

CH 302 – Final Exam

K_{sp} & Q_{sp}

SOLUBILITY PRODUCT, REACTION QUOTIENT, FREE ENERGY

K_{sp} to Molar Solubility

Solid silver phosphate is allowed to equilibrate with water at 25°C until the solution is saturated. What is the silver ion concentration in this saturated solution? K_{sp} for Ag_3PO_4 is equal to 8.9×10^{-19} .

1. $4.3 \times 10^{-5} M$
2. $5.6 \times 10^{-5} M$
3. $1.5 \times 10^{-6} M$
4. $2.8 \times 10^{-6} M$
5. $2.1 \times 10^{-6} M$
6. $1.3 \times 10^{-4} M$

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

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

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

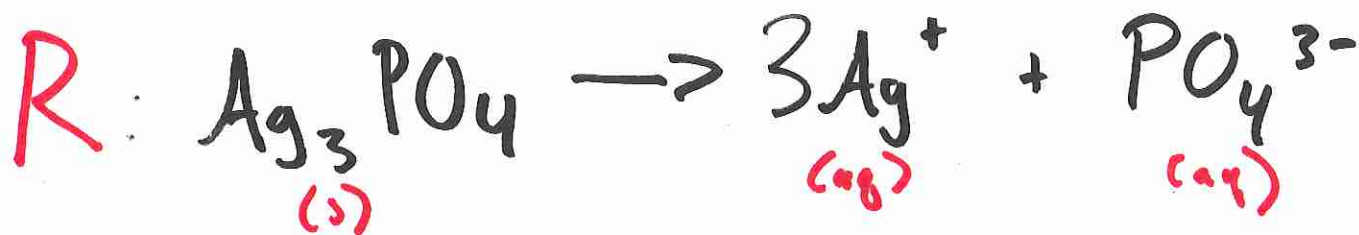
$$\sqrt[4]{\frac{8.9 \cdot 10^{-17}}{27}} = x$$

$$x = 4.26 \cdot 10^{-5} M$$

$$[Ag^+] = 3x = 1.3 \cdot 10^{-4} M$$

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.

$$K_{sp} = 27x^4$$



I a lot

∅

∅

C -x

+3x

+x

E a lot
 -x

$\frac{3x}{\downarrow}$

\downarrow x

$$K = [\text{Ag}^+]^3 [\text{PO}_4^{3-}]$$

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

$$\sqrt[4]{\frac{K_{sp}}{27}} = 4.26 \times 10^{-5} = x$$

$$[\text{Ag}^+] = 3x$$

$$= 1.3 \times 10^{-4} \mu$$

molar solubility

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:**
 1. $Q_{sp} < K_{sp}$ (**unsaturated**) ; more solid can dissolve if added to the solution
 2. $Q_{sp} = K_{sp}$ (**perfectly saturated**) ; your reaction is at equilibrium
 3. $Q_{sp} > K_{sp}$ (**over saturated**) ; precipitation occurs until $Q_{sp} = K_{sp}$

50 mL of 0.05 M sodium phosphate, Na_3PO_4 , is mixed with 50 mL of 0.08 M aluminum chloride, AlCl_3 . What precipitate, if any, forms? $K_{sp}(\text{AlPO}_4) = 9.8 \times 10^{-21}$

1. AlPO_4 and NaCl
2. No precipitate
3. AlPO_4 only
4. NaCl only

50 mL
0.05 M Na_3PO_4 + 50 mL
0.08 M AlCl_3

↓ Dilution x2

100 mL
0.025 M PO_4^{3-}
0.04 M Al^{3+}

$$Q_{sp} = [\text{PO}_4^{3-}][\text{Al}^{3+}]$$

$$0.001 = 0.025 \cdot 0.04$$

$$0.001 \gg 9.8 \times 10^{-21}$$

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



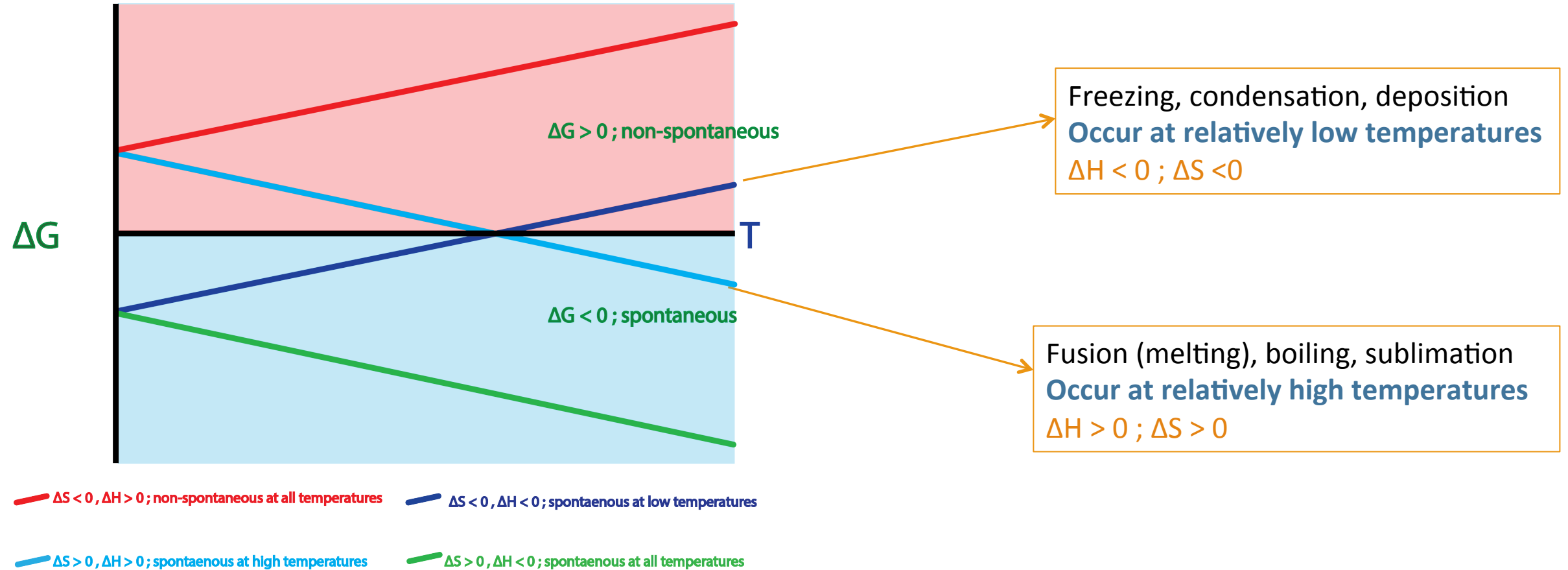
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Phase Changes

EQUILIBRIUM CALCULATIONS, HEATING CURVES, PHASE DIAGRAMS

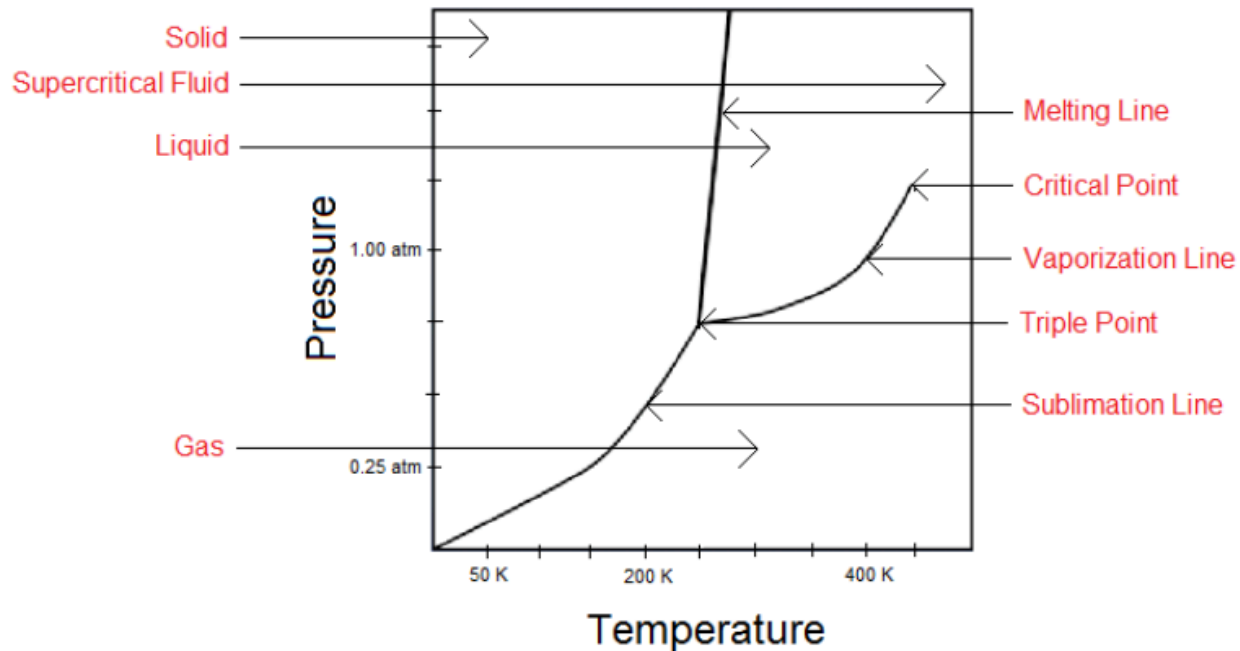
Free Energy: All Conditions Summary

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



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 Big Picture

- 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})

Solution VP < Pure Liquid VP

Higher Temperature = Exponentially Higher Vapor Pressure

- **Changing the surface area, size of the container, amount of water, and so on does not change the pressure.**

Solutions and Colligative Properties

THERMODYNAMICS OF SOLUTIONS, STABILITY OF SOLUTIONS

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)

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

- Molality: moles of solute per kilogram solvent (mol / kg)

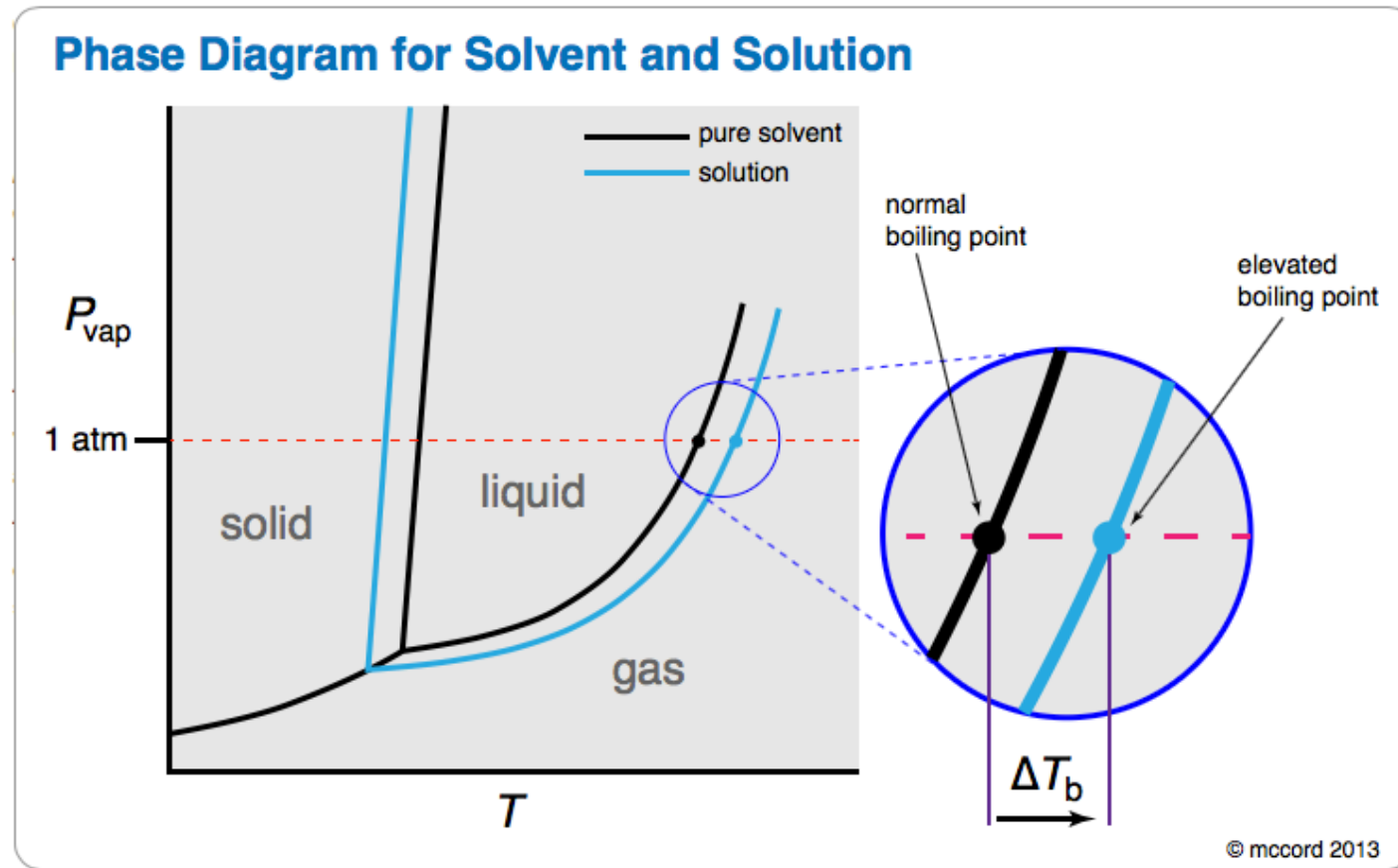
$$m = \frac{\text{mol}}{\text{kg}}$$

- Mole Fraction: moles of a particular species per total moles of solution / mixture (dimensionless)

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

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):

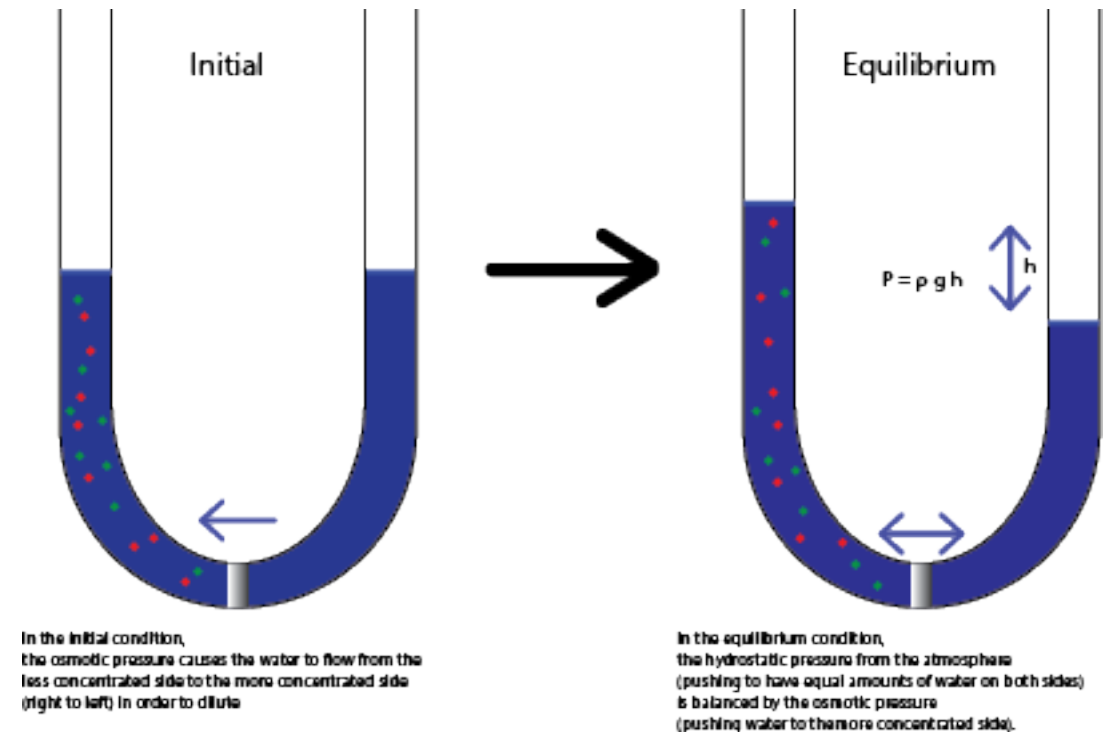
Solves for **the new vapor pressure** (P_A) of a solution, based on the **mole fraction of the solvent** (X_A) and the vapor pressure of the pure solvent (P°_A)

$$P_A = X_A P^\circ_A$$

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.

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).**



$$\Pi = iMRT$$

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

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)
 - $\Pi = iMRT$

A 0.34 *m* solution of lead(IV) nitrate would be expected to have the same boiling point as which of the following solutions?

1. 0.85 *m* CuSO₄
2. 0.34 *m* sucrose
3. 0.34 *m* NaCl
4. 1.7 *m* Ba(NO₃)₂
5. 0.85 *m* K₂SO₄

What will have the HIGHEST BP?

$$\Delta T_b = \underline{i} \cdot \underset{\substack{\downarrow \\ \text{Constant}}}{K_b} \cdot \underline{m}$$

$\left[\frac{\text{moles Solute}}{\text{kg Solute Solvent}} \right]$
 Solve for MW



$$i \cdot m = 5 \cdot 0.34 = 1.7$$



$$i \cdot m = 2 \cdot 0.85 = 1.7$$

Solution

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

Salt:

$$(-) = (+) - \underbrace{T (+)}_{\text{maximize } T \text{ (High } T \text{)}}$$

Gas

$$(-) = (-) - \underbrace{T (-)}_{\text{minimize } T \text{ (Low } T \text{)}}$$

1) Low T ,

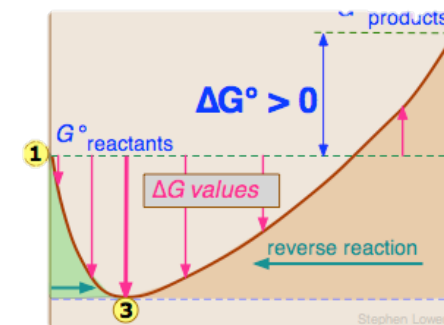
2) High P

Henry's Law

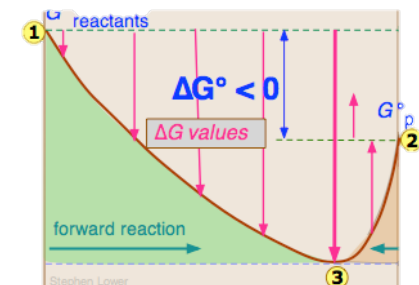
Unit 1 Big Picture: Free Energy and K_{sp}

- 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

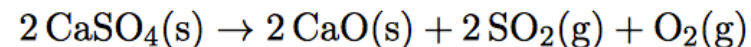
Unit 2: Chemical Equilibrium; Acids & Bases

Q vs K: RICE Tables

1. $Q < K$: “-x” goes on reactant side ;
“+x” goes on product side
2. $Q = K$: reaction is at equilibrium
(just right)
3. $Q > K$: “+x” goes on reactant side ;
“-x” goes on reactant side

Note: The K_p given in this problem is based on bar, not atm. Work the problem in bar.

Consider the following decomposition reaction at 700 K.



If $K_p = 0.032$ at this temperature, what will be the equilibrium overall pressure starting from pure $\text{CaSO}_4(\text{s})$?

1. 0.40 bar
2. 0.20 bar
3. 0.60 bar
4. 0.011 bar
5. 0.22 bar

$$K_p = 0.032$$

$$K_p = \frac{P_{SO_2}^2 \cdot P_{O_2}}{(2x)^2 \cdot x} = \frac{4x^3}{4x^3}$$



I	a lot	0	0	0
C	-2x	+2x	+2x	+x
E	a lot -2x	2x	2x	x

$$K_p = (2x)^2 \cdot x = 4x^3$$

$$\sqrt[3]{\frac{0.032}{4}} = x = 0.2 \text{ bar}$$

$$P_{\text{total}} = P_{SO_2} + P_{O_2} \quad \leftarrow \text{Dalton's Law}$$

$$= 2x + x$$

$$0.4 + 0.2 = 0.6 \text{ bar}$$

Le Chatelier's Principle

1. Adding or removing species:

- Adding: reaction shifts toward the opposite side of the addition
- Removing: reaction shifts toward the same side as the removal

2. Increasing or decreasing the volume (gases):

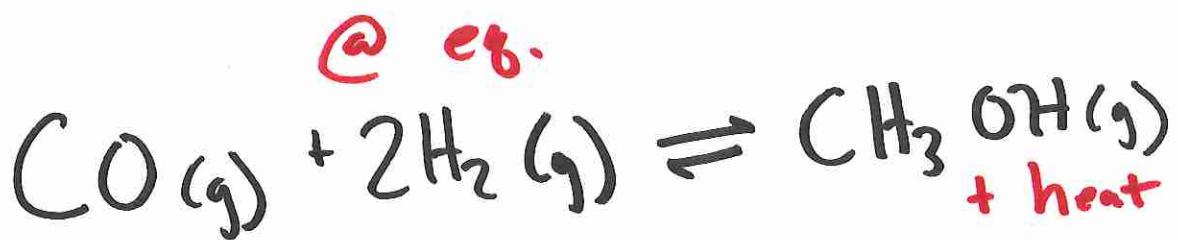
- Increasing volume (decreasing pressure): shifts toward the side with the most gas moles
- Decreasing volume (increasing pressure): shifts toward the side with the least gas moles

3. Diluting or concentration a solution (aqueous):

- Diluting: shifts toward the side of the most aqueous moles
- Concentration: shifts toward the side of least aqueous moles

4. Changing the temperature:

- Endothermic: increasing T shifts toward products ; decreasing T shifts toward reactants
- Exothermic: increasing T shifts toward reactants ; decreasing T shifts toward products



@ RT, $K = 2 \times 10^4$

@ a high T, K is much smaller.

is ΔH positive or negative?

- (1) Add H_2 , shifts right
 - (2) Add CH_3OH , shifts left
 - (3) Double Pressure, shifts right
 - * Least gas moles
 - (4) Double Volume, shifts left
 - * Half pressure
 - * Most gas moles
- } Q

Quantifying Weak Acids and Bases

- For a weak acid, we are dealing with a more interesting equilibrium (additional steps). The approximation formulas are below:

$$[H^+] = \sqrt{C_{HA} \cdot K_a} \qquad [OH^-] = \sqrt{C_B \cdot K_b}$$

- Don't forget that at any time you can convert between different terms:

$$K_w = 1 \cdot 10^{-14} = [H^+][OH^-]$$

$$K_w = K_a K_b$$

$$\frac{K_w}{K_a} = K_b$$

$$\frac{K_w}{K_b} = K_a$$

Quick Concept Check

You have a 1.5 M solution of methylamine, CH_3NH_2 . You expect the concentration of methylammonium ion, CH_3NH_3^+ in this solution to be

1. Slightly greater than 1.5 M
2. Much greater than 1.5 M
3. 1.5 M
4. Much lower than 1.5 M
5. Slightly lower than 1.5 M



↑
Weak base

$K_B \ll 1$

~ 1.5M

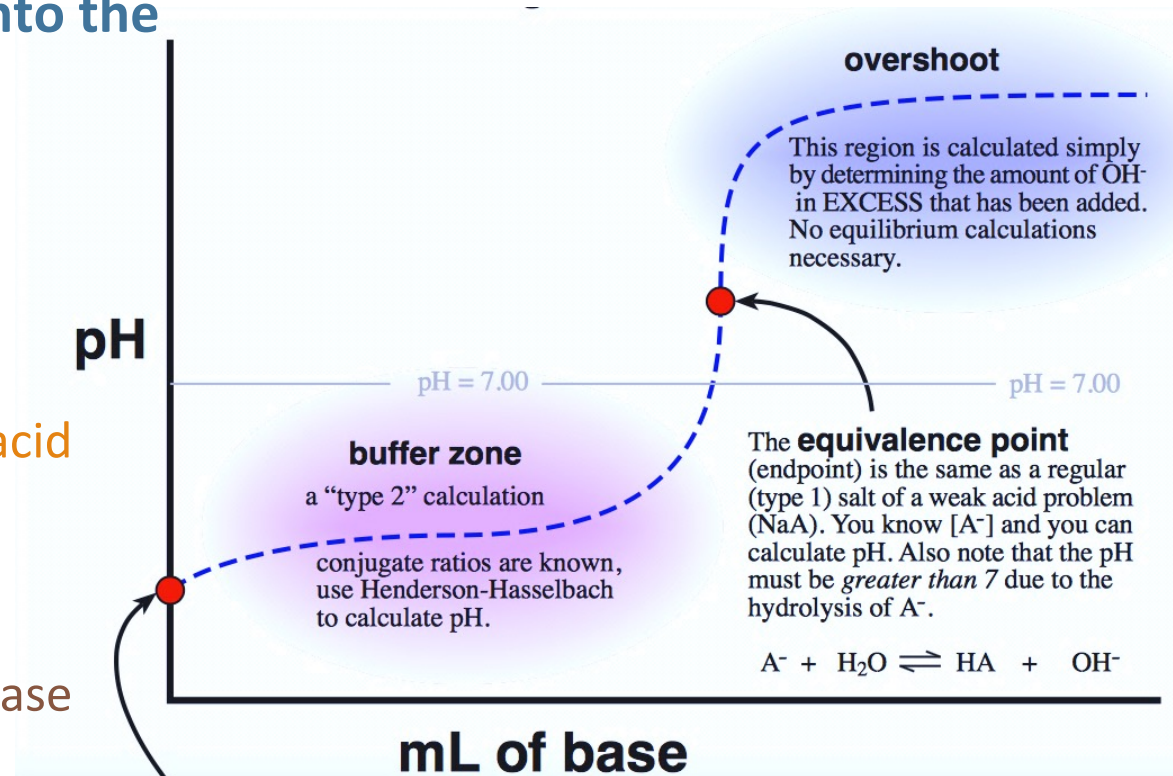
↑
Conj. acid

↑
Very small

Acids and Bases Calculations

Most calculations in the Acid/Base Unit fall into the following categories:

1. Strong Acid Calculation
2. Strong Base Calculation
3. Weak Acid Calculation
 - What is the pH of 0.5M HA?
 - Equivalence point of a weak base – strong acid titration
4. Weak Base Calculation
 - What is the pH of 0.5M B?
 - Equivalence point of a weak acid – strong base titration
5. Buffer problem (mix of weak acid and weak base)



Acid and Base Warm-Up

You mix 10 mL of 3M LiOH with 10 mL of 3M HNO₂. The final solution will be

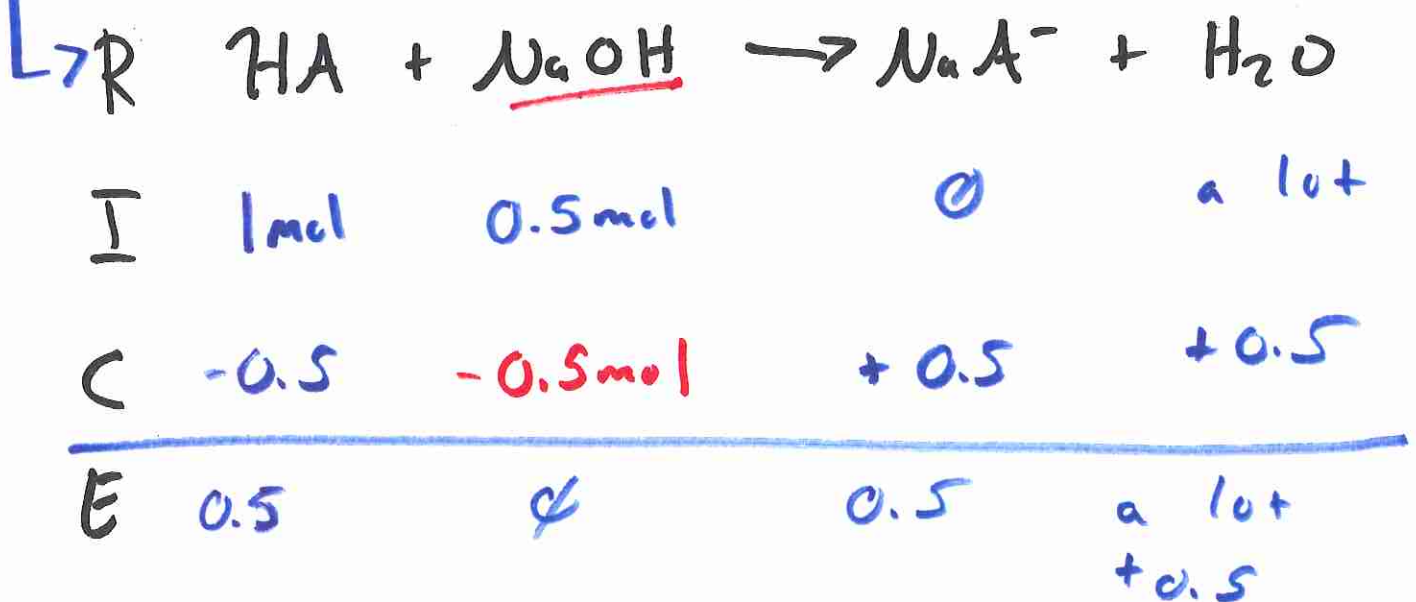
Acid, Neutral, or Basic?

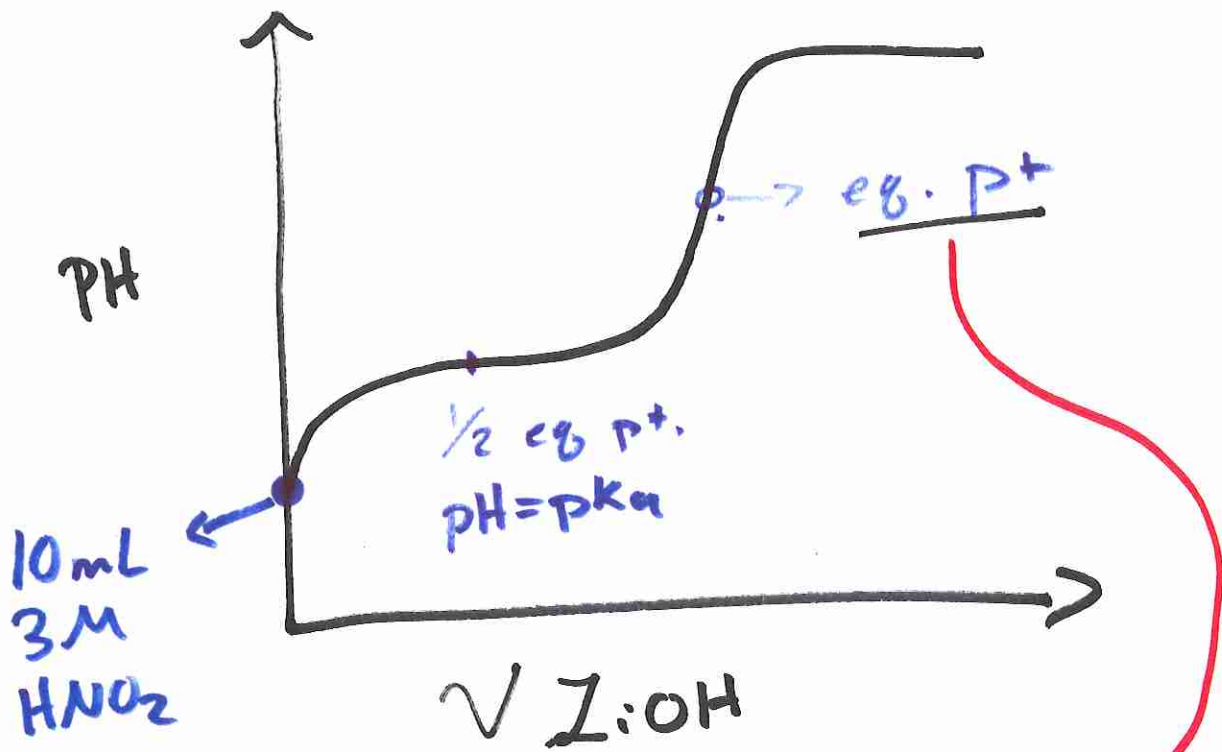
EXTRA: What is the estimated pH of the final solution? K_a for HNO₂ is 5.6×10^{-4}

Great Buffer:

1:1 ratio of weak acid/base : salt

- 0.5 moles HA, 0.5 moles A^-
- 1 mole HA + 0.5 moles NaOH
= 0.5 moles HA, 0.5 moles A^-





100% Li⁺ NO₂⁻ ← conj. base

Diluted, 1.5 M NO₂⁻

$$[OH^-] = \sqrt{K_B \cdot C_B}$$

-log ↓

pOH = 5.3

$$\left(\frac{1 \times 10^{-14}}{5.6 \times 10^{-4}} \right) 1.5 M$$

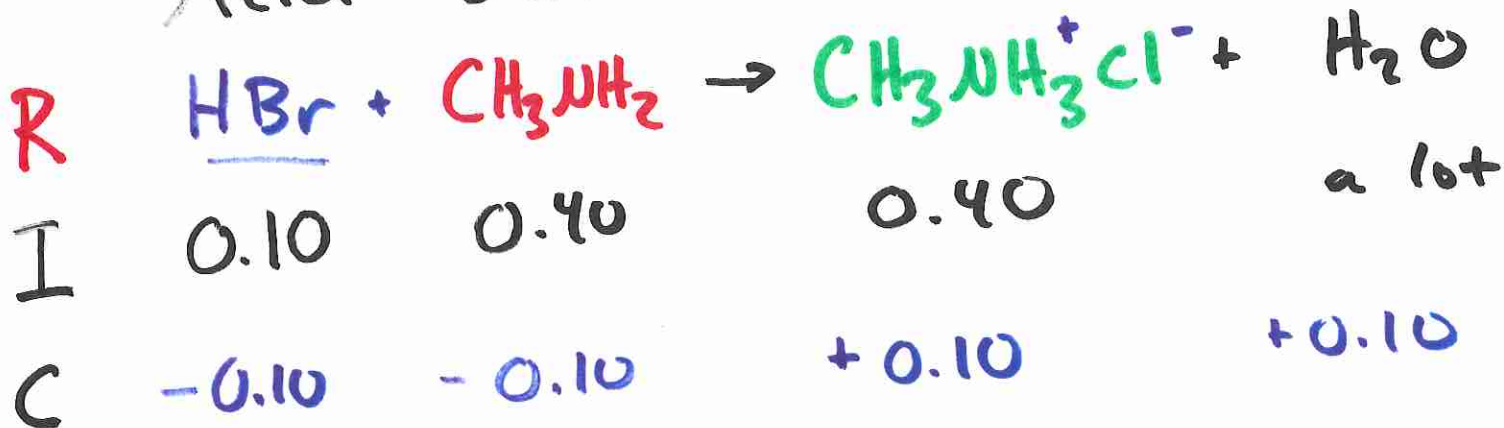
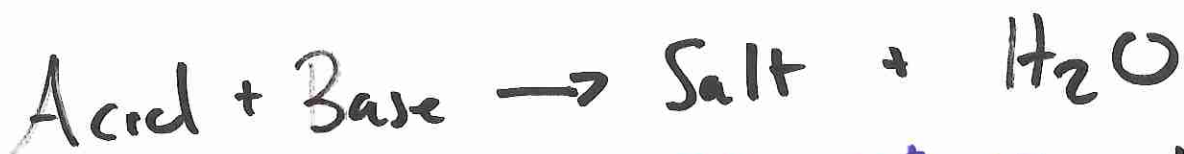
pH = 14 - pOH
= 8.7

→ K_w = K_a · K_B
Memorize

Acid and Base Difficult Question

A buffer was prepared by mixing 0.40 moles of methylamine (CH_3NH_2) and 0.40 moles of methylammonium chloride ($\text{CH}_3\text{NH}_3\text{Cl}$) to form an aqueous solution with a total volume of 800 mL. After that solution came to equilibrium, 0.10 moles of HBr was added to the buffer solution. What is the new pH of the solution?

$$K_B = 4.4 \times 10^{-4}$$



E \emptyset 0.3 0.5 a lot + a little more

$$K_b = 4.4 \times 10^{-4}$$

$$K_w = K_a \cdot K_b$$

$$pH = pK_a + \log \left(\frac{A^-}{HA} \right)$$

$\uparrow -\log K_a$

$$\frac{1 \times 10^{-14}}{4.4 \times 10^{-4}} = K_a$$

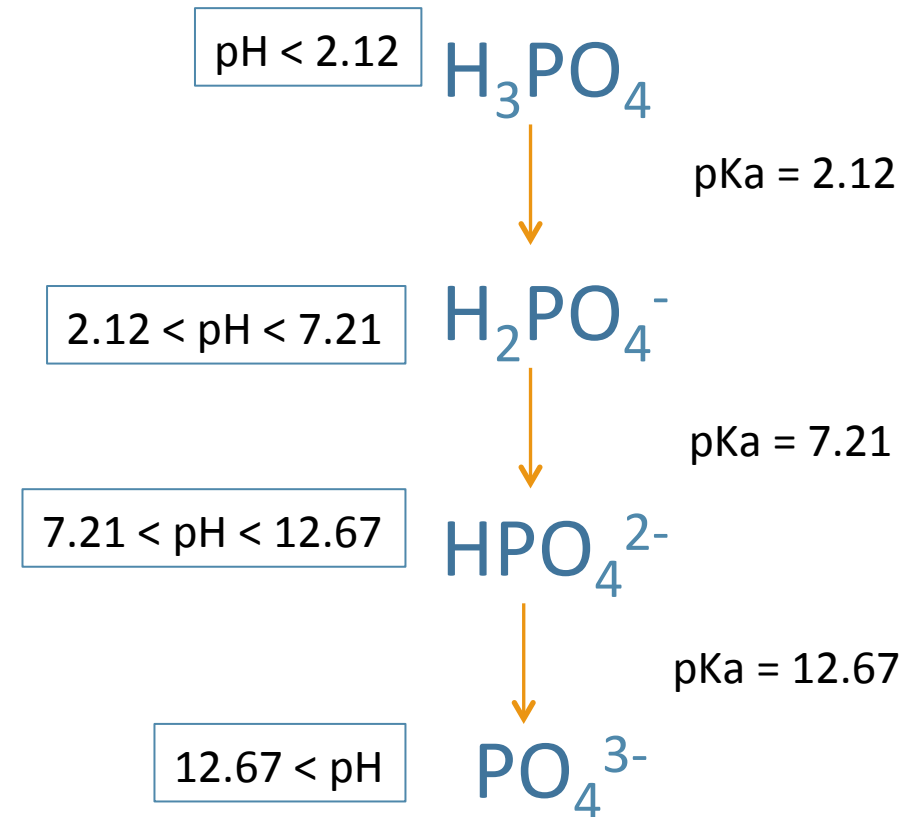
$$10.42 = \underline{10.64} + \log \left(\frac{0.3}{0.5} \right)$$

$pK_a \rightarrow$ when $[CH_3NH_2] = [CH_3NH_3Cl]$

Dominant Species Fundamentals

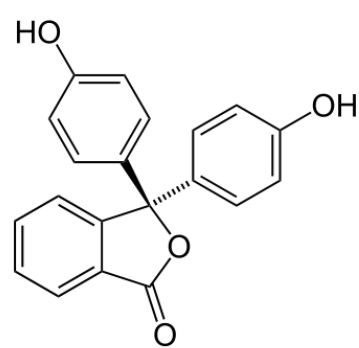
- For polyprotic acids, two simple rules go a long way when identifying the dominant species in solution:

- If $\text{pH} < \text{pK}_a$** : you have too many hydrogen ions in solution for it to be favorable for a hydrogen ion on your molecule to “pop off”
 - Think about it: when the environment is more acidic, it is more “proton-donating,”
 - Your molecule will be protonated
- If $\text{pH} > \text{pK}_a$** : the environment around your molecule is thirsty for hydrogen ions, so it is favorable for a hydrogen ion on your molecule to pop off
 - Think about it: when the environment is more basic, it is more “proton-accepting.”
 - Your molecule will be deprotonated

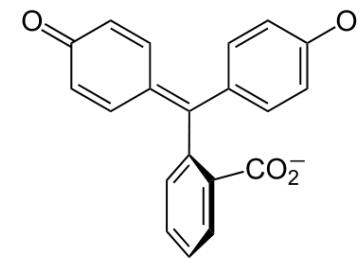
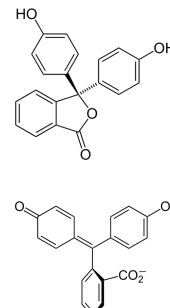


Dominant Species: Indicators

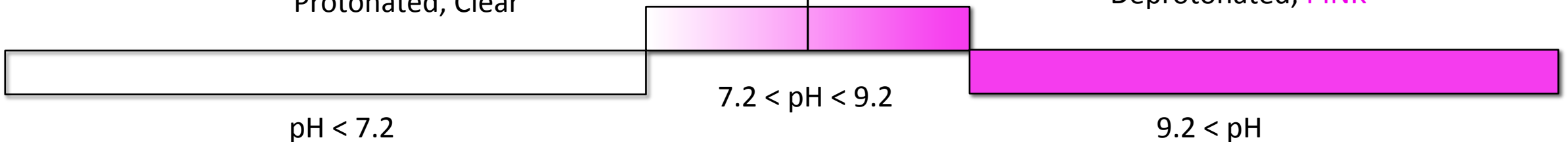
- The purpose of an indicator is to change color in a particular pH range (color change occurs +/- 1 pH unit from the pKa). The protonated and deprotonated forms of the molecule will have different colors. **Therefore, the color of solution will represent the dominant species in solution.**
- Consider phenolphthalein, pKa = 8.2:



Protonated, Clear



Deprotonated, PINK



Unit 3: Nuclear & Kinetics

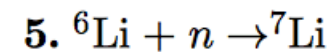
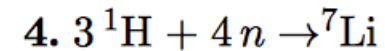
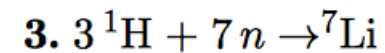
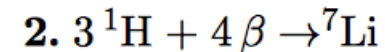
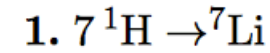
NO INORGANIC

Nuclear Fundamentals

There are four types of nuclear reactions that we discuss in this class:

1. **Fission: a large atom splits into medium nuclei**
 - Fission reactions are exothermic with atoms larger than iron
 - Common with large, unstable nuclei such as uranium
2. **Fusion: small nuclei join to form larger nuclei**
 - Fusion reactions are exothermic with atoms smaller than iron
 - Common with hydrogen isotopes (tritium, deuterium) and helium in extreme conditions (such as in stars)
3. **Nuclear Decay: an unstable nucleus reaches a lower energy state by spontaneously releasing ionizing radiation (beta decay, positron decay, alpha decay, electron capture)**
4. **Transmutation: a less stable nucleus is created by **non-spontaneously** bombarding it with ionizing radiation (opposite of nuclear decay)**

The nuclear binding energy for lithium-7 is the energy released in the nuclear reaction

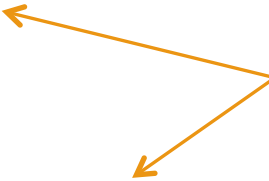


The Four Factors that Affect Rates

1. Nature of reactants/ Availability of the molecules

- Larger surface area = faster rate
- Ex: this is the reason why we chew our food (mechanical digestion)

Increase the rate without changing the rate constant



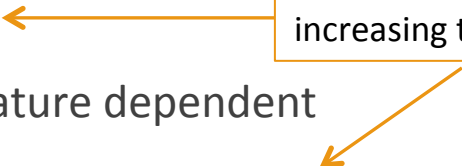
2. Concentration (and pressure)

- Higher concentration, higher rate **if your reaction is first order or higher**
- Increases the rate based on the fact that the rate law is concentration dependent

3. Temperature

- Higher temperature, higher rate **always** (in this class)
- Increases the rate based on the fact that the **rate constant** is temperature dependent

Increase the rate by increasing the rate constant



4. Catalysts

- Catalysts decrease the **activation energy**, which increases the rate based on the Arrhenius Equation
- Increases the rate based on the fact that the rate constant is proportional to the **negative activation energy**

Rate Laws & Integrated Rates

- **First Order: general formula, slope-intercept formula, half life**

$$\text{rate} = k[A]$$

$$\ln \frac{[A]_0}{[A]} = kt$$

$$\ln[A] = -kt + \ln[A]_0$$

$$\frac{\ln(2)}{k} = t_{1/2}$$

- **0th Order: general formula, slope-intercept formula, half life**

$$\text{rate} = k$$

$$[A]_0 - [A] = kt$$

$$[A] = -kt + [A]_0$$

$$\frac{[A]_0}{2k} = t_{1/2}$$

- **2nd Order: general formula, slope-intercept formula, half life**

$$\text{rate} = k[A]^2$$

$$\frac{1}{[A]} - \frac{1}{[A]_0} = kt$$

$$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$$

$$\frac{1}{k[A]_0} = t_{1/2}$$

Half-Lives of Integrated Rate Laws

- **First Order Half-Life: Independent of concentration**

$$\frac{\ln(2)}{k} = t_{1/2}$$

- **0th Order Half-Life: Directly related to concentration**

$$\frac{[A]_0}{2k} = t_{1/2}$$

- **2nd Order Half-Life: Inversely related to concentration**

$$\frac{1}{k[A]_0} = t_{1/2}$$

$$\ln \left(\frac{[A]_0}{[A]} \right) = kt$$



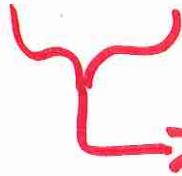
ratio:

amounts, mass

Concentration

radioactivity units

"activities"



must match

s^{-1} , s

m^{-1} , m

hr^{-1} , hr

Unit 4: Electrochemistry

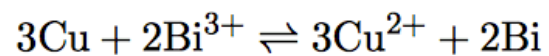
$$\frac{d \cdot t}{n \cdot F} = \text{moles plated}$$

Charge applied (c)

Charge required (c)
mol metal

Equilibrium Constant Problem

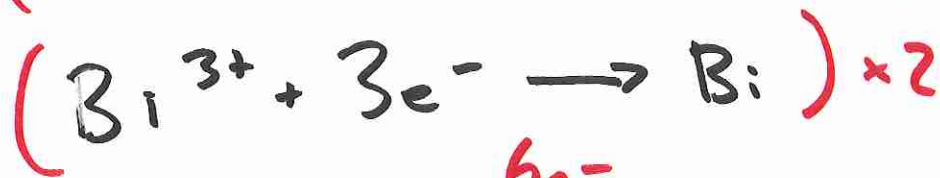
Calculate the equilibrium constant for the following reaction by using a table of standard potentials.



Cu^{2+}/Cu ; potential = 0.34V

Bi^{3+}/Bi ; potential = 0.20V

1. 4.3×10^{-3}
2. 8.0×10^{-8}
3. 6.3×10^{-15}
4. 1.8×10^{-5}
5. 1.3×10^7
6. 1.6×10^{14}



$$E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$$

$$-0.14\text{V} = 0.2 - 0.34$$

$$\Delta G^{\circ} = -RT \ln K$$

$$\frac{-nFE^{\circ}}{-nF} = \frac{-RT \ln K}{-nF}$$

$$E^{\circ} = \frac{RT}{nF} \ln K$$

$$\cancel{E} = E^{\circ} - \frac{0.05916}{n} \log \cancel{K}$$

$$\Downarrow$$

$$0$$

$$\Downarrow$$

$$K$$

$$E^{\circ} = \frac{0.05916}{n} \log K$$

$$\Downarrow$$

$$10^{\frac{-0.14 \cdot 6}{0.05916}} = K$$

$$K = 6.33 \times 10^{-15}$$