Properties of Solutions

Reading:	Ch 11, section 8	Homework:	Chapter 11: 85*, 87
	Ch 12, sections 1-8		Chapter 12: 29, 33, 35, 41, 51*, 53, 55, 63*, 65, 67*, 69, 71, 75*, 79*, 81

* = 'important' homework question

Types of Solutions and Solubility

Discussion: What *very* 'general' kinds of solutes can you dissolve in a solvent (say water) to make a solution? Provide examples.

_____ + water	_____ + water	_____ + water

Quick aside: What happens when one solution is mixed with another, or a solution is mixed with more additional solvent?

Spontaneous Mixing

When the barrier is removed, spontaneous mixing occurs, producing a solution of uniform concentration.

Na^+ Cl^- H_2O

(a)   (b)
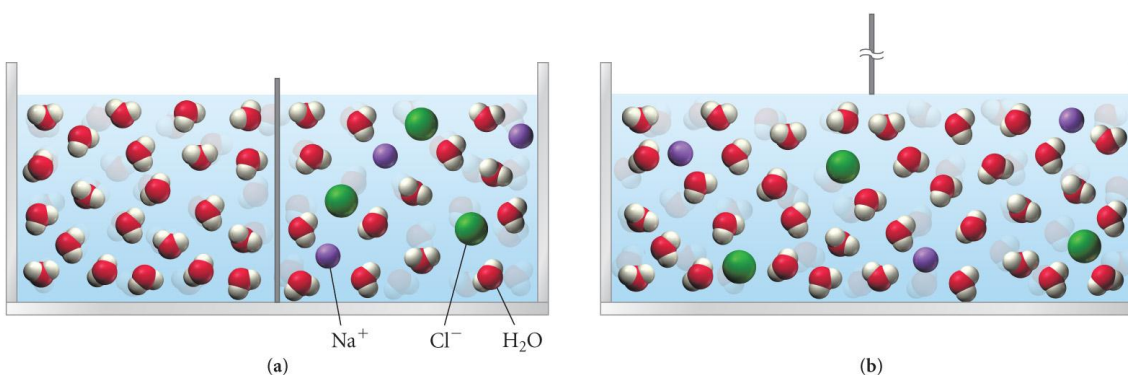
Why do the solutions mix, what's the 'pay off'?

On a *molecular level* the final solution is more 'randomized' (has more ENTROPY*). Chemical systems that possess a higher degree of entropy are more *thermodynamically stable*. 'Nature likes stable'!

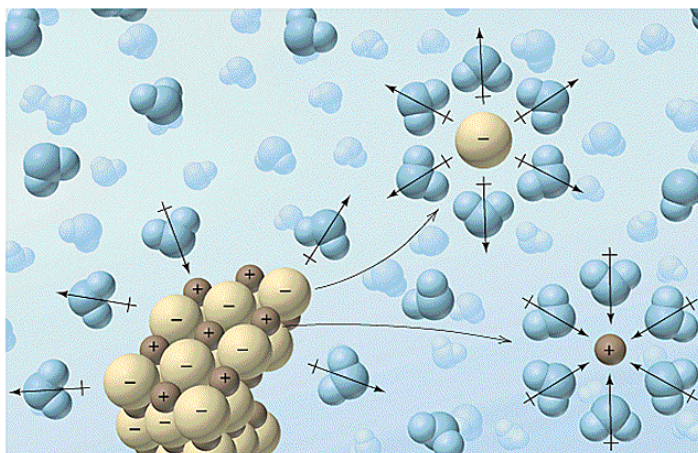*More on Entropy in *Chemical Thermodynamics*

OK, back to it….

Based on your current knowledge (recall the intermolecular forces work from CHM 101), *simply* explain why certain classes of compounds will or will not dissolve in water.
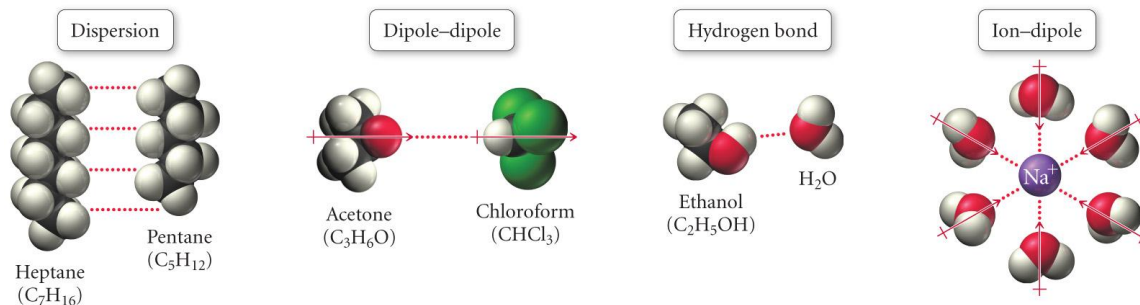<u>*Hint*</u>: *'like dissolves in like' - old chemistry saying**

*Recall the 'ions' slide, plus basic details on solutions (see Appendix).

These forces may contribute to or oppose the formation of a solution.

Dispersion

Dipole–dipole

Hydrogen bond

Ion–dipole

Heptane
(C_7H_{16})

Pentane
(C_5H_{12})

Acetone
(C_3H_6O)

Chloroform
($CHCl_3$)

Ethanol
(C_2H_5OH)

H_2O

Na^+

Solution Interactions

Solvent–solvent
interactions

Solute–solute
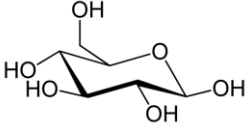interactions

Solvent–solute
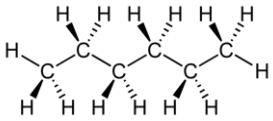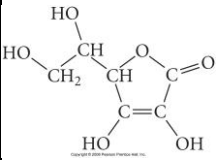interactions
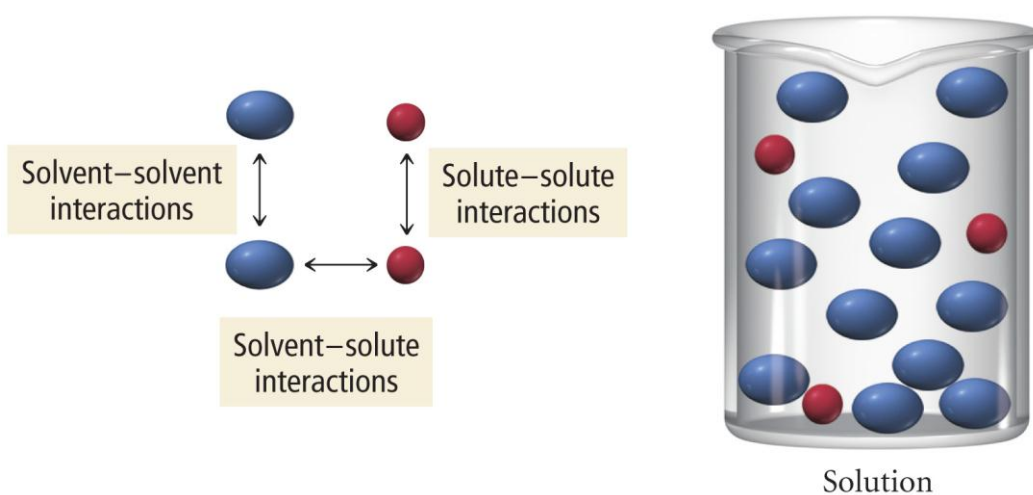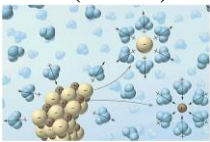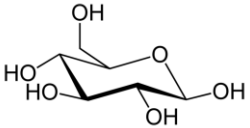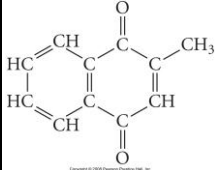
Solution

TABLE 12.2 Relative Interactions and Solution Formation

Solvent–solute interactions	>	Solvent–solvent and solute–solute interactions	Solution forms
Solvent–solute interactions	=	Solvent–solvent and solute–solute interactions	Solution forms
Solvent–solute interactions	<	Solvent–solvent and solute–solute interactions	Solution may or may not form, depending on relative disparity

Task: predict whether the following pairs of compounds are soluble, insoluble, miscible or immiscible. *What's the difference*??

Mixture	Details
Salt (NaCl) with water	
Sugar with water	
Sugar with hexane	
Hexane with water	
Vitamin C with water	
Vitamin K$_3$ with water	

Summary: Recall that '*Nature likes stable*'! Or, in other words, the 'winner' (in terms of the relative strengths of respective intermolecular force combinations) *typically* determines whether the solute /solvent pair are soluble or insoluble.

Solution Energetics

Recall from the CHM 101 *Thermochemistry* material that a difference in stored chemical potential energy (ΔH) – i.e. the change in the amount of energy stored within chemical bonds when reactants → products in a reaction is either released (*exo*thermic) or absorbed (*endo*thermic) as an equivalent amount of heat energy (q). This leads to the First law of thermodynamics:

$$-\Delta H = +q \text{ (exothermic reaction)}$$

A similar approach can be applied to the formation of solutions, and (similarly) be represented in terms of familiar enthalpy (Hess' Law) relationships and diagrams

Heat of Hydration
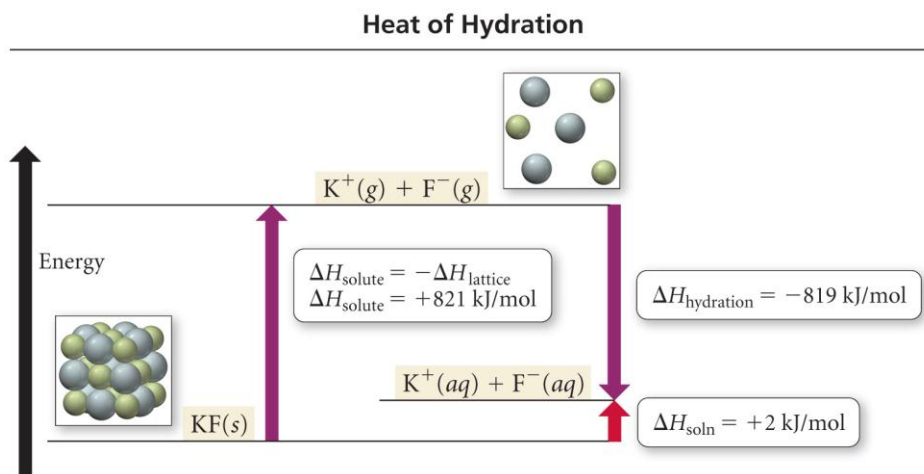
$$\Delta H_{soln} = \Delta H_{solute} + \underbrace{\Delta H_{solvent} + \Delta H_{mix}}$$

$$\Delta H_{soln} = \underset{\substack{\text{endothermic} \\ \text{(positive)}}}{\Delta H_{solute}} + \underset{\substack{\text{exothermic} \\ \text{(negative)}}}{\Delta H_{hydration}}$$
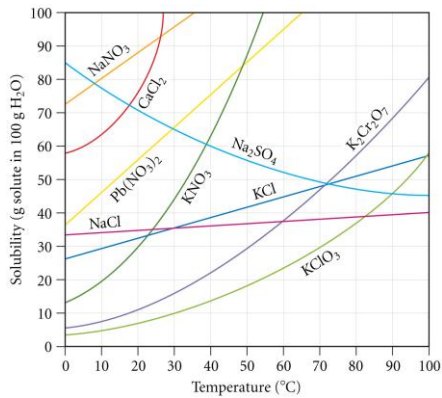
Task: Prove it to yourself; calculate ΔH_{soln} using the ΔH_{solute} and $\Delta H_{hydration}$ values listed above.

Factors Affecting Solubility

Or, in other words, stuff you already know from everyday observation……

<u>Temperature</u>

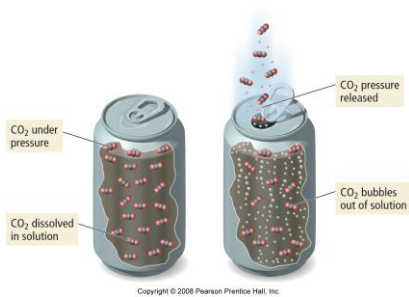How are the solubility of solids and gasses *typically* affected by an increase in temperature?

<u>Solids</u>:

<u>Gasses</u>:

<u>Pressure</u>

How is the solubility of a gas affected by an increase or decrease in pressure?

Expressing Solution Concentration

Overview: There are four ways of expressing the concentration or 'strength' of a solution – **Mola*rity*** (M, mols/L), **% mass**, **ppm** (parts per million) and **Mola*lity*** (mols/kg). **It is important to know how to determine and convert between these concentration types.**

Familiar Units – Molarity and % mass

1. Molarity**:**

Mola*rity** (**M**) = number moles of *solute* per Liter of *solution*

* The Molarity (mol/L conc.) is most often printed on lab reagent solution bottles, e.g. 9.0 M H_2SO_4 (aq)

i.e.   **M**olarity = $\dfrac{\text{Moles Solute}}{\text{Liters Solution}}$ Units: mol/L or just **M**

Example: What is the concentration (molarity, M) of a solution made by dissolving 25 g of NaCl in water and making the final volume of the solution equal to 750 mL?

2. % Mass

$$\% \text{ Mass} = \frac{\text{Mass Solute}}{\text{Mass Solution}} \times 100 \% \qquad (\text{units of } \%)$$

Example: What is the % mass concentration of an NaCl in a solution made by dissolving 25 g of NaCl in water and making the final volume of the solution equal to 750 mL? Assume the final solution has a density of 1.15 g/mL

New Units – ppm and Molality

Discussion: Why learn these new unit types? What are they used for?

3. ppm (parts per million)

The ppm unit is simply a mass ratio: 'grams per million grams', i.e. there is a 'difference factor' of 10^6 between mass solute and mass solution. **A better way to express this would be mg solute per kg solution**

Parts per million = ppm = mg solute per kg of solution

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i.e.   **ppm** =   mg solute   Units: ppm or mg/kg
                  kg solution
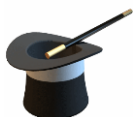
Regular molarity (mol/L) concs can be easily converted to ppm if the density of the solution is known. Recall that mass = density x volume

---

Example: What is the ppm concentration of NaCl in a solution made by dissolving 25 g of NaCl in water and making the final volume of the solution equal to 750 mL? Assume the final solution has a density of 1.15 g/mL

1. Find mass solution

2. Divide mass of solute (in mg) by mass solution (in kg)

4. Molality:

m = Mola*lity* = number moles of *solute* per kg of *solvent*

i.e.   **m**olality = $\dfrac{\text{Moles Solute}}{\text{kg solvent}}$ Units: mol/kg or m

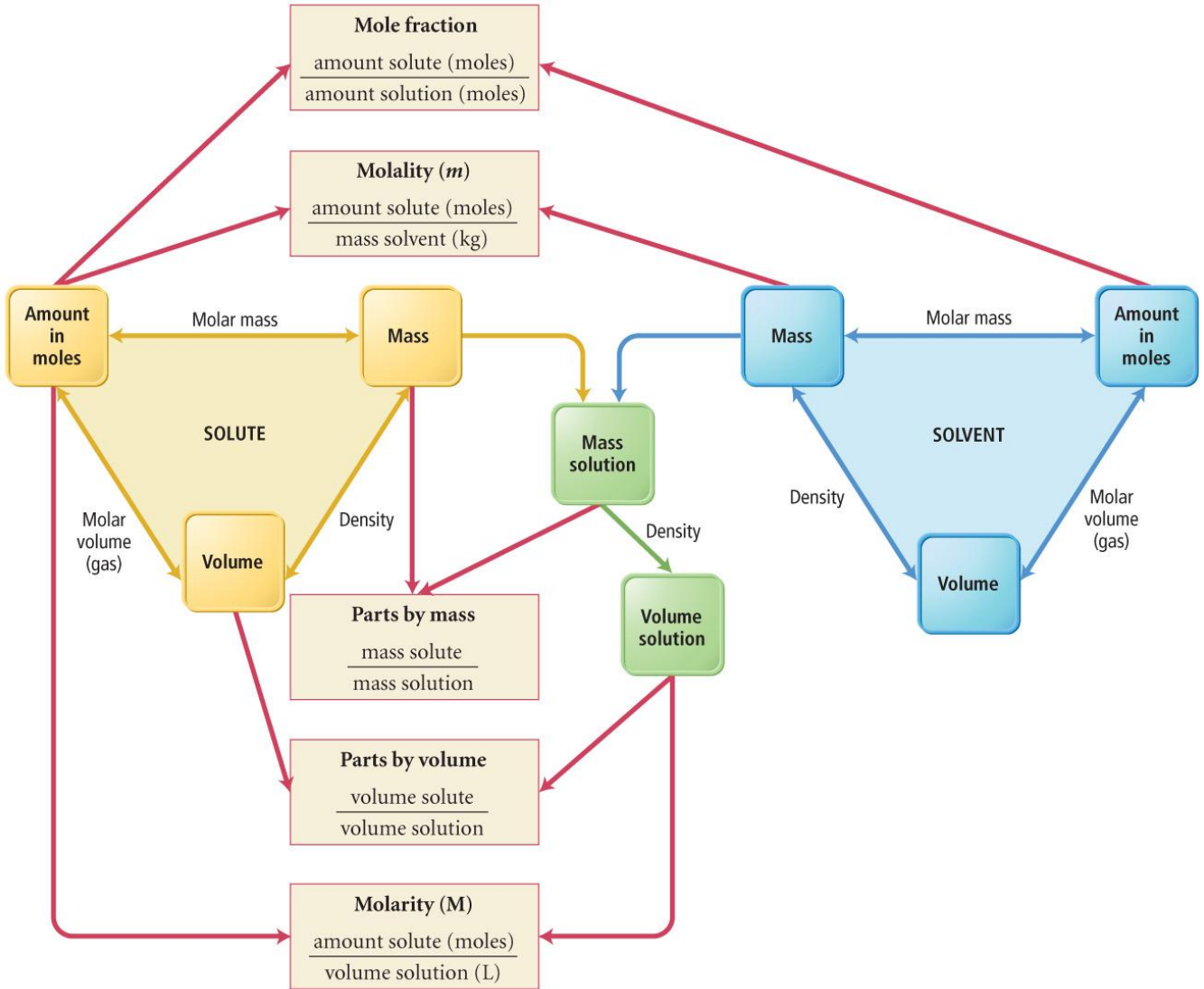Example: What is the molality of an HCl solution that is 36% by mass?

When presented with a % mass concentration, assume that you have 100 g of this solution. The % mass of solute is than the same numerical value as the mass (in g) of solute in the solution

Mass solute =

Mass SOLVENT =

Molality of solution

Units of Concentration and Solution Quantities

Mole fraction

$$\frac{\text{amount solute (moles)}}{\text{amount solution (moles)}}$$

Molality (m)

$$\frac{\text{amount solute (moles)}}{\text{mass solvent (kg)}}$$

SOLUTE

Amount in moles — Molar mass — Mass

Molar volume (gas)

Volume

Density

Mass solution

Density

Volume solution

SOLVENT

Mass — Molar mass — Amount in moles

Density

Molar volume (gas)

Volume

Parts by mass

$$\frac{\text{mass solute}}{\text{mass solution}}$$

Parts by volume

$$\frac{\text{volume solute}}{\text{volume solution}}$$

Molarity (M)

$$\frac{\text{amount solute (moles)}}{\text{volume solution (L)}}$$

Colligative Properties

Definition: A property of a solution that **_only_** depends on the number of particles dissolved in solution (i.e. concentration), **_not_** the type of particle or their respective chemistries (ions, molecules etc.)

Application 1: Boiling Point Elevation / Freezing Point Depression

Discussion: Why is salt added to pasta water, why is salt spread on the roads in winter?

The change in bpt. or fpt. (ΔT) of a solution is proportional to its molality. Bpt. elevation and fpt. depression are colloidal properties – they depend only on the *number* (molality) of solute particles disrupting intermolecular forces between the solvent molecules. It is the solvent's bpt or fpt that is affected.

Equations

Bpt. Elevation

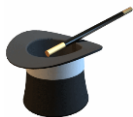$$\Delta T = K_b\, m$$

Fpt. Depression

$$\Delta T = K_f\, m$$

Where: ΔT = *change* in bpt. or fpt. of the solution compared to the pure solvent
K_b = boiling point elevation constant for the solvent
K_f = freezing point depression constant for the solvent
m = molality of the solution

Water is the most common solvent. Its cryoscopic constants are:

K_b (H_2O) = 0.51 $^{\circ}$C/m K_f (H_2O) = 1.86 $^{\circ}$C/m

Example: Calculate the fpt. of a 30 % by mass ethylene glycol ($C_2H_6O_2$) solution (this is what you probably have in your car, or perhaps in your wine rack)

Ionic Solutes

Unlike molecular solutes (like ethylene glycol), ionic solutes dissociate into *more than one* solvated particle when dissolved.

Eg: NaCl(s) → Na⁺ (aq) + Cl⁻ (aq) (x2 as many ions in solution)

**The higher concentration of solvated particles (ions) in solution *must* be accounted for in elevation / depression problems**

Example: What is the boiling point of a solution that has a 2.5 m NaCl conc? What about 2.5 m $CaCl_2$ (sold as 'Quick Melt')

<u>Recall</u>: Phase Diagrams

🔑 **A Phase Diagram relates the physical state (s, l, g) of a material to pressure and temperature conditions.**

Generic Phase Diagram (see appendix)
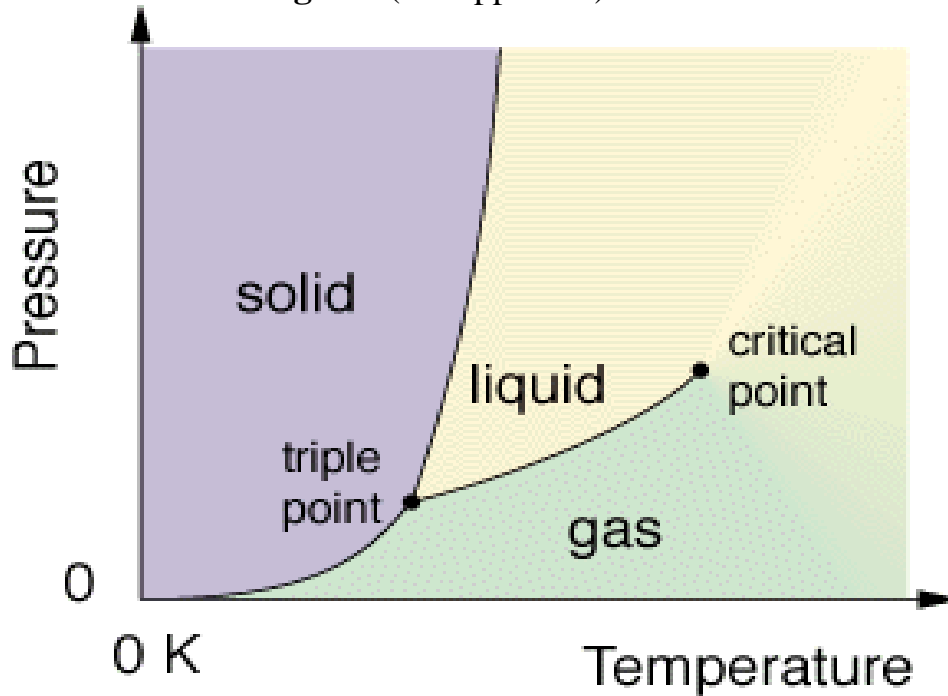
<u>Features of the Graph</u>

<u>Boiling point (l ↔ g)</u>   <u>Triple point</u>
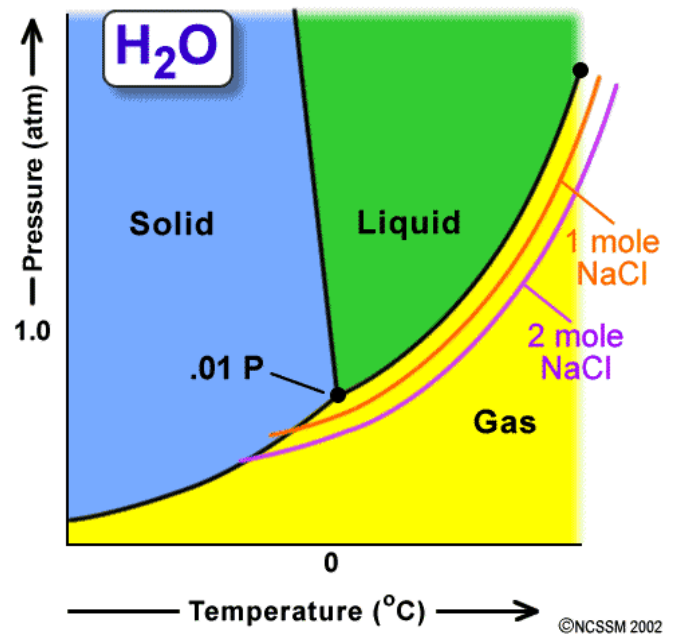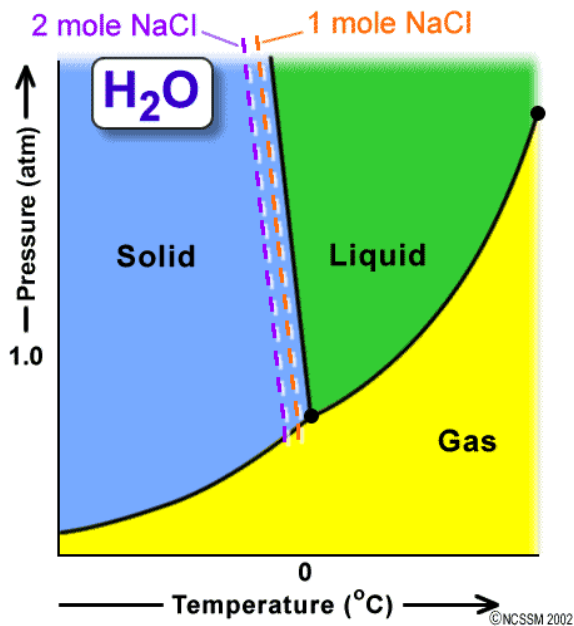
<u>Freezing point (s ↔ l)</u>
                                               <u>Critical point</u>

<u>Sublimation Point (s ↔ g)</u>

Discussion: How would the phase diagram of water be affected if some NaCl was dissolved in the water being studied? Hint: Think about the effects of bpt. and fpt. changes.

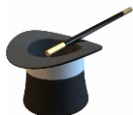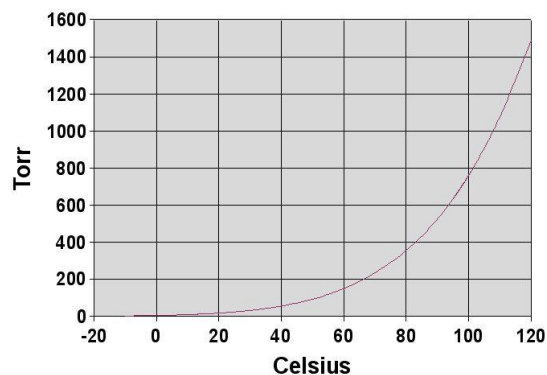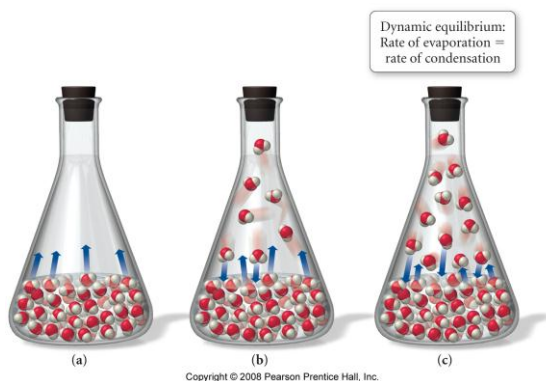Phase Diagrams for an NaCl (aq) solution (see appendix)

Application 2: Vapor Pressure Lowering

> 🔑 **Vapor Pressure = pressure of a gas 'above'
> a liquid when the two are in dynamic equilibrium***

*more on this in the *Equilibrium* packet, also recall Ch.11.

Dynamic equilibrium:
Rate of evaporation =
rate of condensation

(a) (b) (c)
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> 🎩 <u>Think of vapor pressure like humidity</u> – there is always a ***fixed***
> amount (partial pressure) of gaseous material 'above' any liquid
> (in a closed container) at a specific temp – recall the CHM 101
> 'humidity' plot… *What is the vapor pressure of water at 100^oC?*

Think about it. Does the vapor pressure / equilibrium
idea help to explain why clothes on a washing line dry
faster on *warm* and *windy* days??

Raoult's Law Definition: (Recall partial pressure work from CHM 101)

1. Volatile solutes (e.g. ethanol, benzene)
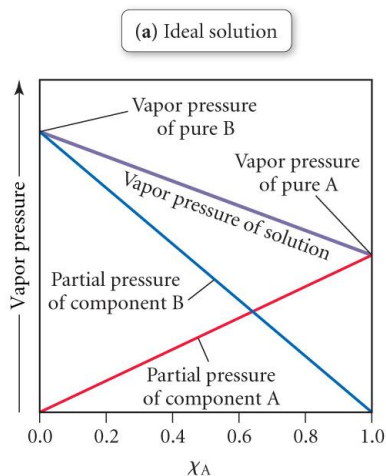
'Using words'

1.

2.

'Using math'

1.   2.

Worked Example (HWK 12.73): A solution contains 50.0 g heptane (C_7H_{16}) and 50.0 g of octane (C_8H_{18}) at 25°C. The vapor pressures of pure heptane and pure octane at 25°C are 45.8 Torr and 10.9 Torr, respectively. Assuming ideal behavior, calculate:

a. The vapor pressure of each of the solution components in the mixture

b. The total pressure above the solution

c. The composition of the vapor in mass percent

Recall that $p \propto n$, and then let 1 mole. = 1 torr

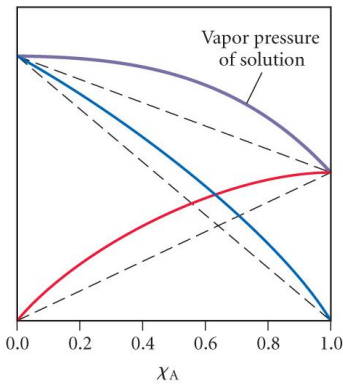d. Why is the composition of the vapor different than that of the solution

Deviating from Raoult's Law

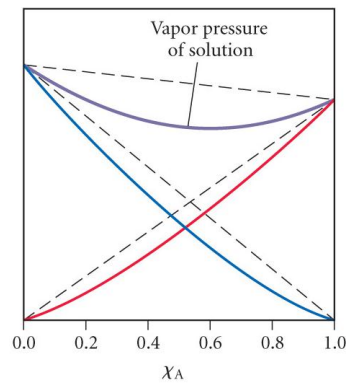|	
🗝️	*Solutions* do not necessarily follow IDEAL (i.e. pure solute or solvent) behavior with regard to their Vapor Pressure v Composition plots – this is called deviating from **Raoult's Law**.

Discussion: What *microscopic* events would cause a deviation from Raoult's Law, i.e. the vapor pressure for the solution to become greater or less than the partial pressure contributions expected from its pure components?
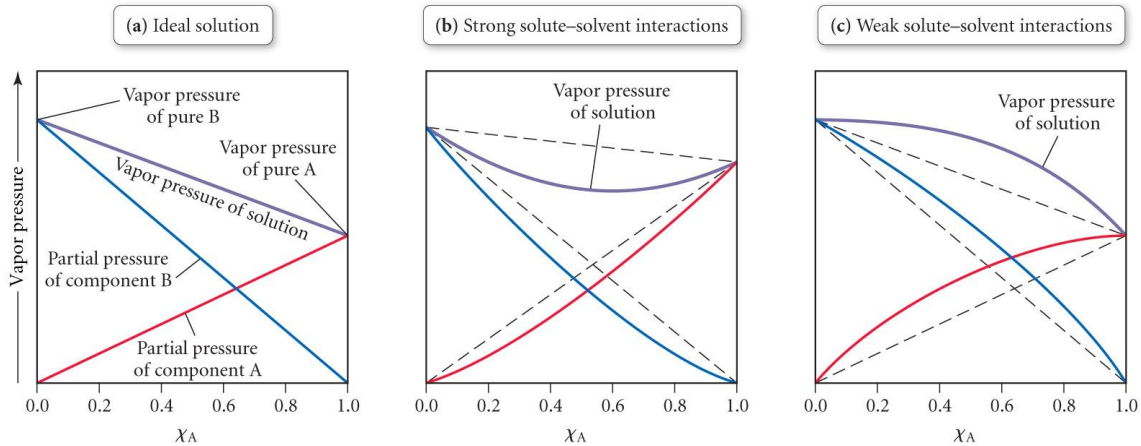
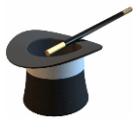## Positive Deviation

Ans:

Negative Deviation

Ans:

Summary

Deviations from Raoult's Law

(a) Ideal solution

(b) Strong solute–solvent interactions

(c) Weak solute–solvent interactions

2. Non-Volatile solutes (e.g. sucrose, table salt)

Since non-volatile solutes will **not** generate a respective vapor above the mixture, only the solvent (now with a reduce mole fraction) will generate a slightly reduced, (compared to its pure state) vapor pressure.

Worked Example: Calculate the vapor pressure at $25^{\circ}C$ of a solution containing 95.5 g sucrose ($C_{12}H_{22}O_{11}$) and 300.0 mL water. The vapor pressure water at $25^{\circ}C$ is 23.8 Torr, assume density $H_2O = 1.00$ g/mL

Plan:

Execute:

<u>Task</u>: Calculate the vapor pressure at 25°C of a solution containing 55.3 g ethylene glycol ($C_2H_6O_2$) and 285.2 mL water. The vapor pressure water at 25°C is 23.8 Torr, assume density H_2O = 1.00 g/mL.
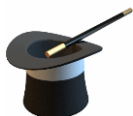
Recall that for ionic solutions, the concentration of colloidal particles in solution is 'multiplied out' by the number of ions of the formula unit. *Be sure to remember this when answering questions pertaining to ionic solutes.*

e.g. Since NaCl(s) → Na^+(aq) + Cl^-(aq) ($i \approx 2$), the effective concentration of particles in 0.20 M NaCl (aq) is…

Ion pairing

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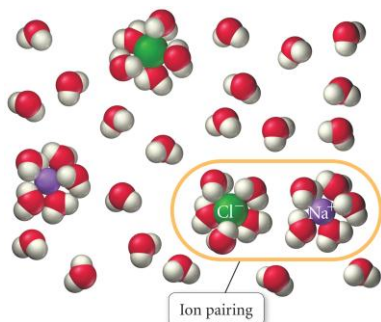
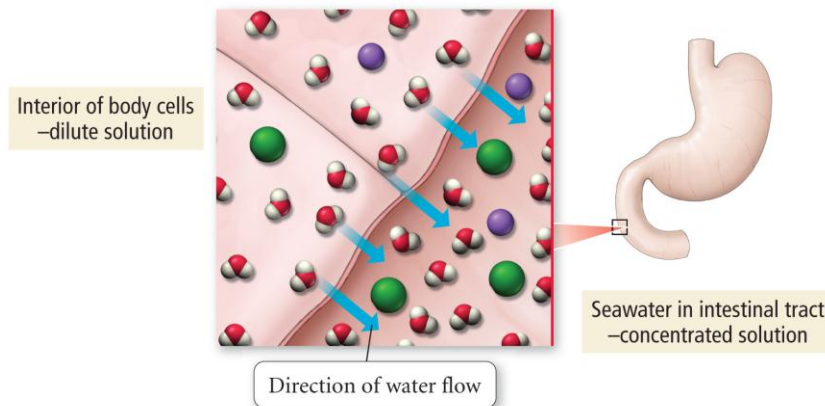*see appendix for measured i values
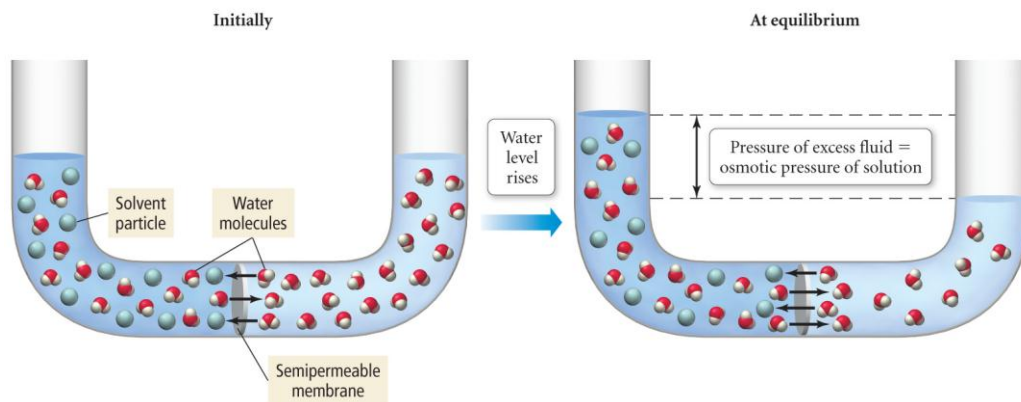
Application 3: Osmotic Pressure
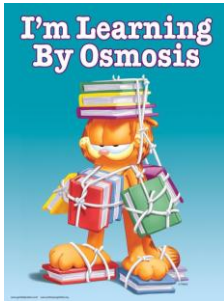
Discussion: Please explain the joke / observation that: "I'm learning through osmosis"
Scientific hint: recall the earlier discussion about mixing solutions

Observation: 'Seawater and Hangovers'

Interior of body cells –dilute solution

Seawater in intestinal tract –concentrated solution

Direction of water flow

Osmosis and Osmotic Pressure

Initially

At equilibrium

Solvent particle

Water molecules

Semipermeable membrane

Water level rises

Pressure of excess fluid = osmotic pressure of solution

<u>Osmotic Pressure Math</u>

$$\Pi = i\text{MRT}$$

<u>Where:</u> Π = osmotic pressure

i = number of ions per formula unit (ionic solutes only)

M = Molarity (mol/L)

R= gas constant (0.0821 Latm/mol K)

T= temp in K

<u>Worked Example</u>: The osmotic pressure of a solution containing 5.87 mg of an unknown protein (per 10.0 mL of solution) was 2.45 Torr at 25°C. Find the molar mass of the protein.

<u>Extra credit (2 points)</u>: Type a brief (less than 100 words) report detailing how *reverse osmosis* works. Include at least one diagram.

""Bloody Solution"

The following question was taken from your 1st practice midterm:

Question 5 (30 points): Calculate the osmotic pressure of a solution containing 20.5 mg of hemoglobin in 15.0 mL of solution at $25^{o}C$. The molar mass of hemoglobin is 6.5×10^{4} g/mol.

<u>Appendix</u>

Chem. 101 Review Material: **Strong, Weak and Non-Electrolytic solutions**

<u>Strong Electrolytes</u>: **Salts**

Cl^-

Na^+

NaCl (aq)
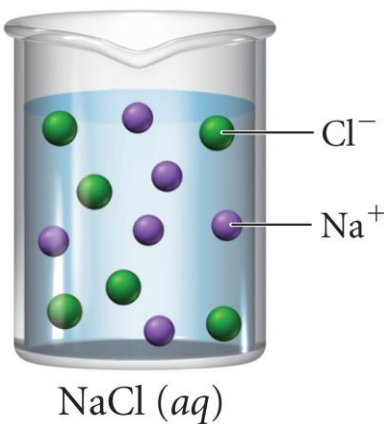
> **Strong electrolytes contain *very* large numbers of dissociated ions when dissolved**

Strong electrolytes are formed from the dissolution of SALTS (e.g. NaCl), which typically <u>undergo complete (100%) dissociation</u>
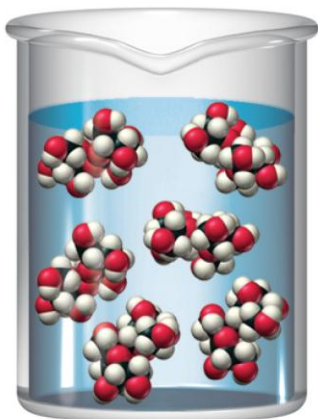
<u>Weak Electrolytes</u>: **Molecular acids**

$C_2H_3O_2^-$

$HC_2H_3O_2$

H^+
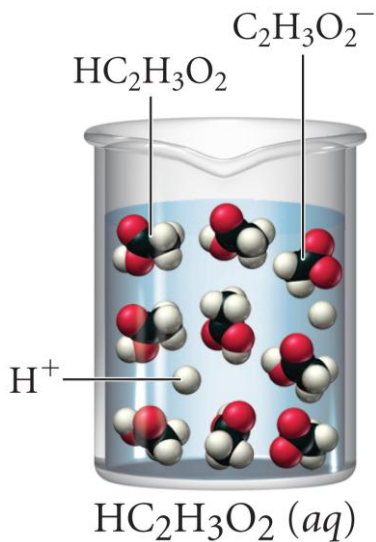
$HC_2H_3O_2$ (aq)

> **Weak electrolytes contain 'smaller' numbers of dissociated ions when dissolved**

Weak electrolytes are formed from the dissolution of MOLECULAR ACIDS (generic formula HA, e.g. $H(C_2H_3O_2)$ or HCl), which typically <u>undergo partial (<100%) dissociation</u>
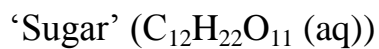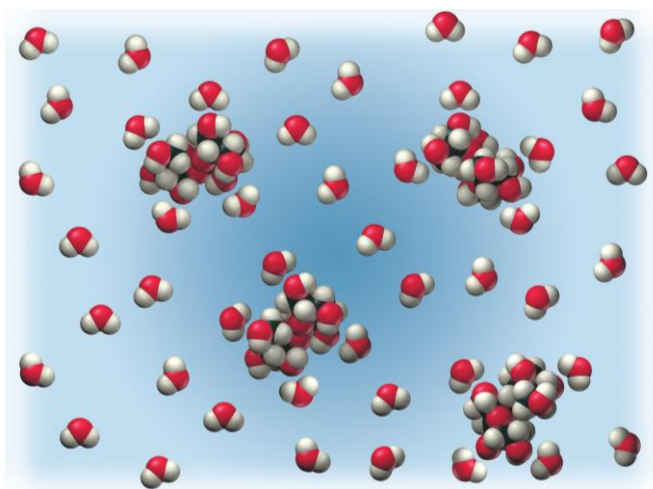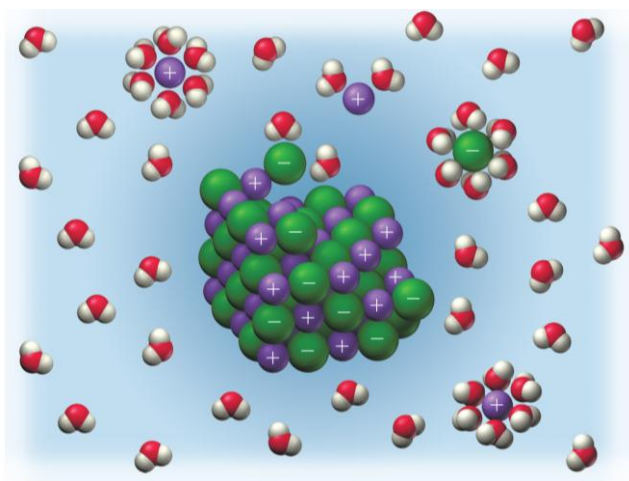
Non Electrolytes: **Molecular Materials**

$C_{12}H_{22}O_{11}$ (aq)

Non-electrolytes contain NO dissociated ions when dissolved, so CANNOT conduct electricity.

$\Rightarrow$ **Since non-electrolytes do NOT contain ions they must be MOLECULAR. As it** *cannot* **dissociate, molecular material remains INTACT when it dissolves (see below comparison)**

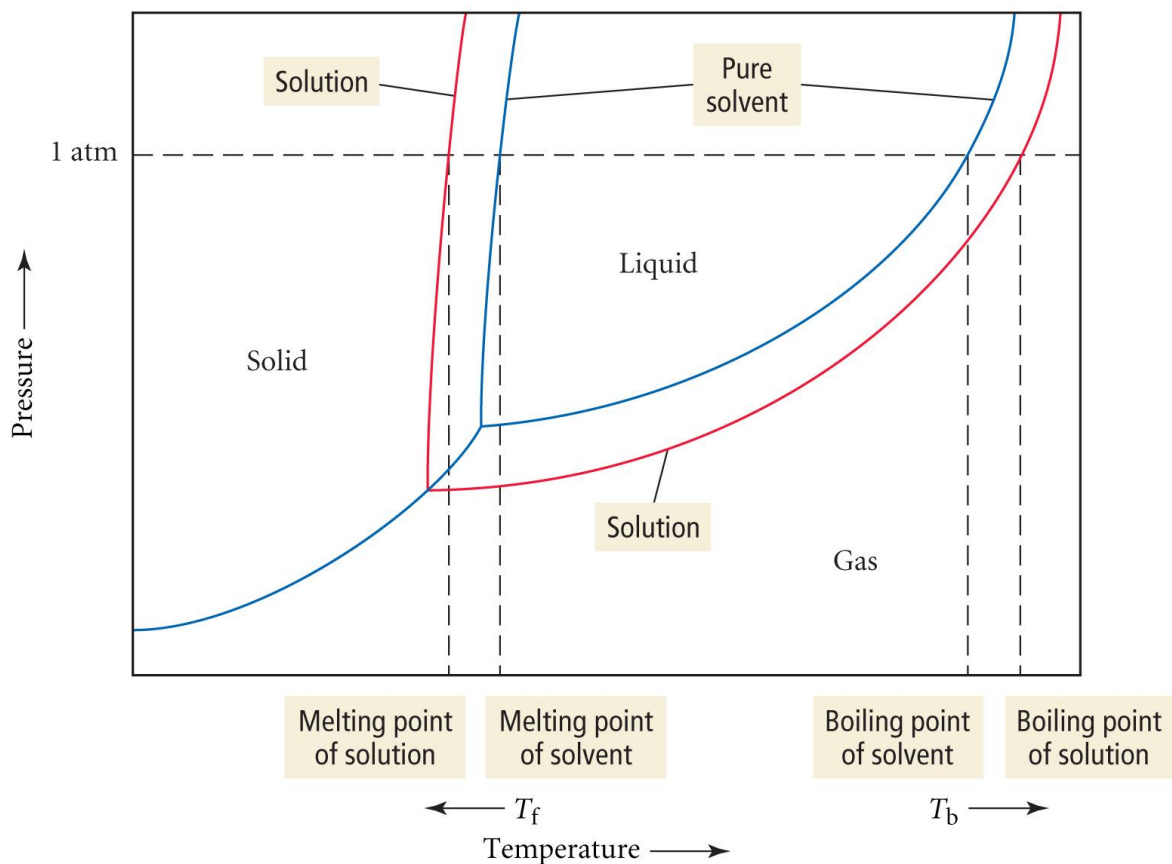Comparison of (a) ionic and (b) molecular dissolution processes

NaCl(aq)

'Sugar' ($C_{12}H_{22}O_{11}$ (aq))

Solution

Pure solvent

1 atm

Pressure →

Solid

Liquid

Solution

Gas

Melting point of solution

Melting point of solvent

Boiling point of solvent

Boiling point of solution

← T_f

T_b →

Temperature →

TABLE 12.9 Van't Hoff Factors at 0.05 *m* Concentration in Aqueous Solution

Solute	*i* Expected	*i* Measured
Nonelectrolyte	1	1
NaCl	2	1.9
$MgSO_4$	2	1.3
$MgCl_2$	3	2.7
K_2SO_4	3	2.6
$FeCl_3$	4	3.4

Ion pairing