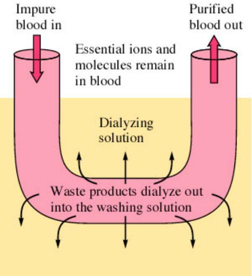
Expected = 5

Experimental = 4.4

APPLICATIONS OF OSMOSIS

Dialysis

A phenomenon in which a semipermeable membrane allows transfer of both solvent molecules and small solute molecules and ions. Occurs in walls of most plant and animal cells.

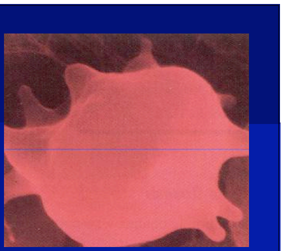


Kidney dialysis is one of most important applications. Waste molecules move into the "wash" solution and filter the blood.

Isotonic Solution

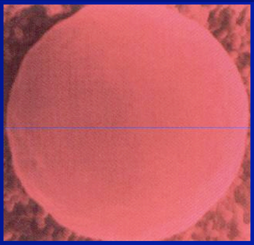
Solutions that have the same osmotic pressure. (Ex. IV fluids)

Hypertonic



Solution has higher osmotic pressure (cells bathed in a hypertonic solution would shrivel –crenation). Treating the surface of food with salt causes this to happen to bacteria.

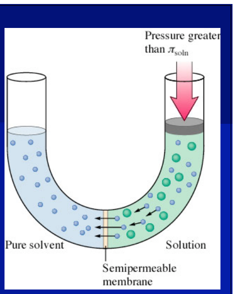
Hypotonic



Solution has lower osmotic pressure (cells bathed in a hypotonic solution would burst—hemolysis).

Reverse Osmosis

The process occurring when the high external pressure on a solution causes a net flow of solvent through a semipermeable membrane from the solution to the solvent.



Used in desalination (the membrane here acts as a "molecular filter" to remove solute particles). The need for this process will probably increase as the need for drinkable water increases.

Colloids (also called Colloidal Dispersions)

Thomas Graham, 1860--albumin, starch, gelatin and glue diffuse only very slowly and could not be crystallized. He called these substances colloids.

"A suspension of tiny particles in some medium."

The dispersed colloidal particles are larger than a simple molecule but small enough to remain distributed and not settle out.

A colloidal particle has a diameter between 1 and 1000 nm and may contain many atoms, ions, or molecules.

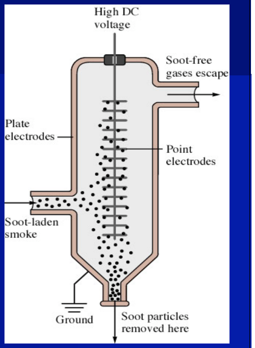
Because of their small particle size, colloids have an enormous total surface area.

The particles stay suspended because of electrostatic repulsion.

Hydrophobic/Hydrophilic ends

Coagulation, destruction of a colloid, occurs by heating (particles collide so hard that they stick together) or by the addition of an electrolyte (neutralizes ion layers).

This process is important in removal of soot from smoke so that air quality has improved somewhat in industrialized cities.



Tyndall Effect

The scattering of light by particles.

Used to distinguish between a suspension and a true solution.

A true solution has particles that are too small to scatter light.

Brownian Motion

A characteristic movement in which the particles change speed and direction erratically (solvent molecules collide with the colloidal particles).

Suspensions are temporary solutions. They will settle eventually. Colloids will not do this.

Solutions are permanent. Particles are really small. Colloids lie in between solutions and suspensions!

Examples of Some Common Colloids

Foam- colloidal dispersion of a gas dispersed in a liquid or solid (ex. Whipped cream and marshmallows)

Aerosol- colloidal dispersion of a liquid or solid dispersed in a gas (ex. Fog and smoke)

Emulsion- colloidal dispersion of a liquid dispersed in a solid or liquid (ex. Butter and milk)

Solution- colloidal dispersion of a solid dispersed in a liquid or solid (ex. Paint or ruby)

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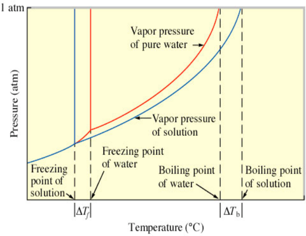
i = van't Hoff factor (moles of electrolyte must be multiplied by this)
Number of moles particles in solution/number of moles particles dissolved.

There are fewer solvent molecules on the surface to escape.



This can be mathematically expressed by Raoult's Law:

For instance, if we had 1 mole of NaCl as the solute, we would use 2 moles of particles for our mole fraction calculations.

For nonelectrolytes, i= 1.

For electrolytes, i = the number of particles formed when one formula unit of the solute dissolves in the solvent.

The experimental value of i is often less than the expected value of i because of a phenomenon called "**ion pairing**".

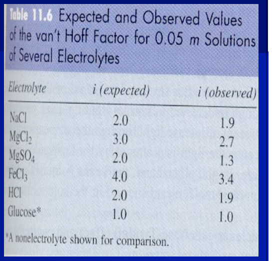


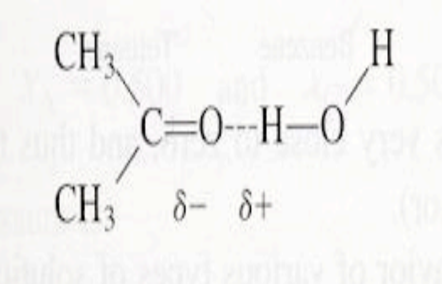
Table 11.6 Expected and Observed Values of the van't Hoff Factor for 0.05 *m* Solutions of Several Electrolytes

Electrolyte	*i (expected)*	*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

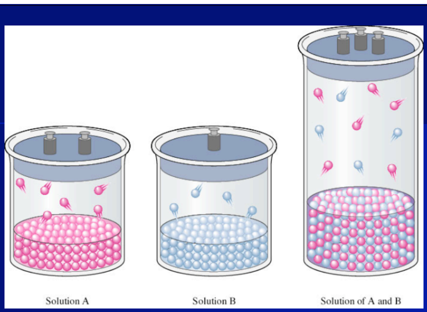
*A nonelectrolyte shown for comparison.

Especially in concentrated solutions, oppositely charged ions can pair up and thus, we have fewer particles than expected.

If hydrogen bonding occurs between solute and solvent, vapor pressure is less than expected. We call this a *negative deviation from Raoult's law*. This can often be predicted when an enthalpy of the solution formation is large and negative (exothermic).



A great example of this negative deviation is acetone and water.

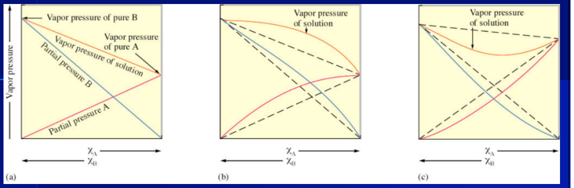


Both solute and solvent contribute to the vapor pressure.

If the solute is more volatile than the solvent, the vapor pressure of the solution is higher than the vapor pressure of the solvent. In this case, the molecules have a higher tendency to escape than expected.

We call this a <u>positive deviation from Raoult's law.</u>

The enthalpy of solution for this type of deviation is positive. (endothermic)



[illegible]

(same as Dalton's Law)

Exercise 7 Calculating the Vapor Pressure of a Solution Containing Two Liquids

A solution is prepared by mixing 5.81 g acetone (C_3H_6O, molar mass = 58.1 g/mol) and 11.9 g chloroform ($HCCl_3$, molar mass = 119.4 g/mol). At 35°C, this solution has a total vapor pressure of 260. torr.

Is this an ideal solution?

The vapor pressures of pure acetone and pure chloroform at 35°C are 345 and 293 torr, respectively.

Solution

Not an ideal solution.

Solutions in which both solute and solvent are liquid and the liquids are volatile, do not behave ideally.

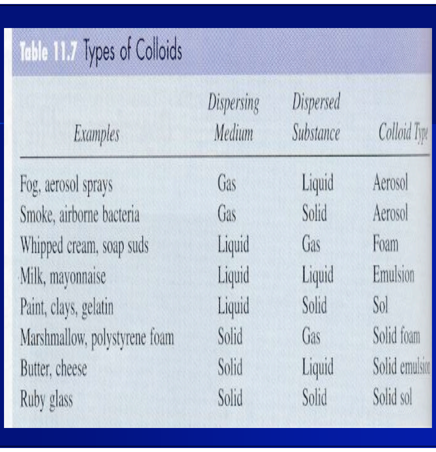


Table 11.7 Types of Colloids

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