

CH 302 – Exam 1 Review

PHYSICAL EQUILIBRIUM, SOLUBILITY

Doing Well on Exam One

- Learn through repetition: the more you practice, the better you will do on the exam
- **Know how to use your calculators. Be comfortable with large exponents and natural log.**
- Be able to make calculations ; be able to explain what the calculations are saying and why they are important
 - For example: colligative properties are easy quantitative questions. Do you understand why boiling point increases, how we make a hypertonic solution, etc.?
- Don't forget the basics: thermodynamics is still important for conceptual questions, especially for solubility

Exam One Learning Outcomes

Learning Outcomes for Physical Equilibrium

Students will be able to...

Demonstrate mastery of and compound and reaction stoichiometry (mole to mole conversion and grams to mole conversions).

Predict the sign of ΔG , ΔH , and/or ΔS for physical change

Understand the concept of spontaneous change and equilibrium in the context of phase changes, including calculating phase transition temperatures from standard thermodynamic data.

Interpret heating curves and calculate heat required for phase transitions and temperature changes.

Describe phase transitions (macroscopically and microscopically).

~~Understand phase in the context of Boltzmann distribution.~~

Understand how intermolecular forces, temperature, and solute concentration affect vapor pressure.

Interpret phase diagrams and identify normal boiling and melting point, critical point, and triple point.

Describe the factors that favor the dissolution process in terms of intermolecular forces and thermodynamics (eg.: enthalpies of solution, hydration, lattice energy, entropies of solution, free energy of solution, and temperature).

Describe how T and P (Henry's Law) each affect solubility.

Define and perform calculations for common concentration units molarity, molality, and mole fraction.

Perform calculations and understand the concepts of the 4 colligative properties: vapor pressure lowering, boiling point elevation, freezing point depression, and osmotic pressure.

Describe the dissociation of ionic compounds in solution and the effects on colligative properties (van't Hoff factor, i).

Learning Outcomes for Solubility Equilibrium

Students will be able to...

Understand the concept of the solubility product, K_{sp} .

Write total and net ionic equations to identify spectator ions.

Quantitatively determine solubility from K_{sp} and vice versa.

Estimate molar solubility from K_{sp} .

Understand and apply the "common ion effect" on solubility.

Given concentrations of specific ions, predict if a precipitate will form (amount or concentration) using Q_{sp} vs K_{sp} .

K_{sp} vs. Q_{sp}

SOLUBILITY PRODUCT, REACTION QUOTIENT, FREE ENERGY

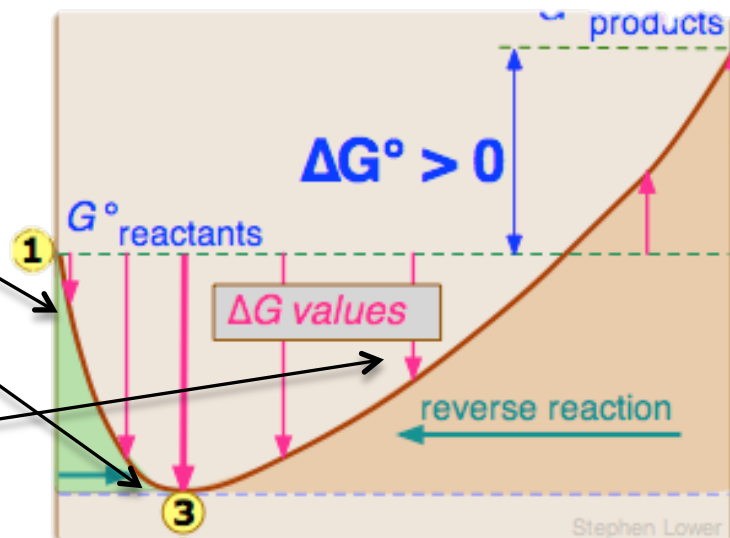
K_{sp} , Q_{sp} , and Saturation - Definitions

- **Solubility Product (K_{sp}):** K_{sp} is a constant that represents the product of all ion concentrations at equilibrium **specific to a given salt**.
- **Molar Solubility:** Solved from K_{sp} , molar solubility represents the maximum amount of solute that can dissolve for a reaction in terms of Molarity (M). This term is represented by the “x” in K_{sp} calculations.
- **Common Ion Effect:** When an ion is already present in solution, the molar solubility of a salt containing that ion significantly decreases.
- **Reaction Quotient Solubility Product (Q_{sp}):** Q_{sp} is a variable that is calculated by the product of all ion concentrations **at a point away from equilibrium**. Solved in the same way as K_{sp} , Q_{sp} uses experimental values rather than “ideal” values.
- **Saturation:** when the maximum amount of ions are present in solution ($K_{sp} = Q_{sp}$)
 - Saturation is an equilibrium position.
 - Dissolution: when $Q_{sp} < K_{sp}$ and your reaction moves forward (solid becomes ions) ←
 - Precipitation: when $Q_{sp} > K_{sp}$ and your reaction moves backward (ions become solid) ←

NOT equilibrium

Saturation: Q_{sp} vs. K_{sp}

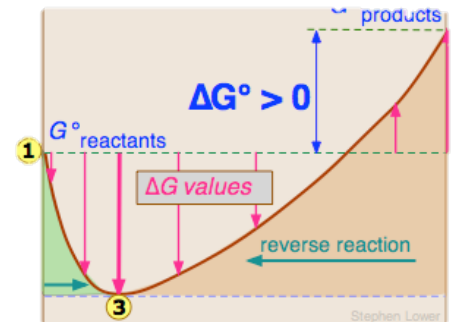
- K_{sp} represents the ion product of a saturated solution in terms of molar solubility (x). You can think of it as a measurement of the maximum saturation capacity of a solution.
- Q_{sp} represents the ion product of the actual concentrations of ions at any given time. You can control these concentrations experimentally. **You can think of Q_{sp} like a starting point**
- K_{sp} is a fixed value ; Q_{sp} is dependent on your actual concentrations. **Therefore, your value of Q_{sp} in relationship to K_{sp} will describe what happens:**
 - $Q_{sp} < K_{sp}$ (**unsaturated**) ; more solid can dissolve if added to the solution
 - $Q_{sp} = K_{sp}$ (**perfectly saturated**) ; your reaction is at equilibrium
 - $Q_{sp} > K_{sp}$ (**over saturated**) ; precipitation occurs until $Q_{sp} = K_{sp}$



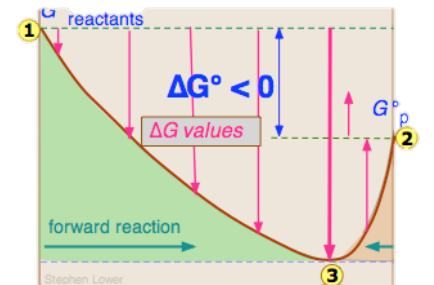
Final Point: Free Energy and K_{sp}

- When K_{sp} is very small (less than 1), only a tiny fraction of your solid product dissociated into ions. This means that the solid reactant is favored.
- When K_{sp} is large (greater than 1), a greater amount of ions are formed than the amount of solid that remains. This means that the dissociated ions are favored.

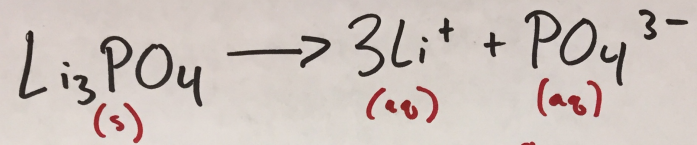
When the reactant is favored, the free energy change for the reaction is positive.



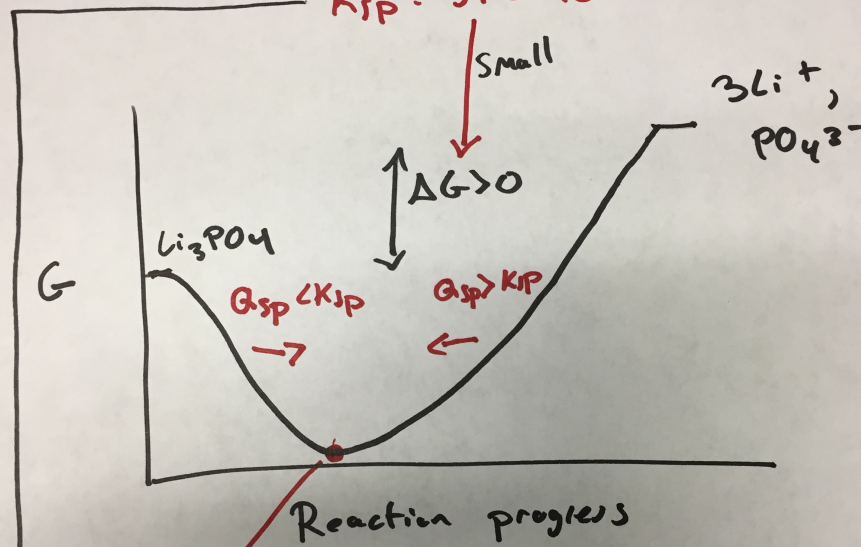
When the product is favored, the free energy change for the reaction is negative.



The exact relationship will be discussed next unit; but understand this conceptually



$$K_{sp} = 3.2 \times 10^{-9}$$



$$K_{sp} = [\text{Li}^+]^3 [\text{PO}_4^{3-}]$$

- Lowest energy $K_{sp} = Q_{sp}$
- Equilibrium

$K_{sp} < 1$; small $\Delta G > 0$
$K_{sp} > 1$; <u>large</u> $\Delta G < 0$

K_{sp} to Molar Solubility

What is the molar solubility of Li_3PO_4 ? The K_{sp} of Li_3PO_4 is 3.2×10^{-9} .

$$K_{sp} = [\text{Li}^+]^3 [\text{PO}_4^{3-}]$$

$$K_{sp} = (3x)^3 x = 27x^4$$

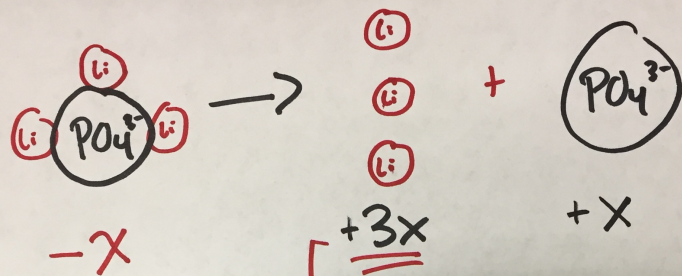
K_{sp} is the “Solubility Product,” which is a constant unique to a particular compound that represents the product of ion concentrations that are present at equilibrium

$$\sqrt[4]{\frac{K_{sp}}{27}} = x$$

$$x = 3.3 \cdot 10^{-3} M$$

x represents the “Molar Solubility,” which is a direct measurement of solubility. Molar solubility is the concentration of a solute that dissolves in molarity (M) for a reaction.

$$K_{sp} = [Li^+]^3 [PO_4^{3-}]$$



$$K_{sp} = \underline{\underline{[Li^+][Li^+][Li^+][PO_4^{3-}]}}$$

$$\underline{\underline{K_{sp} = (3x)^3 x}}$$

$$[Li^+] = 3x$$

K_{sp} and the common ion effect

What is the apparent molar solubility of Li_3PO_4 when added to a 0.5M solution of LiCl ? The K_{sp} of Li_3PO_4 is 3.2×10^{-9} .

$$K_{sp} = [\text{Li}^+]^3 [\text{PO}_4^{3-}]$$

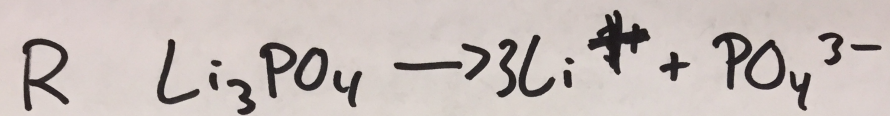
$$K_{sp} = (0.5)^3 x$$

K_{sp} remains constant (because it is a constant). Therefore, you should predict that the presence of a common ion decreases the overall “apparent” molar solubility of your compound.

$$x = \frac{K_{sp}}{(0.5)^3} = \frac{K_{sp}}{.125}$$

Notice how the molar solubility here is much less than that of the last problem we solved.

$$x = 2.56 \cdot 10^{-8} M$$



I Lots 0.5M 0

C -x +3x +x

E Lots -x 0.5M + 3x 0 + x

↪ negl. s. ble

$$K_{sp} = (0.5M)^3 x$$


$$\frac{K_{sp}}{(0.5)^3} = \underline{\underline{x}}$$

↓
"apparent"
molar solubility

K_{sp} vs. Q_{sp}

What happens when you mix 135mL 0.2M lithium nitrate and 250mL 0.1M potassium phosphate? The K_{sp} of Li_3PO_4 is 3.2×10^{-9} .

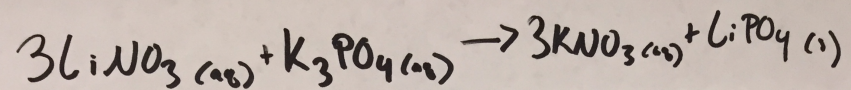
Here you are given “starting point” concentrations of lithium and phosphate ions. Therefore, your ion product will be Q_{sp} .


$$Q_{sp} = [Li^+]^3 [PO_4^{3-}]$$

$$Q_{sp} = (0.07M)^3 (0.065M) = 2.2 \cdot 10^{-5}$$

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

You have oversaturated your solution. The reaction will run backwards until equilibrium is reached, **resulting in a solid Li_3PO_4 precipitate.**



Spectator ions: K^+ , NO_3^-

$$K_{sp} = 3.2 \times 10^{-9}$$

$$Q_{sp} = ?$$

moles

$$135 \text{ mL} \times \frac{0.2 \text{ mol LiNO}_3}{1000 \text{ mL}} = 0.027 \text{ moles}$$

$$+ 250 \text{ mL} \times \frac{0.1 \text{ mol K}_3\text{PO}_4}{1000 \text{ mL}} = 0.025 \text{ mol}$$

$$385 \text{ mL} = \text{total volume} = .385 \text{ L}$$

molarity

$$\frac{0.027 \text{ mol}}{.385 \text{ L}} = 0.07 \text{ M} = [\text{Li}^+]$$

$$\frac{0.025 \text{ mol}}{.385 \text{ L}} = 0.065 \text{ M} = [\text{PO}_4^{3-}]$$

Q_{sp}

$$Q_{sp} = (0.07 \text{ M})^3 (0.065 \text{ M})$$
$$= 2.2 \times 10^{-5}$$

K_{sp} Solubility Comparison

Which of the following salts is more soluble?



or



K_{sp} Solubility Comparison

Which of the following salts is more soluble?



$$K_{sp} = (3x)^3 x = 27x^4$$

$$\sqrt[4]{\frac{K_{sp}}{27}} = x$$

$$x = 3.3 \cdot 10^{-3} M$$

or



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

$$\sqrt[3]{\frac{K_{sp}}{4}} = x$$

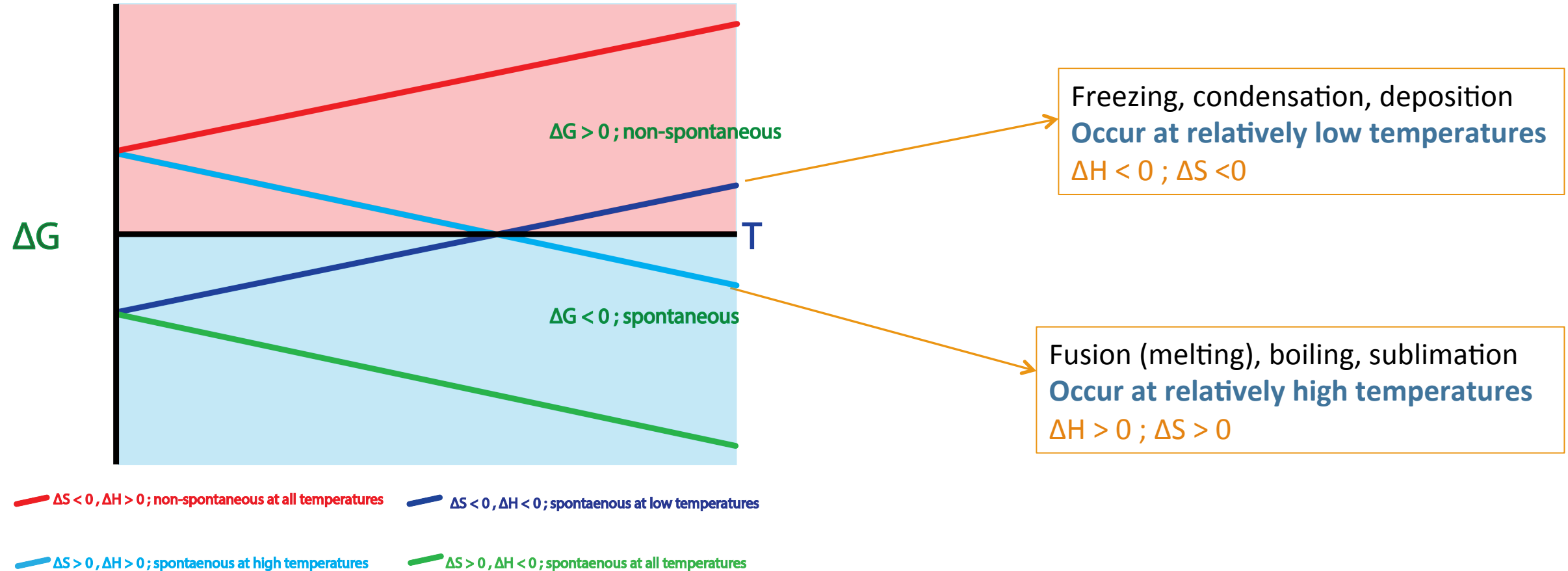
$$x = 1.2 \cdot 10^{-4} M$$

Phase Changes

EQUILIBRIUM CALCULATIONS, HEATING CURVES, PHASE DIAGRAMS

Free Energy: All Conditions Summary

$$\Delta G = \Delta H - T\Delta S$$



Free Energy: Physical Equilibrium Equations

$$\Delta G = \Delta H_{trans} - T \Delta S_{trans}$$

$$\Delta G = 0$$

$$\Delta H_{trans} = T \Delta S_{trans}$$

Be able to calculate the ΔH , ΔS , and T for a phase change

$$\Delta S_{trans} = \frac{\Delta H_{trans}}{T_{trans}}$$

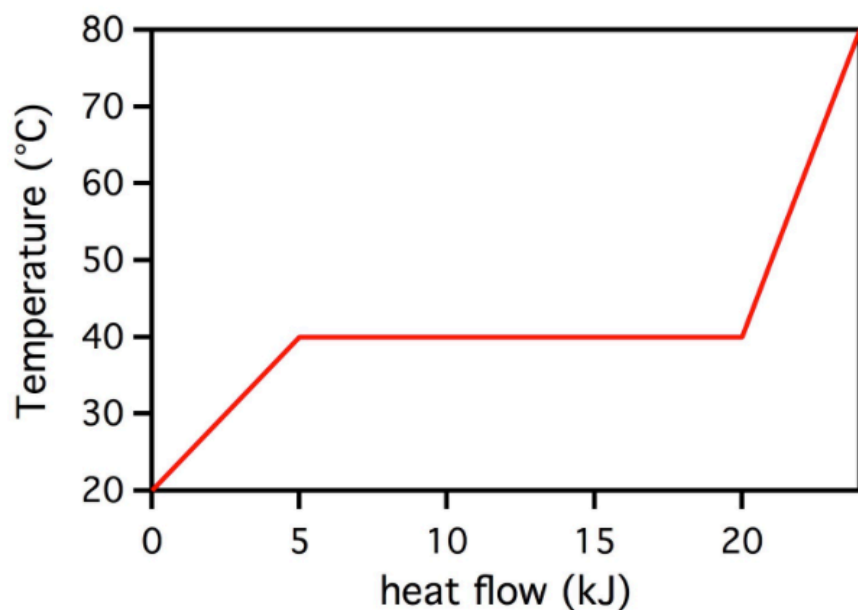
The entropy change of a phase transition given an enthalpy and temperature value

$$T_{trans} = \frac{\Delta H_{trans}}{\Delta S_{trans}}$$

The temperature change of a phase transition (boiling point, freezing points, etc.) given the enthalpy and entropy

Heating Curves Checklist

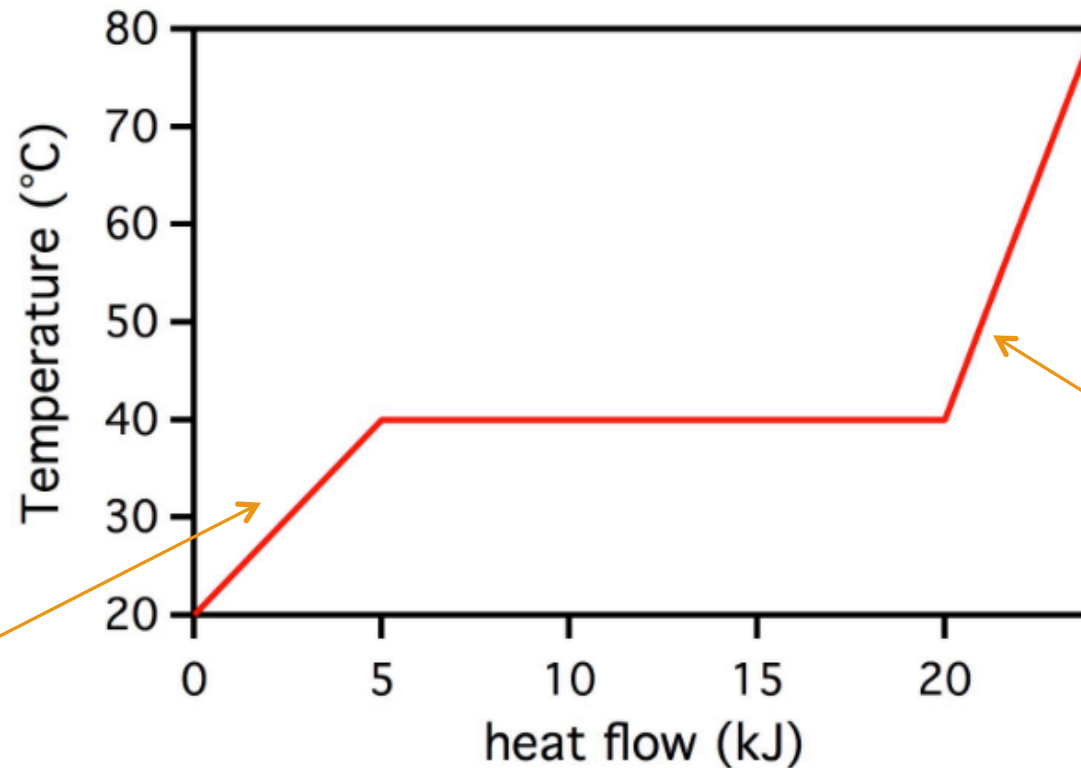
- Heating Curves are a 301 concept that show the two equations necessary to calculate the total heat of a single or multiple phase changes for a substance.



- Calculating Heat:
 - Use your two calculations ($q = mc\Delta T$ and $q = m\Delta H$)
 - Be able to do this same calculation for cooling, even though we are used to doing it for heating (many mistakes on 301 exams)
- Reading the graph:
 - Understanding heat capacity / slope of the heating curves
 - Determine the value of heat without making a calculation

Heating Curves Checklist – Heat Capacity

Heat capacity can be thought of as a substance's resistance to change in temperature. Consider the heating curve for a liquid being heated to the gas phase:



A high heat capacity results in a smaller slope on a heating curve (substance resists change in temperature when heat is applied)

A low heat capacity results in a steeper slope on a heating curve (substance does not do a good job resisting change in temperature when heat is applied)

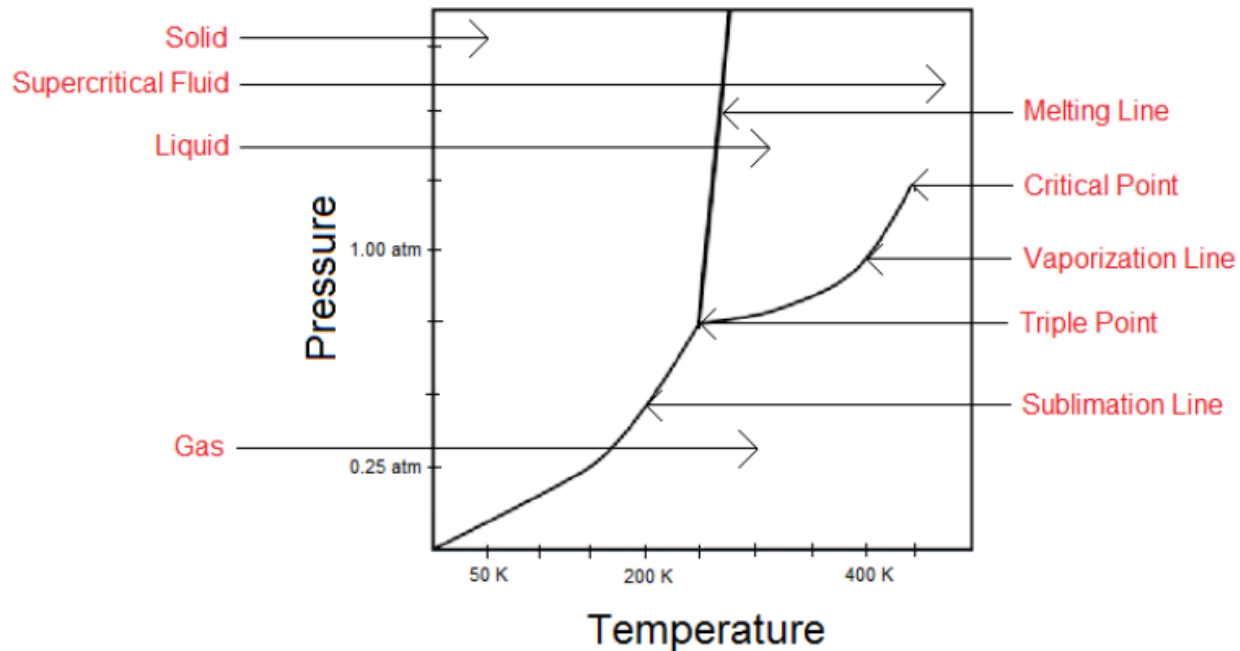
Therefore, the gas of this substance has a lower heat capacity than the liquid.

Phase Diagram Checklist

- Phase diagrams show the lowest free energy phase of a substance at a given temperature and pressure.
- Identify the key features of the diagram:
 - What is the stable phase at a certain temperature and pressure?
 - Identify the triple point
 - Identify the critical point
 - What phase transition does a specific line represent?
- Moving along the diagram:
 - What phase transitions do you go through if you go from point A to point B on the graph?

Phase Diagram Checklist

- Phase diagrams show the lowest free energy phase of a substance at a given temperature and pressure.



Identify the key features of the diagram:

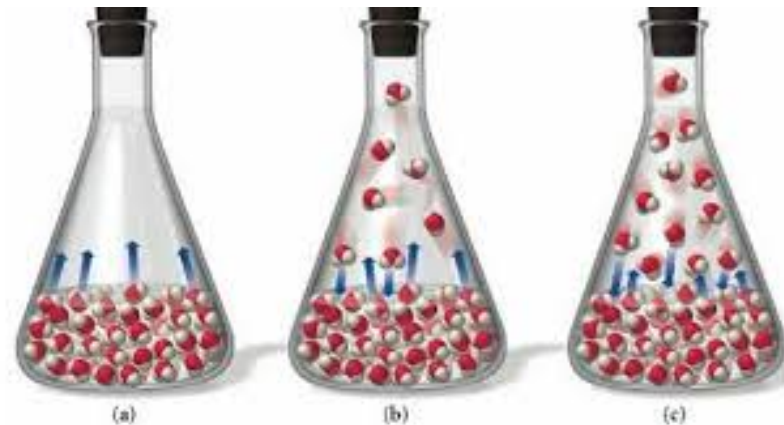
- What is the stable phase at a certain temperature and pressure?
- Identify the normal boiling point, melting point, etc.
- Identify the triple point
- Identify the critical point
- What phase transition does a specific line represent?
- How does this change for a solution versus a pure solvent?

Moving along the diagram:

- What phase transitions do you go through if you go from point A to point B on the graph?

Vapor Pressure

- For any given liquid sample in a closed container, a certain amount of that sample exists in the gas phase. This is what is known as the **vapor pressure**.
- **These molecules have enough kinetic energy to “escape” the attractions of other molecules on the surface.**
- Vapor pressure is a function of dynamic equilibrium between the gas and the surface molecules of a liquid.



- The Vapor Pressure is a function of **the IMF's of the liquid (which results in a higher ΔH_{vap})** and **the temperature**.

Vapor Pressure and IMF's

- If Vapor Pressure is the pressure of gas above a liquid in a closed container at a given temperature, we can easily determine that a sample with High IMF's will have a Low VP (less molecules able to overcome the IMFs and be "lifted into the gas phase).

Strong IMF - > low VP (and high boiling point, high ΔH_{vap})

Weak IMF -> high VP (and low boiling point, low ΔH_{vap})

IMF Review

Dispersion Forces < Dipole Forces < Hydrogen-Bonding

You can see in this equation also that as ΔH_{vap} increases, P_{vap} decreases

Vapor Pressure and Temperature

- Mathematically, the vapor pressure for a given liquid is only dependent on a change in temperature.

Higher Temperature = Exponentially Higher Vapor Pressure $P_{\text{vap}} = K \cdot e^{\frac{-\Delta H_{\text{vap}}}{R \cdot T}}$

- Changing the surface area, size of the container, amount of water, and so on does not change the pressure.
- Of all the derivations used to model this relationship, the most important equation to you will be the Clausius-Clapeyron Equation:

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T_1} - \frac{1}{T_2} \right)$$

Note: the order of P_2 / P_1 and $(1 / T_1 - 1/T_2)$ is important. If you forget the order, remember that as you increase temperature, you are increasing vapor pressure. You are taking the difference of the inverse temperature, so you need to switch the order.

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:
 - 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 in water.**

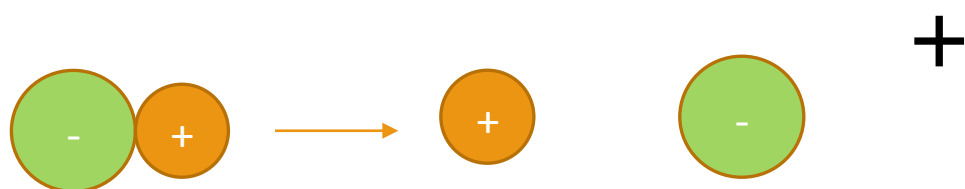
Enthalpy of Solution – Ion Dissolution

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

Usually +
But can be -

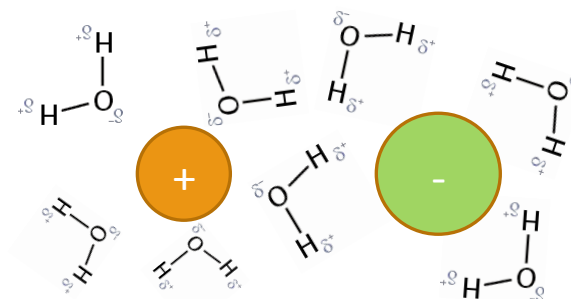
Always +

Always -



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

Step one: Lattice Energy
breaks apart ionic compound



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

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

Enthalpy of Solution – Gas Dissolution

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

Always -

Always 0

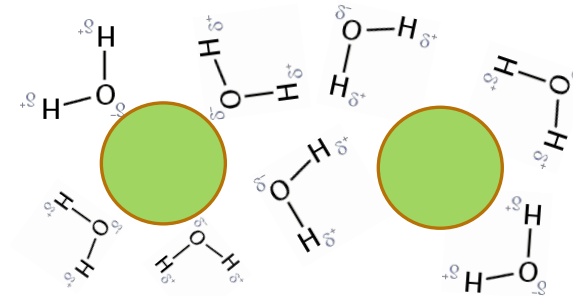
Always -



$\Delta H_{\text{lattice}} = 0$; boring

Step one: There is no lattice energy, so nothing really happens here!

+

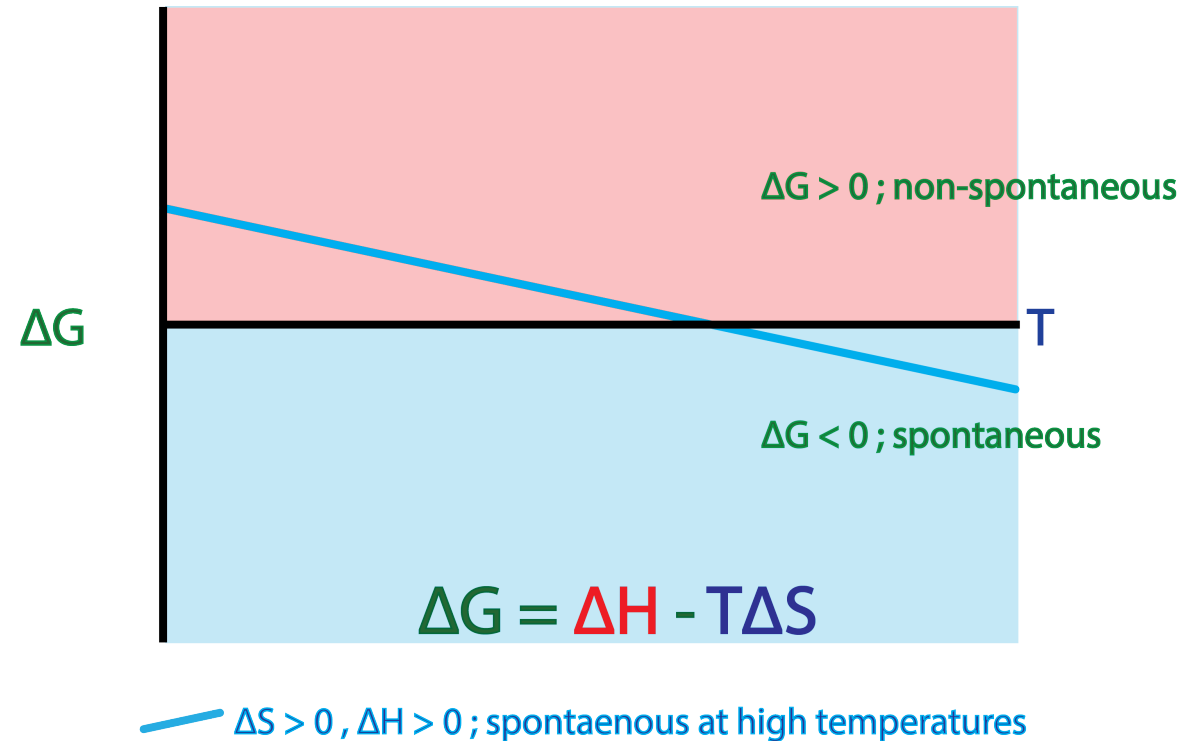


+ $\Delta H_{\text{solvation}}$ (negative value)

Step two: Solvation Energy is released when gas dissolves in water

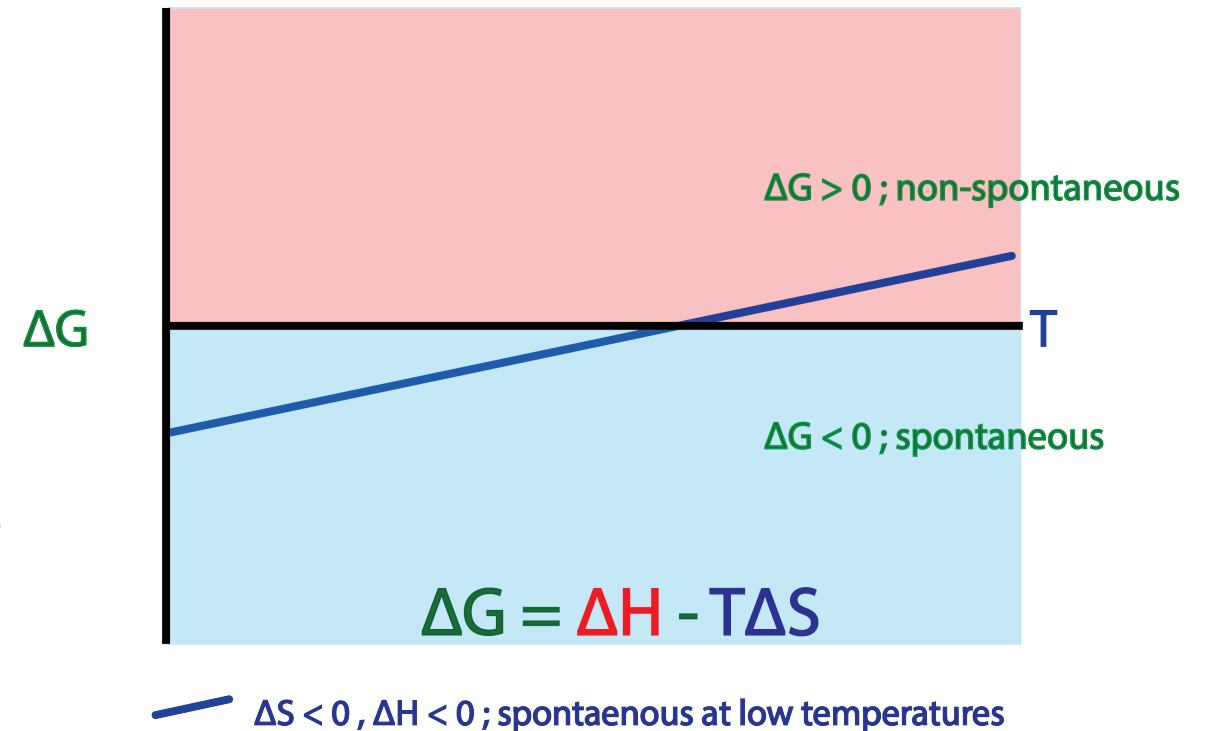
Free Energy of a Salt Dissolving in Water: $+\Delta H$, $+\Delta S$

- The majority of salts have a positive $\Delta H_{\text{solution}}$
- In all cases, the $\Delta S_{\text{solution}}$ 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: $-\Delta H$, $-\Delta S$

- For a gas dissolving in liquid, the reaction is exothermic ($\Delta H_{\text{solution}} < 0$) 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

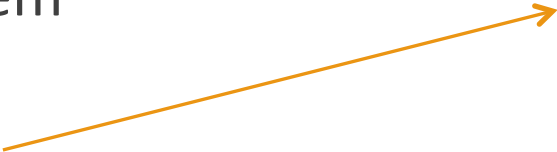
- **Gases dissolving in a liquid is favored at low temperatures.**
 - For example: an open bottle of soda will stay carbonated longer if you keep it chilled.
- **The solubility of a gas also depends on the partial pressure of the gas above a liquid in a closed container – This is Henry's Law.**
 - For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

Units of 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)


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


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


$$X_A = \frac{\text{mol}_A}{\text{mol}_{\text{total}}}$$

Yes, there will be a question that is a pure unit conversion.

Colligative Properties

CREATING A SOLUTION INCREASES THE STABILITY OF A SOLVENT

$$P_A = \chi_A P_A^\circ \quad \left[\begin{array}{l} \text{Salt in} \\ \text{water} \end{array} \right]$$

\downarrow
 $\frac{\text{moles A}}{\text{moles A} + \underline{\underline{i \times \text{moles solute}}}}$

$$\Delta T_f = i K_f m \quad \rightarrow \frac{\text{moles solute}}{\text{kg solvent}}$$

$$\Pi = i M R T$$

$\uparrow \quad \quad \uparrow$
 $\quad \quad \quad \uparrow$
 match Pressure
units

Can solve for:

- molarity
- molar mass
- mole fraction
- etc.

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)
 - $P_A = X_A P_A^\circ$

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)
 - $\Pi = iMRT$

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**

$$\Delta T_f = i k_f m$$

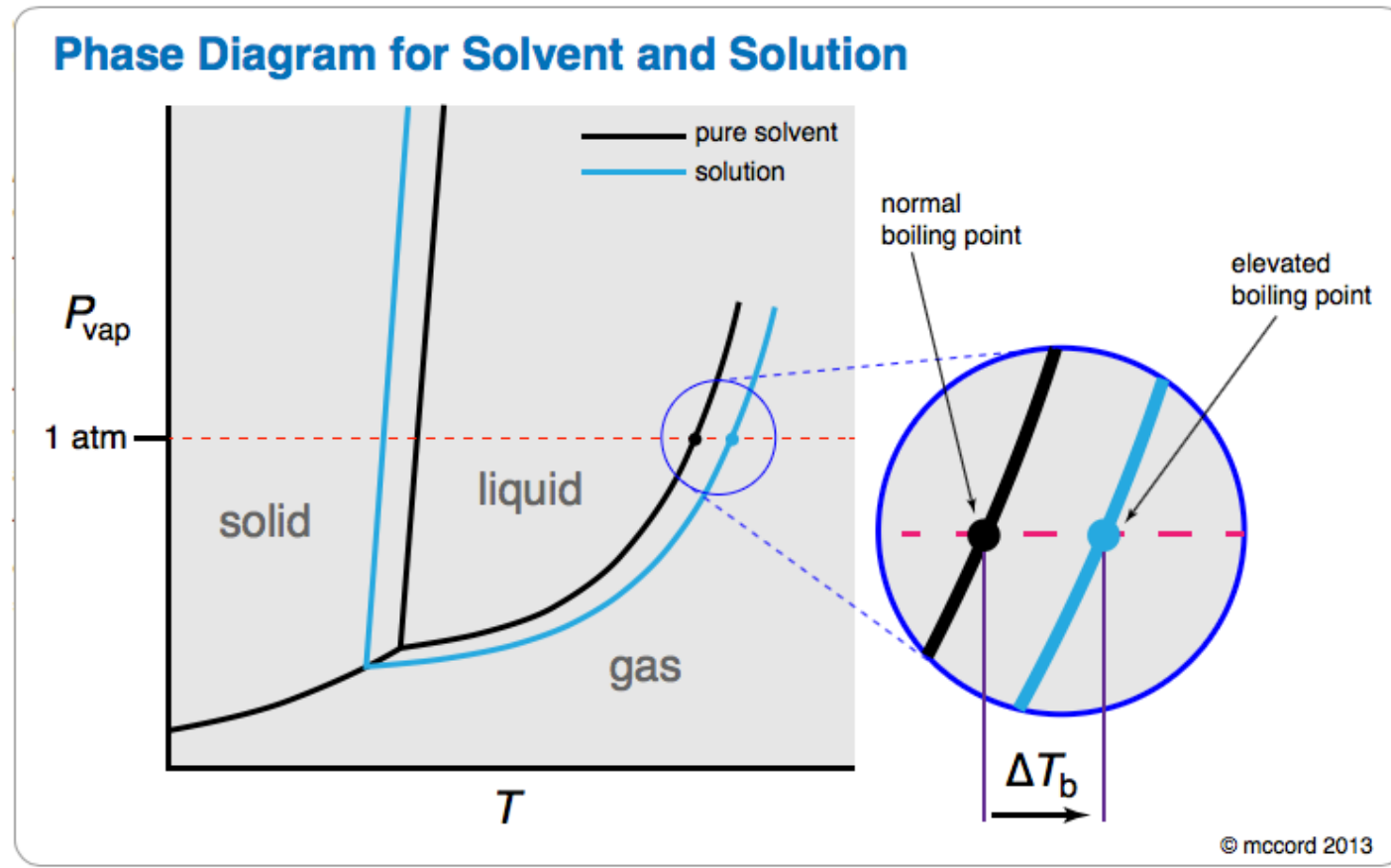
Examples:

- 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



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)

$$\Delta T_f = i k_f m$$
$$T_f = T_f^\circ - \Delta T_f$$

Boiling Point Elevation:

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

$$\Delta T_b = i k_b m$$
$$T_b = T_b^\circ + \Delta T_b$$

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)

$$P_A = X_A P^\circ_A$$

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 Volatile Liquids

- The vapor pressure of a binary liquid (A + B) must take into account the vapor pressure of both liquids.
- **Mathematically, this follows Dalton's Law of Partial Pressures:**

Vapor Pressure Lowering (Raoult's Law) + Dalton's Law:

$$P_A = X_A P_A^\circ \qquad P_B = X_B P_B^\circ$$

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

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.

Vapor Pressure Lowering (Raoult's Law):

Solves for **the total vapor pressure**

$$P_A = X_A P_A^\circ$$

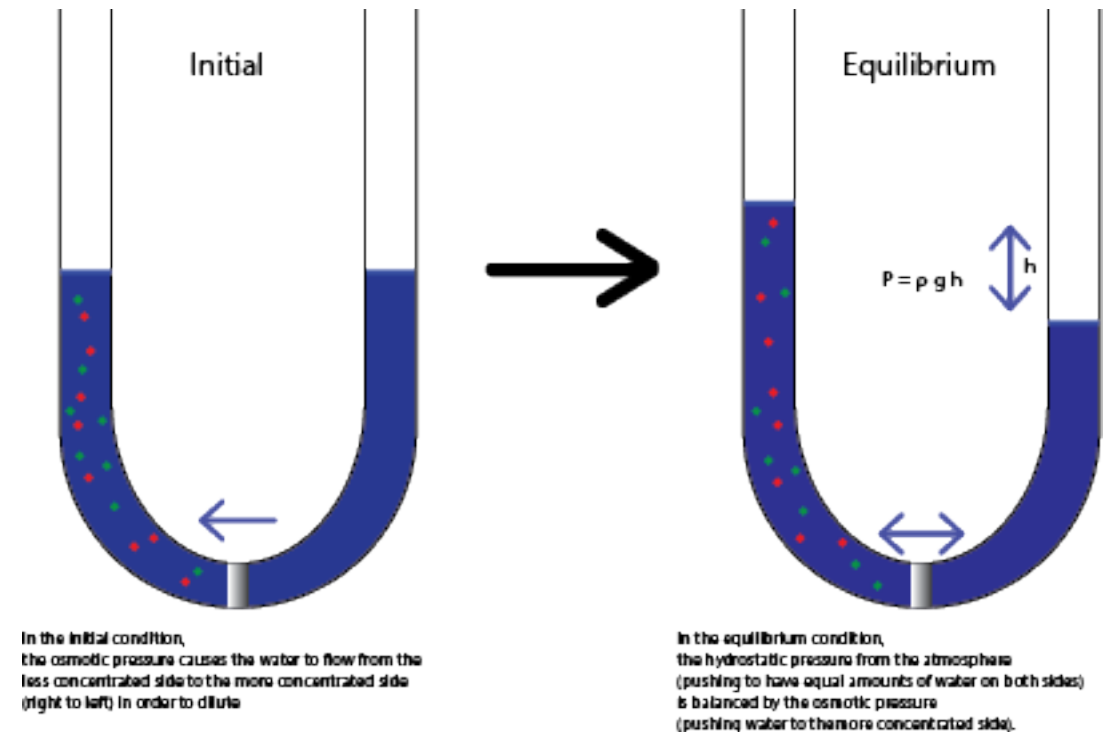
$$P_B = X_B P_B^\circ$$

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

Dalton's Law
(CH301)

Osmotic Pressure

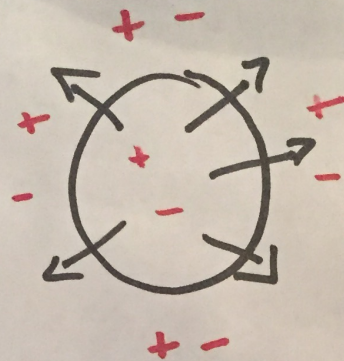
- **Osmotic pressure is the pressure exerted by a fluid to restore osmotic equilibrium.**
- The basic idea is that fluid will flow from the less concentrated to the high concentrated side of a semipermeable membrane (only allows the flow of the solvent; blocks solute).
- Again, this property is due to the fact that the solution is lower in energy. **This is why water flows toward the solution (going from high to low energy).**



$$\Pi = iMRT$$

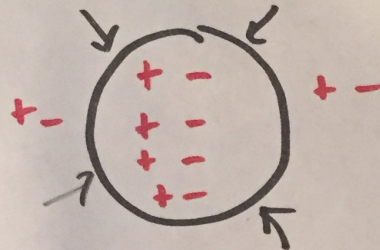
Osmotic Pressure – Biological Membranes

- 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

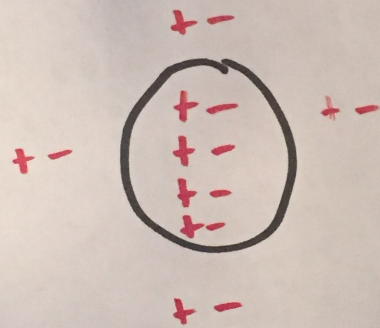


Salted
beef

Shrinking
shriveling



hypodermic
needle



ISO
↓
Same