CH 302 – Unit 1 – Review II

SOLUTIONS, COLLIGATIVE PROPERTIES, ION PRODUCT

Questions we will answer today

1. Review Solutions and thermodynamic relationships
    - Conceptual: Will it dissolve?
2. Stability of solutions and colligative Properties
    - How does creating a solution affect the physical properties (vapor pressure, boiling point, freezing point, and osmotic pressure) of a solution?
3. Introduction to Ion Product and Molar Solubility
    - Quantitative: How much will dissolve?

Solutions

QUALITATIVE: DOES IT DISSOLVE?

Introduction to Solutions

- A solution is a homogenous mixture consisting of a solute (can be gas, liquid, or solid) dissolved in a liquid solvent.
- Solubility is a measurement of how much solute dissolves in a particular solvent
  - **The most important term you will learn here is "like-dissolves-like"**
  - **Solubility is highest when the IMF's of the solute match the IMF's of the solvent**
- Some basic rules:
  - Electrostatic interactions generally pair well with hydrogen bonding (example: salts in water)
  - Solvents with dominant hydrogen bonding don't dissolve nonpolar solutes (and vice-versa)
  - Large organic molecules that are dominated by dispersion forces (example: fats) dissolve best in nonpolar solvents
  - **Salts formed with sodium (Na^+), potassium (K^+), and nitrate (NO_3-) ions are soluble.**

Qualitative Solubility

In the following double-displacement percipitate reaction, write the net ionic equation, the total ionic equation, and identify the phases associated with the products.

$$Fe(NO_3)_3(aq) + 3NaOH(aq) \rightarrow Fe(OH)_3 + 3NaNO_3$$

Basic Rules:

1. Total ionic equations involve all aqueous ions and other products
2. Net ionic equations involve only the non-spectator ions and solid product(s)

$$\mathrm{Fe(\underline{NO_3})_{3\,(aq)} + 3\,NaOH_{(aq)}}$$

$$\mathrm{\longrightarrow \underset{(s)}{Fe(OH)_3} + 3\,\underset{(aq)}{NaNO_3}}$$

Total Ionic:

$$\mathrm{Fe^{3+}_{(aq)} + \cancel{3\,NO_3^-{}_{(aq)}} + \cancel{3\,Na^+{}_{(aq)}} + 3\,OH^-_{(aq)}}$$

$$\mathrm{\longrightarrow Fe(OH)_{3\,(s)} + \cancel{3\,Na^+{}_{(aq)}}}$$

$$\mathrm{+ \cancel{3\,NO_3^-{}_{(aq)}}}$$

Net Ionic: only species "doing chemistry"

$$\underline{\mathrm{Fe^{3+}_{(aq)} + 3\,OH^-_{(aq)} \longrightarrow Fe(OH)_{3\,(s)}}}$$

Qualitative Solubility

Which of the following molecules would be the most miscible in water?

a. $CH_3(CH_2)_4OH$
b. $CH_3(CH_2)_6OH$
c. CH_3CH_2OH
d. C_6H_6
e. $CH_3(CH_2)_4CH_3$

Qualitative Solubility

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e. $CH_3(CH_2)_4CH_3$

Enthalpy of Solution

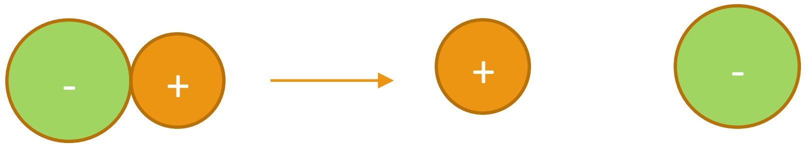
$$\Delta H_{solution} = \Delta H_{lattice} + \Delta H_{solvation}$$

Always +

Always -

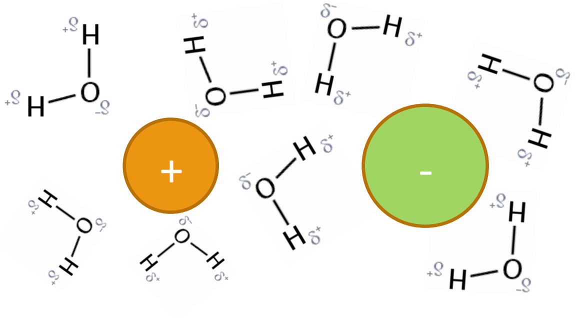
Step one: Lattice Energy breaks apart ionic compound

Step two: Solvation Energy is released when solvent dissolves positive and negative charges



+ $\Delta H_{lattice}$ (positive value)

+



+ $\Delta H_{solvation}$ (negative value)

Introduction to Solutions

- Some of the concentration units you should know for solutions are (gchem fundamentals chapter):
  - Molarity (M): moles of solute per liter solution (mol/L)
  - Molality: moles of solute per kilogram solvent (mol / kg)
  - Mole Fraction: moles of a particular species per total moles of solution / mixture (dimensionless)

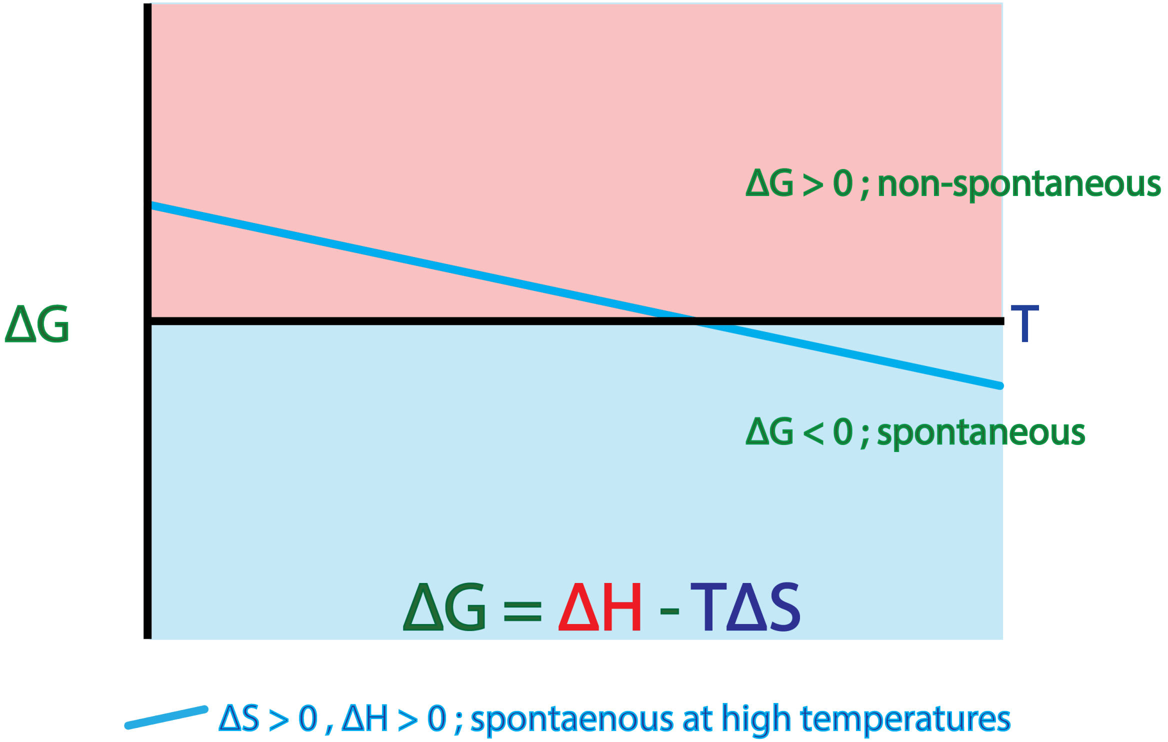
$$M = \frac{mol}{L}$$

$$m = \frac{mol}{kg}$$

$$X_A = \frac{mol_A}{mol_{total}}$$

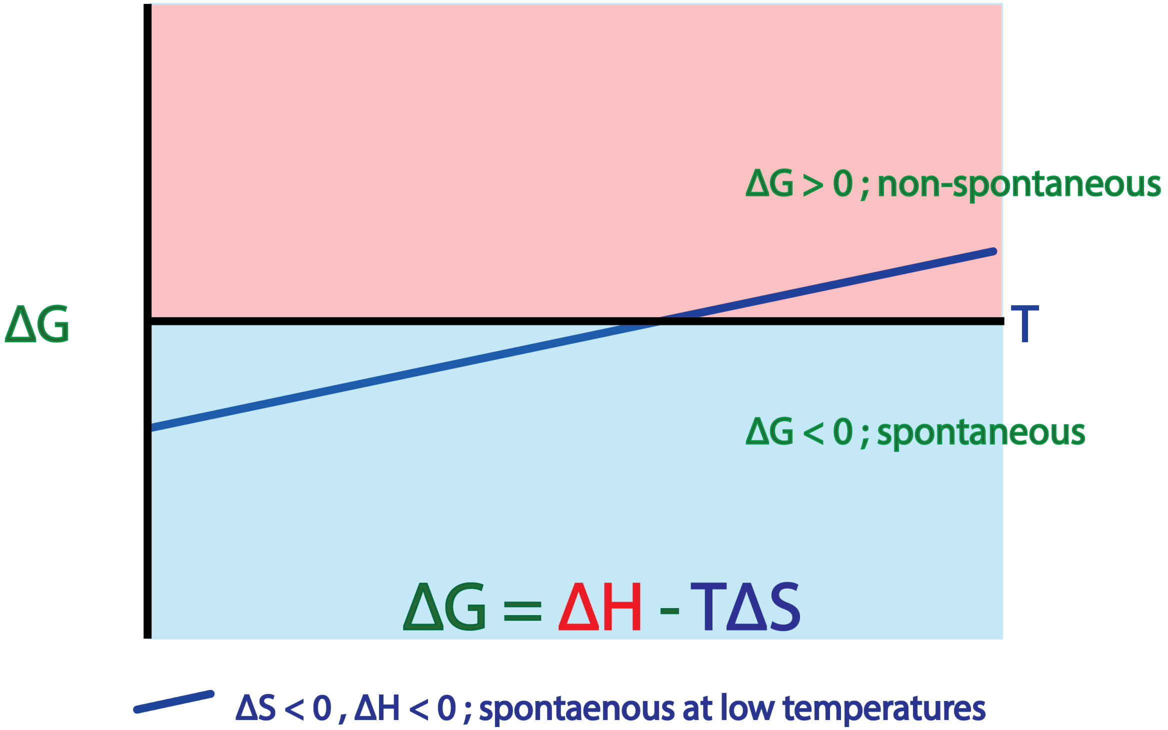
Free Energy of a Salt Dissolving in Water: $+\Delta H$, $+\Delta S$

- The majority of salts have a positive $\Delta H_{solution}$
- In all cases, the $\Delta S_{solution}$ is positive (solid to aqueous is a positive entropy change)
- **Dissolution is favored at high temperatures for all salts dissolving in water.**



Free Energy of a Gas Dissolving in Water: -ΔH , -ΔS

- For a gas dissolving in liquid, the reaction is exothermic ($\Delta H_{solution} < 0$) because there is no lattice energy and a negative solvation energy.
- There is a negative change in entropy ($\Delta S < 0$) because you are going from gas to aqueous
- **Therefore, dissolution is favored at low temperatures.**



Henry’s Law Gas Dissolving in a Liquid

- **Gases dissolving in a liquid is favored at low temperatures.**
  - **For example: an open bottle of soda will stay carbonated longer if you keep it chilled.**
- **The solubility of a gas also depends on the partial pressure of the gas above a liquid in a closed container – This is Henry’s Law.**
  - **For example: a closed bottle of soda will stay carbonated until you open it (release pressure)**
  - There is a mathematical relationship here:

$$P_{gas} = KX_{gas}$$

The mole fraction of the gas dissolved in a liquid (X_{gas}) is directly proportional to the partial pressure of the gas above the liquid (P_{gas}).

Does it Dissolve (thermo)?

Most solids, liquids

$$\Delta G = \underset{(+)}{\Delta H} - \underset{(+)}{\left(T\Delta S\right)} \rightarrow \text{driving force}$$

→ (−) at High T

$\qquad (-) \qquad\qquad (+)$

→ (−) always

Gas

$$\Delta G = \underset{(-)}{\Delta H} - \underset{(-)}{\left(T\Delta S\right)} \rightarrow \text{this term "hurts you"}$$

→ (−) at Low T

→ Henry's Law, Dissolves @ High P

Colligative Properties

CREATING A SOLUTION INCREASES THE STABILITY OF A SOLVENT

Colligative Property Summary

Vapor Pressure Lowering (Raoult’s Law):

- Solves for **the *new* vapor pressure** (P_A) of a solution, based on the **mole fraction of the solvent** (X_A)
  - $P_A = X_A P°_A$

Freezing Point Depression:

- Solves for the ***negative change* in the freezing point** (ΔT_f), based on the **molality of the solute** (m)
  - $\Delta T_f = i\, k_f\, m$

Boiling Point Elevation:

- Solves for **the *positive change* in the boiling point** (ΔT_b), based on **the molality of the solute** (m)
  - $\Delta T_b = i\, k_b\, m$

Osmotic Pressure:

- Solves for the pressure exerted by a fluid to restore osmotic equilibrium, based on **the molarity of the solute** (M)
  - $\Pi = iMRT$

$$\Delta T_f = i\ k_f\ m$$

Van’t Hoff Factor

- Colligative properties depend on the number of moles of solute in the final solution.
- **Therefore, in the case of electrolytes (salts), colligative properties depend on the concentration of ions rather than the initial amount of the solid salt.**
- We make this “correction” by using the Van’t Hoff Factor (i) in our colligative properties calculations
- **The Van’t Hoff Factor is the total number of solute species in solution**

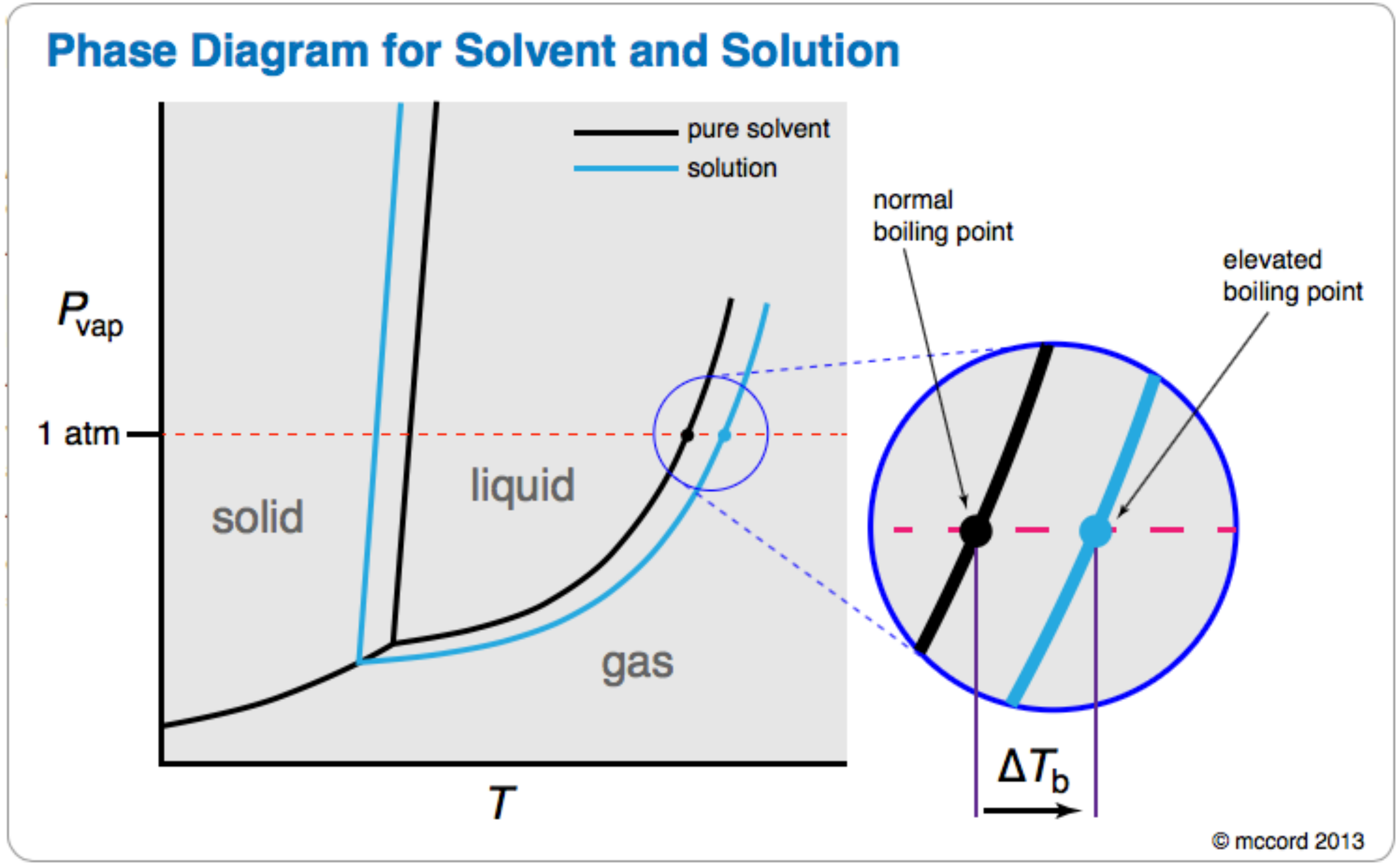
Examples:

- NaCl: *I* = 2
- **Sucrose: *I* = 1**
- PbI_2: *I* = 3
- **Na_2SO_4: *I* = 3***

*Remember that polyatomic ions stay together and don’t dissociate in solution

Boiling Point Elevation, Freezing Point Depression

- Creating a solution from a pure solvent increases the stability of your substance in the liquid phase.
- This has two effects:
  1. **The freezing point decreases**
  2. **The boiling point increases**
- You can see in the diagram to the right that the liquid phase is favored in a larger range of temperatures



Phase Diagram for Solvent and Solution

Boiling Point Elevation, Freezing Point Depression

- Using the following equations, you are solving for the change in the freezing point or boiling point. **Remember: you are solving for a change (ΔT_f is always negative, ΔT_b is always positive) and you are NOT solving for the final temperatures.**

Freezing Point Depression:

Solves for the ***negative change* in the freezing point** (ΔT_f), based on the **molality of the solute** (*m*)

$$\Delta T_f = i\ k_f\ m$$

Boiling Point Elevation:

Solves for **the *positive change* in the boiling point** (ΔT_b), based on **the molality of the solute** (*m*)

$$\Delta T_b = i\ k_b\ m$$

Colligative Properties Calculation

The freezing point of an aqueous calcium chloride solution is -1.4°C. The K_f for water is 1.86°C/*m*. What is the molality of calcium chloride?

What molality of sucrose would be necessary to make the same temperature difference starting with pure water?

$\Delta T_f = i K_f m$

$CaCl_2, \; i = 3$

$\frac{1.4\,°C}{3 \times 1.86} = (3)\left(1.86\,\frac{°C}{m}\right) m$

$= 0.25\,m$

×3

Sucrose, $i = 1$

$\frac{1.4\,°C}{1.86} = 1 \cdot 1.86 \cdot m$

$= 0.75\,m$

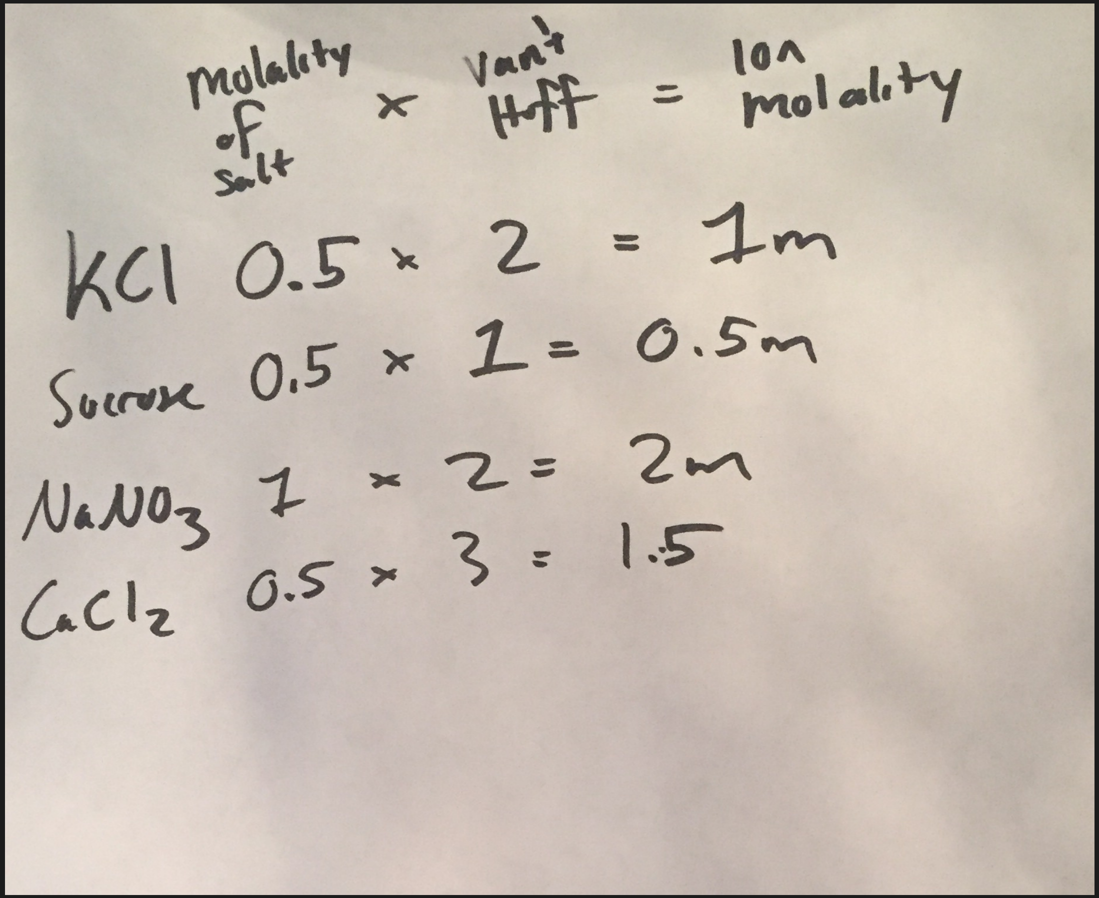
Colligative Properties Calculation

The freezing point of an aqueous calcium chloride solution is -1.4°C. The K_f for water is 1.86°C/*m*. What is the molality of calcium chloride? 0.25m

What molality of sucrose would be necessary to make the same temperature difference starting with pure water? 0.75m

Colligative Properties Conceptual

Rank the boiling points of the following aqueous solutions from least to greatest: 0.5m KCl, 0.5m sucrose, 1m $NaNO_3$, 0.5m $CaCl_2$



Molality of Salt × Van't Hoff = Ion molality

KCl $0.5 \times 2 = 1m$

Sucrose $0.5 \times 1 = 0.5m$

$NaNO_3$ $1 \times 2 = 2m$

$CaCl_2$ $0.5 \times 3 = 1.5$

Colligative Properties Conceptual

Rank the boiling points of the following aqueous solutions from least to greatest: 0.5m KCl, 0.5m sucrose, 1m $NaNO_3$, 0.5m $CaCl_2$

Sucrose < KCl < $CaCl_2$ < $NaNO_3$

Vapor Pressure Lowering

- Vapor Pressure is **lower when a liquid is more stable**. Therefore, it should make sense that when you create a lower free energy solution from a pure solvent, the vapor pressure goes down.
- **Mathematically, vapor pressure looks like this:**

Vapor Pressure Lowering (Raoult's Law):

Solves for **the *new* vapor pressure** (P_A) of a solution, based on the **mole fraction of the solvent** (X_A) and the vapor pressure of the pure solvent ($P°_A$)

$$P_A = X_A P°_A$$

You WILL have to account for electrolytes in the "total moles" of this mole fraction term, even though you don't see a Van't Hoff Factor here.

Vapor Pressure Lowering: Mixing Liquids

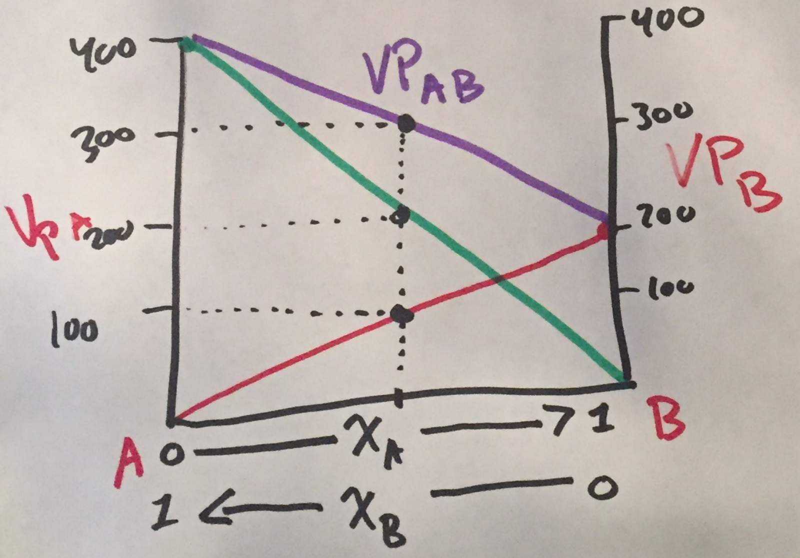
- When you mix two miscible liquids, you will get a new vapor pressure value for your solution. There are two ways you might be asked to determine this value.
- Consider two liquids, A and B. Liquid A has a vapor pressure of 200 torr. Liquid B has a vapor pressure of 400 torr. Calculate the vapor pressure when the concentrations of A and B are equal. Then use a vapor pressure diagram to prove your answer.

A = 200 torr
B = 400 torr

$$P_{total} = P_A + P_B$$

$$\to P_A = \chi_A P^o_A \,, \quad P_B = \chi_B P^o_B$$

$$\underline{300\text{torr}} = \overset{\chi_A \downarrow}{.5}(200) + \overset{\chi_B \downarrow}{.5}(400)$$



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Vapor Pressure Lowering (Raoult's Law):

Solves for **the total vapor pressure**

$$P_A = X_A P^\circ_A$$

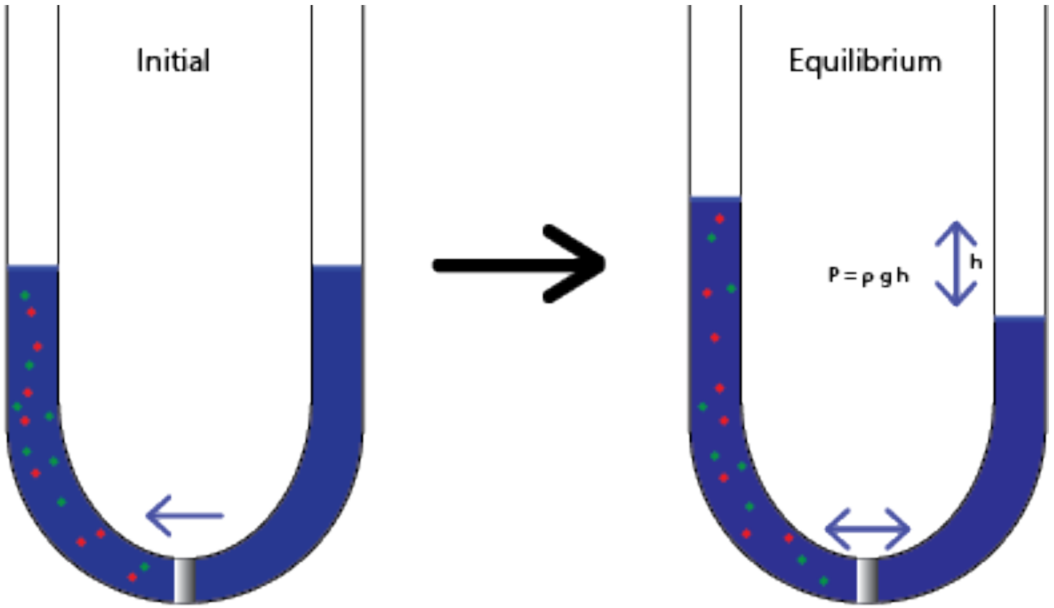
$$P_B = X_B P^\circ_B$$

$$P_{total} = P_A + P_B$$

Dalton's Law (CH301)

Osmotic Pressure

- **Osmotic pressure is the pressure exerted by a fluid to restore osmotic equilibrium.**
- The basic idea is that fluid will flow from the less concentrated to the high concentrated side of a semipermeable membrane (only allows the flow of the solvent; blocks solute).
- **You should understand this mathematically, based on a diagram in a U-Tube, and in real-life context**



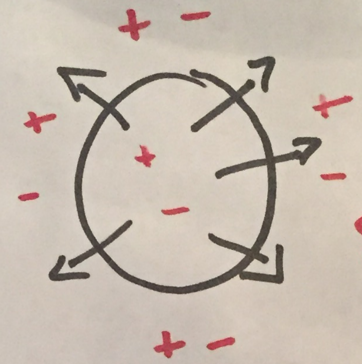
In the initial condition,
the osmotic pressure causes the water to flow from the less concentrated side to the more concentrated side (right to left) in order to dilute

In the equilibrium condition,
the hydrostatic pressure from the atmosphere (pushing to have equal amounts of water on both sides) is balanced by the osmotic pressure (pushing water to the more concentrated side).

$$\Pi = iMRT$$

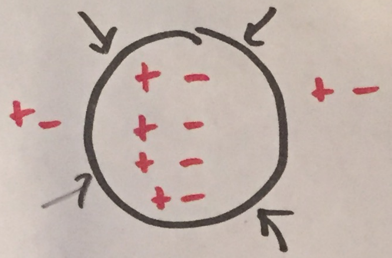
Osmotic Pressure – Biological Membranes

- **In biology, osmosis is the process of water flowing from low to high solute concentrations.**
- The driving force of this process is the osmotic pressure and the chemical ion gradient established between the inside and outside of a cell.
- **The direction and outcome of osmosis depends on the ion gradient of the solution:**
  1. **Hypertonic solutions:** high solute concentration on the outside of a cell ; water flows OUT ; results in cells shrinking
  2. **Hypotonic solutions:** high solute on the inside of the cell ; water flows IN ; results in cells swelling
  3. **Isotonic solutions:** equal solute concentrations on the inside and outside of a cell ; no net flow of water ; no change

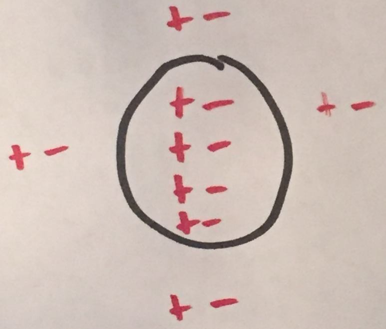


Salted beef

Shrinking
shriveling



hypo dermic
needle



iso
↓
same

Ion Product and Solubility

QUANTITATIVE: HOW MUCH OF A SALT WILL DISSOLVE?

Free Energy and "K"

K is known technically as the "Equilibrium Constant"

- If we say a reaction is spontaneous ($\Delta G < 0$), that means the reaction progresses forward. However, we need a new term that tells us how much a reaction moves forward.
- **Many reactions do not go to "completion" – instead, they stop at particular equilibrium concentrations. This is what K is for.**
- **For salts, K_{sp} is simple the product of your ion concentration raised to the power of their coefficients.**

$$PbI_2 \rightarrow Pb^{2+} + 2I^-$$

$$\downarrow$$

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

$$\downarrow$$

$$K_{sp} = x(2x)^2 = 4x^3$$

Introduction to Ion Product

K_{sp} is a measurement of solubility that answers the question:
"How much does a salt dissolve at a given temperature?"

The generic equation for K_{sp} can be written as:

$$K_{sp} = [M^{y+}]^x[A^{x-}]^y$$

Don't try to memorize this formula. Instead, learn this topic through repetition (practice)

Where M is our metal cation,
A is our non-metal anion
y is the charge on M, and
x is the charge on A

K_{sp} to Molar Solubility

The K_{sp} of silver chromate is 1.1×10^{-12}. What is the molar solubility?

1) $Ag_2CrO_{4\,(s)} \rightarrow \underset{+2x}{2Ag^+} + \underset{\underline{\underline{+X}}}{CrO_4^{2-}}$

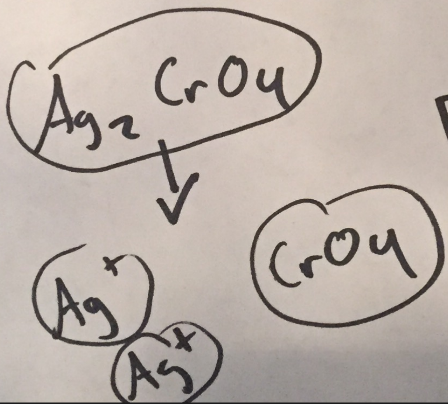
$$\underline{K_{sp}} = [Ag^+]^2[CrO_4]$$

$$K_{sp} = (2x)^2 \; x$$

$$1.1\times10^{-12} = 4x^3$$

$x \rightarrow$ molar solubility

$$\sqrt[3]{\frac{1.1\times10^{-12}}{4}} = \underline{\underline{6.5\times10^{-5}M}}$$



$$[Ag^+][Ag^+][CrO_4]$$

$$(2x)^2 \; x$$