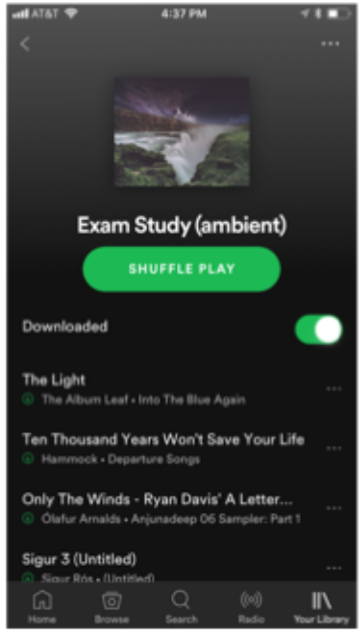
# CH 302 –Final Exam Review

WE MADE IT! (ALMOST)

# It was a great year ;')



**Exam Study (ambient)**

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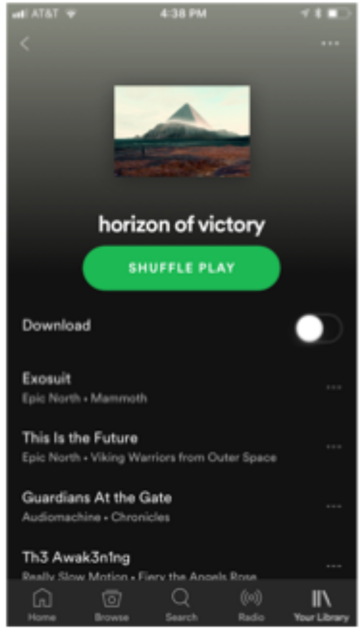
Sigur 3 (Untitled)
Sigur Rós • (Untitled)



**horizon of victory**

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Epic North • Viking Warriors from Outer Space

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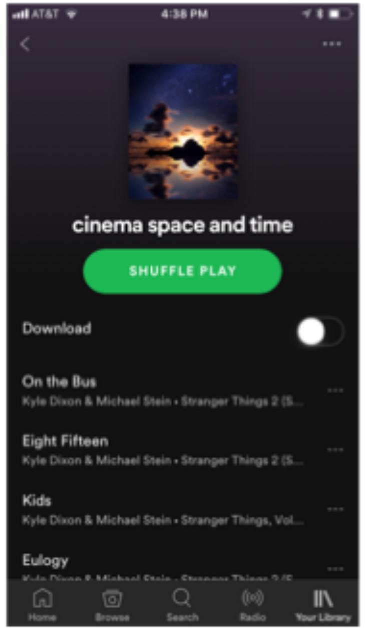

**cinema space and time**

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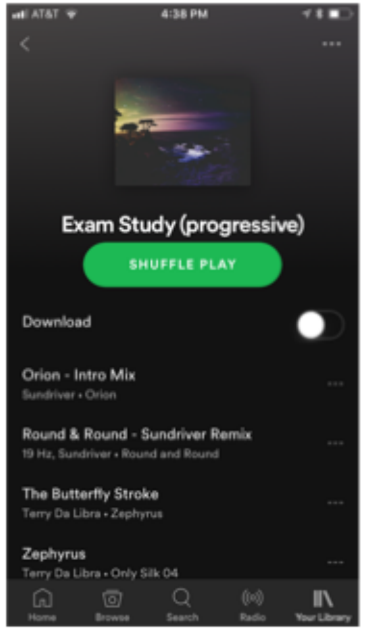
On the Bus
Kyle Dixon & Michael Stein • Stranger Things 2 (S...

Eight Fifteen
Kyle Dixon & Michael Stein • Stranger Things 2 (S...

Kids
Kyle Dixon & Michael Stein • Stranger Things, Vol...

Eulogy



**Exam Study (progressive)**

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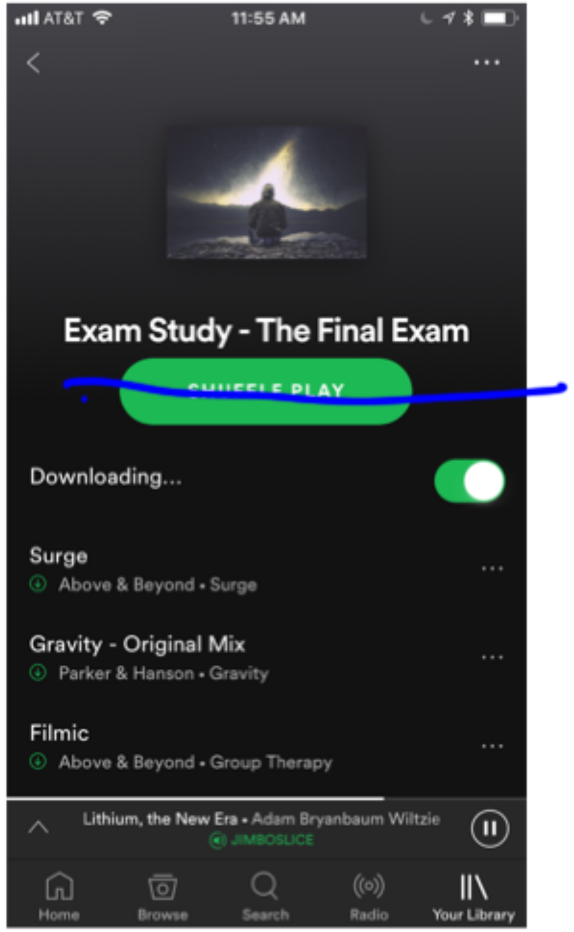
Orion - Intro Mix
Sundriver • Orion

Round & Round - Sundriver Remix
19 Hz, Sundriver • Round and Round

The Butterfly Stroke
Terry Da Libra • Zephyrus

Zephyrus
Terry Da Libra • Only Silk 04



**Exam Study - The Final Exam**

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Surge
Above & Beyond • Surge

Gravity - Original Mix
Parker & Hanson • Gravity

Filmic
Above & Beyond • Group Therapy

Lithium, the New Era • Adam Bryanbaum Wiltzie
JIMBOSLICE

# Conquering the Final Exam

- **Study the formula sheet**
  - Know what is on it and what is missing
- **Be able to put all equations and concepts in your own words**
  - The final exam is heavily conceptual, so make sure you don't overlook the fundamental relationships that underlie the equations
- **When you study the midterms, don't just study the questions. Also make sure you understand the underlying concepts**
  - You're going to see variations of midterm questions on the exam, but not duplicates. Be able to apply the equations or concepts in midterm questions to unique questions
- As always, put in the (genuine) work and you will be rewarded

$\underbrace{\text{50 Q's}}_{\text{3 hours}}$

Even distribution across 5 midterms

Dr. B

↓

Inorganic ×2

# Semester Big Picture

This semester we examined the relationship between ΔG, K, and E°

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

$$\Delta G_r^\circ = -RT \ln K$$

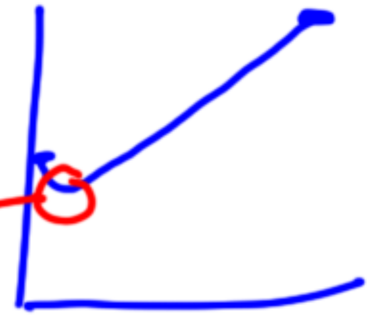
$$\Delta G^\circ = -nF\mathcal{E}^\circ$$

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

$$\underbrace{FeCO_3}_{\text{Insoluble}}{}_{(s)} \longrightarrow Fe^{2+}_{(aq)} + CO_3^{2-}{}_{(aq)}$$

$\Delta G\ (+)$ , $K_{sp} << 1$

mostly $FeCO_3$

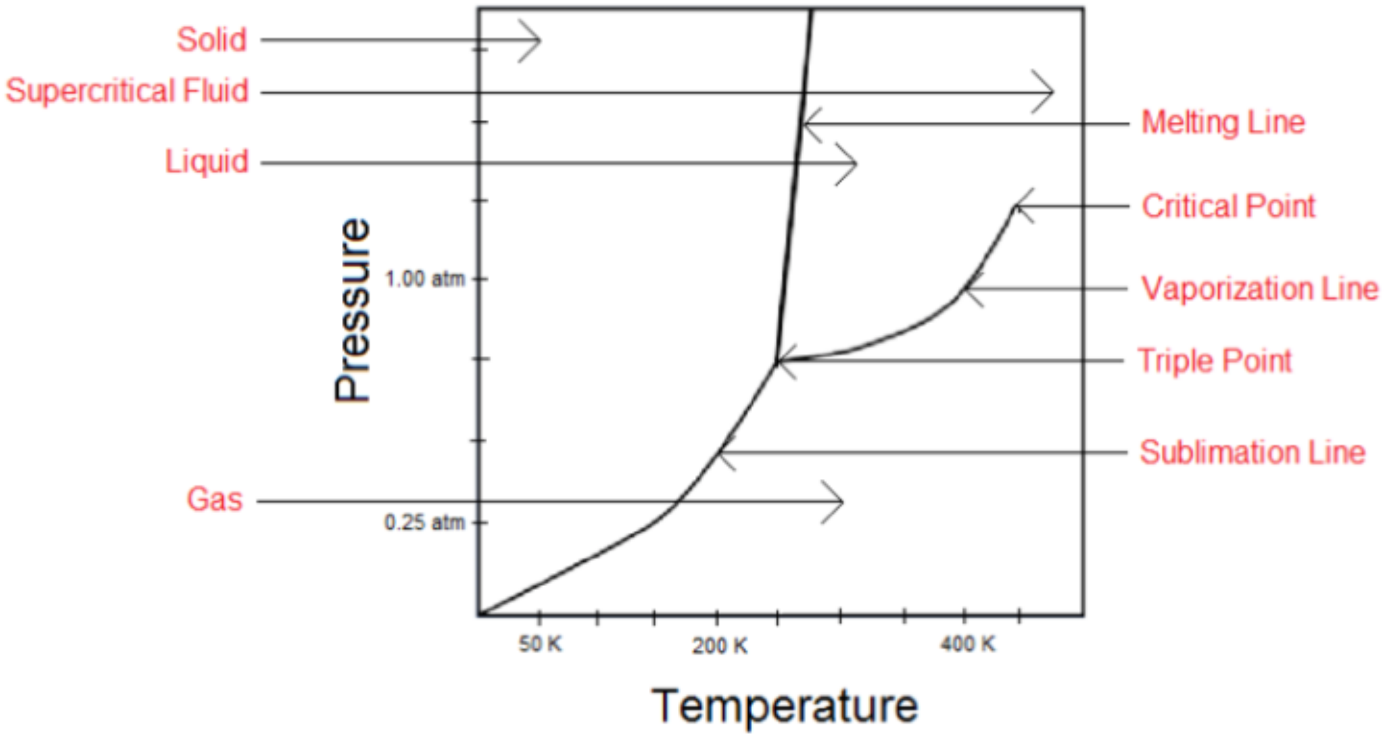


# Unit One: Physical Changes

## VAPOR PRESSURE, FREE ENERGY OF PHYSICAL CHANGES, STABILITY OF SOLUTIONS

# 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 $\Delta H_{vap}$)

Weak IMF -> high VP (and low boiling point, low $\Delta H_{vap}$)

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 vapor pressure.**

# Free Energy and Spontaneity

- In unit one, we looked at a few types of physical changes and what conditions "favor" spontaneity ($\Delta G < 0$):

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

Also increase pressure

- Fusion, boiling, sublimation: (−) = + − high +
- Freezing, condensation, deposition: (−) = (−) − low (−)
- * Solids dissolving in liquid: (−) = (+) − high (+)
- Gases dissolving in liquid: (−) = (−) − low (−)
- Liquids mixing: (−) = (+) − high (+)

Want to minimize

*Typical Salt dissolution

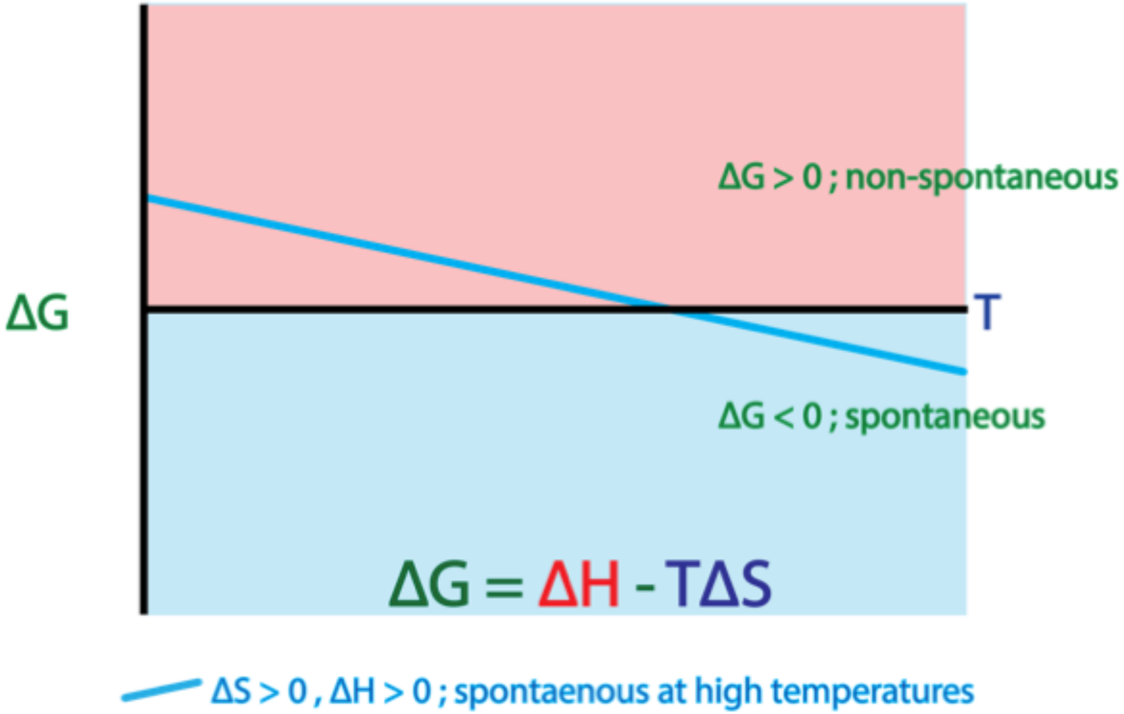
# Melting, Boiling, Sublimation

- **Each of these phase changes has (+)ΔH and (+)ΔS**

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

**What do the signs of ΔG mean?**

1. $\Delta G < 0$ (negative) ; your reaction is spontaneous, the temperature is high enough
2. $\Delta G = 0$ (zero) ; your reaction is at equilibrium, the temperature = $T_{trans}$
3. $\Delta G > 0$ (positive) ; your reaction is nonspontaneous, the temperature is too low



# Freezing, Condensation, Deposition

- **Each of these phase changes has (-)ΔH and (-)ΔS**

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

**What do the signs of ΔG mean?**

1. $\Delta G < 0$ (negative) ; your reaction is spontaneous, the temperature is low enough
2. $\Delta G = 0$ (zero) ; your reaction is at equilibrium, the temperature = $T_{trans}$
3. $\Delta G > 0$ (positive) ; your reaction is nonspontaneous, the temperature is too high

Summary: Temperature is the “balance” between a phase change that is spontaneous or non-spontaneous. Whether you want temperature to be high or low depends on the signs of ΔH, ΔS

* $\Delta H$ solution is 0 for an ideal solution. For your typical salts, it is slightly endothermic. There are plenty of examples of both endothermic AND exothermic solid dissolution processes

# Thermodynamics of Solution

*Salt Dissolving in Water*

$$\Delta H_{\text{solution}} = \underset{(+)}{\Delta H_{\text{lattice energy}}} + \underset{(-)}{\Delta H_{\text{solvation}}} \approx \overset{\text{slightly } (+)}{0^*}$$

$$\Delta S_{\text{solution}} = S_{(\text{aqueous})} - S_{(\text{solid})} = \textbf{Positive}$$

$$\Delta G_{\text{solution}} = \Delta H_{\text{solution}} - T\Delta S_{\text{solution}} = \textbf{Negative}$$

$$\Delta G_{\text{solution}} = (0^*) - \boxed{T}\,(+)$$

Dissolution of salt is typically an entropy-driven process, favored at high temperatures

*Gas Dissolving in Water*

$$\Delta H_{\text{solution}} = \underset{0}{\Delta H_{\text{lattice energy}}} + \underset{(-)}{\Delta H_{\text{solvation}}} = \textbf{Negative}$$

$$\Delta S_{\text{solution}} = S_{(\text{aqueous})} - S_{(\text{solid})} = \textbf{Negative}$$

$$\Delta G_{\text{solution}} = \Delta H_{\text{solution}} - T\Delta S_{\text{solution}} = \textbf{Negative}$$

$$\Delta G_{\text{solution}} = \underline{\underline{(-)}} - T\,(-)$$

Dissolution of gas is typically an enthalpy-driven process, favored at low temperatures and high pressures

# Like-Dissolves-Like: Miscibility

Like the dissolution of a solid, liquids mixing is typically an entropy-driven process, favored at high temperatures:

$$\Delta G_{solution} = \Delta H_{solution} - T\Delta S_{solution} = \textbf{Negative}$$

$$\Delta G_{solution} = (+) - T(+)$$

Once again, this is an entropy-driven process. There are two important points here:

1. **Enthalpy is important when mixing two liquids. Matching the IMF's of two liquids MINIMIZES the ΔH term.**
2. **Increasing temperature increases solubility**

Dispersion forces:

$C_nH_{n+2}$, $CCl_4$, $CO_2$, $F_2$ etc.

Dissolve well in each other

Dipole-Dipole:

$CH_2O$, $CH_3COCH_3$, $AsCl_3$, etc.

H-bonding:

$CH_3OH$, $H_2O$, HF, $NH_3$, etc.

# Free Energy and Spontaneity

- One of those things we forget is what is "driving" the reaction to have a negative ΔG. Here it is outlined:

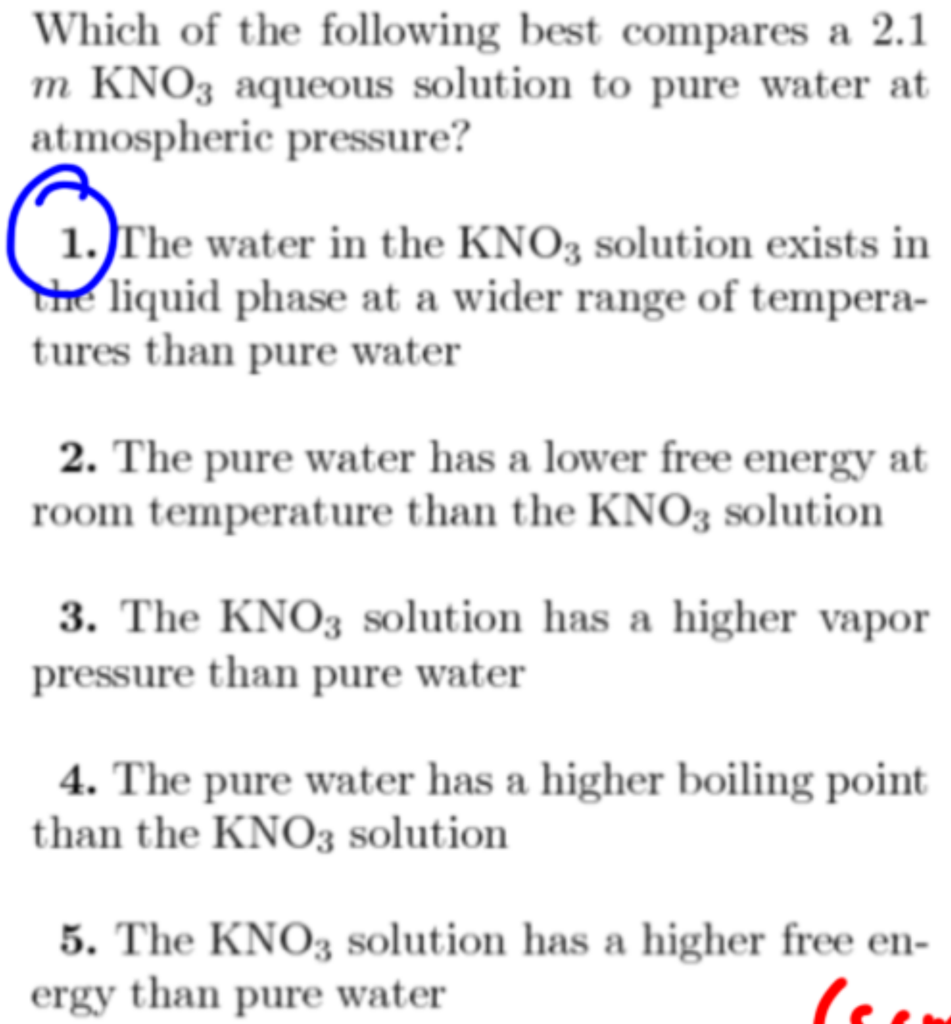
$$\Delta G = \Delta H - T\Delta S$$

- Fusion, boiling, sublimation: +ΔH, +ΔS (entropy driven, high temperatures)
- Freezing, condensation, deposition: -ΔH, -ΔS (enthalpy driven, low temperatures)
- Solids dissolving in liquid: +ΔH, +ΔS (entropy driven, high temperatures*)
- Gases dissolving in liquid: -ΔH, -ΔS (enthalpy driven, low temperatures, & high pressures)
- Liquids mixing: +ΔH, +ΔS (entropy driven, high temperatures, choose two liquids that have similar IMF's to minimize ΔH)

*later we did learn that the $K_{sp}$ for an exothermic reaction will decrease with temperature, so this isn't always true if $\Delta G < 0$, products are more stable

# Free Energy and the Solution

- Focusing on just solutions now, it is important to understand that what we did was show that when a solid spontaneously dissolves in a liquid, the free energy of the reaction system decreased.
- This means that the solution is more stable.
- And this is precisely why the vapor pressure lowers, the freezing point depresses, the boiling point elevates, and an osmotic pressure can be formed across a semipermeable membrane



Which of the following best compares a 2.1 $m$ $KNO_3$ aqueous solution to pure water at atmospheric pressure?

**1.** The water in the $KNO_3$ solution exists in the liquid phase at a wider range of temperatures than pure water

**2.** The pure water has a lower free energy at room temperature than the $KNO_3$ solution

opposite

**3.** The $KNO_3$ solution has a higher vapor pressure than pure water

opposite

**4.** The pure water has a higher boiling point than the $KNO_3$ solution

opposite

**5.** The $KNO_3$ solution has a higher free energy than pure water

opposite (same as 2.)

# Colligative Property Summary

Vapor Pressure Lowering (Raoult's Law):

- Solves for **the *new, lower* 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** ($\Delta T_f$), 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** ($\Delta T_b$), 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 physical equilibrium of osmosis against the hydrostatic pressure, based on **the molarity of the solute** (M)
  - $\Pi = iMRT$

# 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 ($\Delta T_f$ is always negative, $\Delta T_b$ is always positive) and you are NOT solving for the final temperatures.**

**Freezing Point Depression:**

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

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

$$T_f = T^\circ_f - \Delta T_f$$

**Boiling Point Elevation:**

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

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

$$T_b = T^\circ_b + \Delta T_b$$

# 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 ($P°_A$)

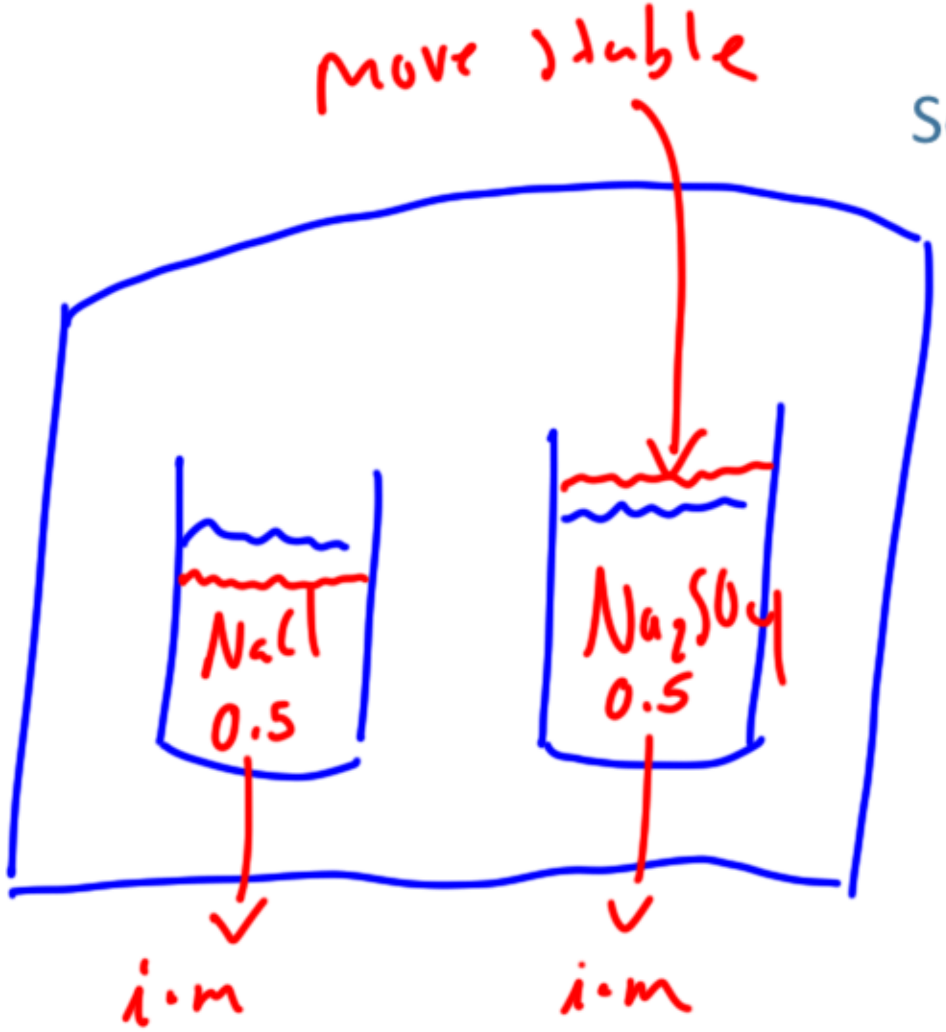
$$P_A = X_A P°_A$$

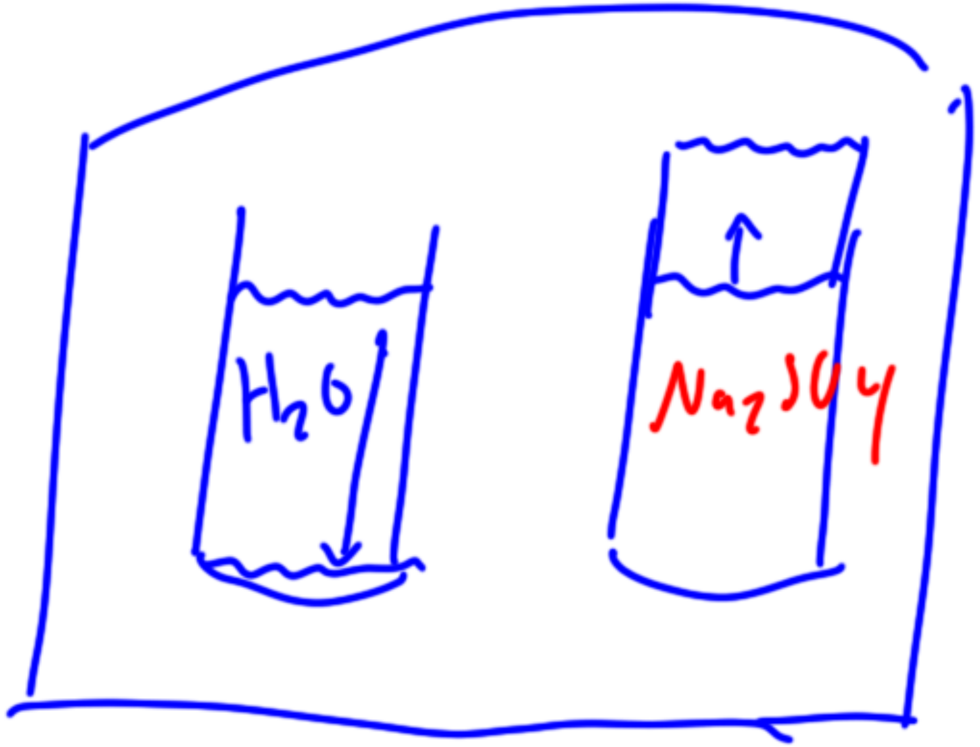
**You WILL have to account for electrolytes in the "total moles" of this mole fraction term, even though you don't see a Van't Hoff Factor here.**

$$\frac{\text{mol A}}{\text{mol A} + \text{mol solute} \times i}$$

# Vapor Pressure Big Picture II

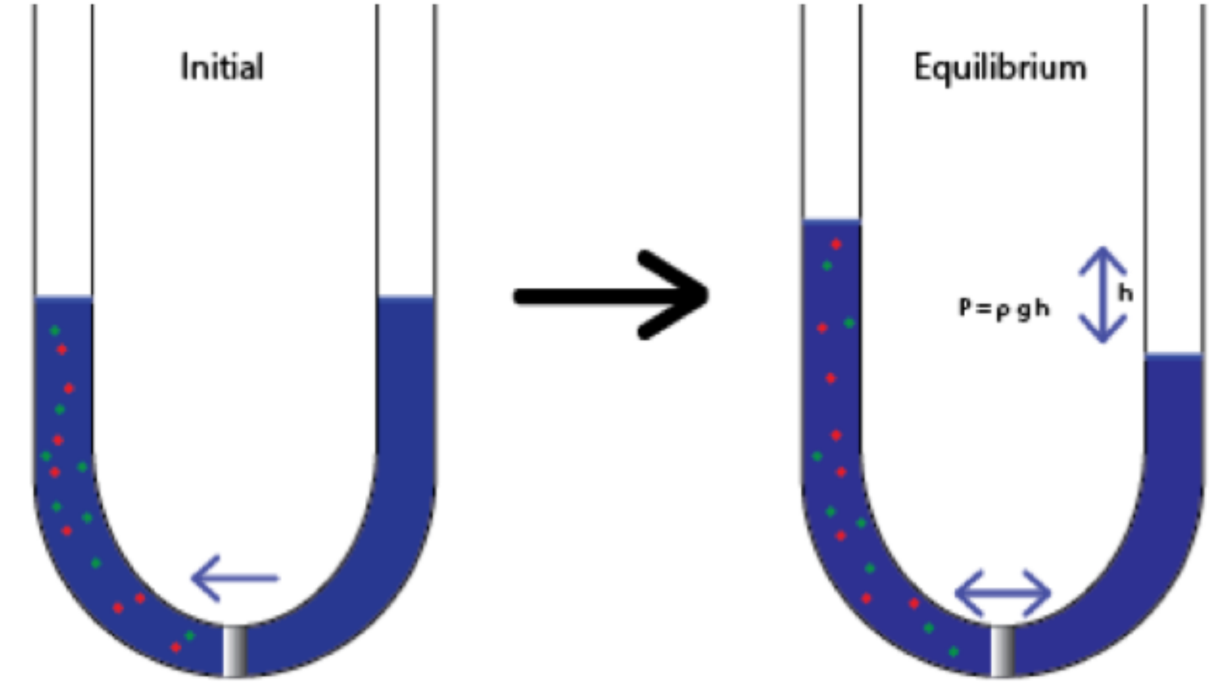
Solution VP < Pure Liquid VP





# 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).**



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).

$$\Pi = iMRT$$

$m_{eff} = i \cdot m_{stated}$

$0.34 \cdot 5 = 1.7$

# van’t Hoff Factor

- The van’t Hoff Factor is our “correction factor” for the colligative properties equations that helps us quantify the effective concentration of ions in solution
- **Big picture:** the reason for this lies in the fact that ΔS is greater for ionic solids that dissociate into more ions, resulting in a greater effect of the colligative property

1 4

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 $m$ $CuSO_4$ $0.85 \cdot 2 = 1.7\ m$

**2.** 0.34 $m$ sucrose

**3.** 0.34 $m$ NaCl

**4.** 1.7 $m$ $Ba(NO_3)_2$ $1.7 \cdot 3 = 5.1$

**5.** 0.85 $m$ $K_2SO_4$

What will have the HIGHEST BP?

# Unit 2,3: Chemical Equilibria

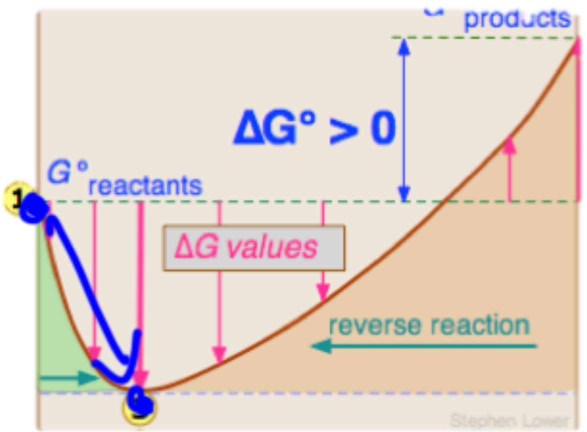
CHEMICAL EQUILIBRIUM, ACID+BASE CHEMISTRY, SOLUBILITY EQUILIBRIUM

# Brief overview of Equilibrium Terminology

- We use K and ΔG˚ to express which side of a reaction is "favored"
  - If $K > 1$, the products are favored (ΔG˚ is negative)
  - If $K < 1$, the reactants are favored (ΔG˚ is positive)
- We use the relationship between Q and K to explain which way a reaction will progress toward equilibrium
  - If the starting point of a reaction is $Q < K$, the reaction moves forward toward equilibrium
  - If the starting point of a reaction is $Q > K$, the reaction moves backward toward equilibrium.
- We stress a system at equilibrium to examine how a reaction will "shift" to oppose the stress
  - Stressing equilibrium can either change Q or K, resulting in more products or reactants formed

# Free Energy vs K

- When K is small (less than 1), only a small fraction of your reactants becomes products. A reaction with a small K reacts to a small extent.



reactant-favored

$\Delta G > 0$

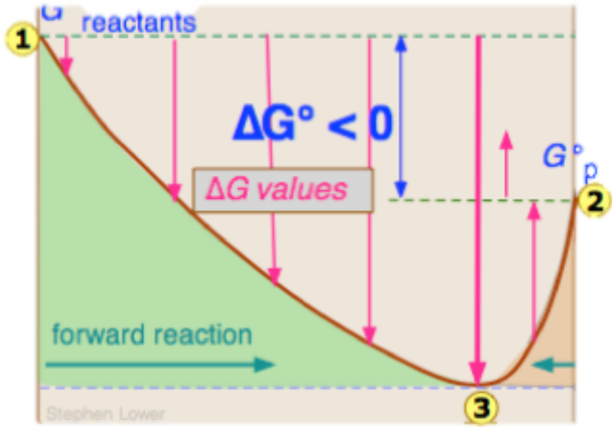
$K < 1$

- When K is large (greater than 1), a greater amount of products are formed than reactants remain. A reaction with a large K reacts to a large extent.

product-favored

$\Delta G < 0$

$K > 1$



$$\boxed{aA + bB \rightleftharpoons cC + dD}$$

$$K = \frac{a_C^c \, a_D^d}{a_A^a \, a_B^b}$$

# Q vs K: Chemical Equilibrium Terminology

1. Q < K : reaction moves forward toward equilibrium +x on product side
2. Q = K : reaction is at equilibrium (lowest energy state)
3. Q > K : reaction moves backward toward equilibrium +x on reactant side

Q = K

Q < K

Forward

Reverse

Q > K

K = 4

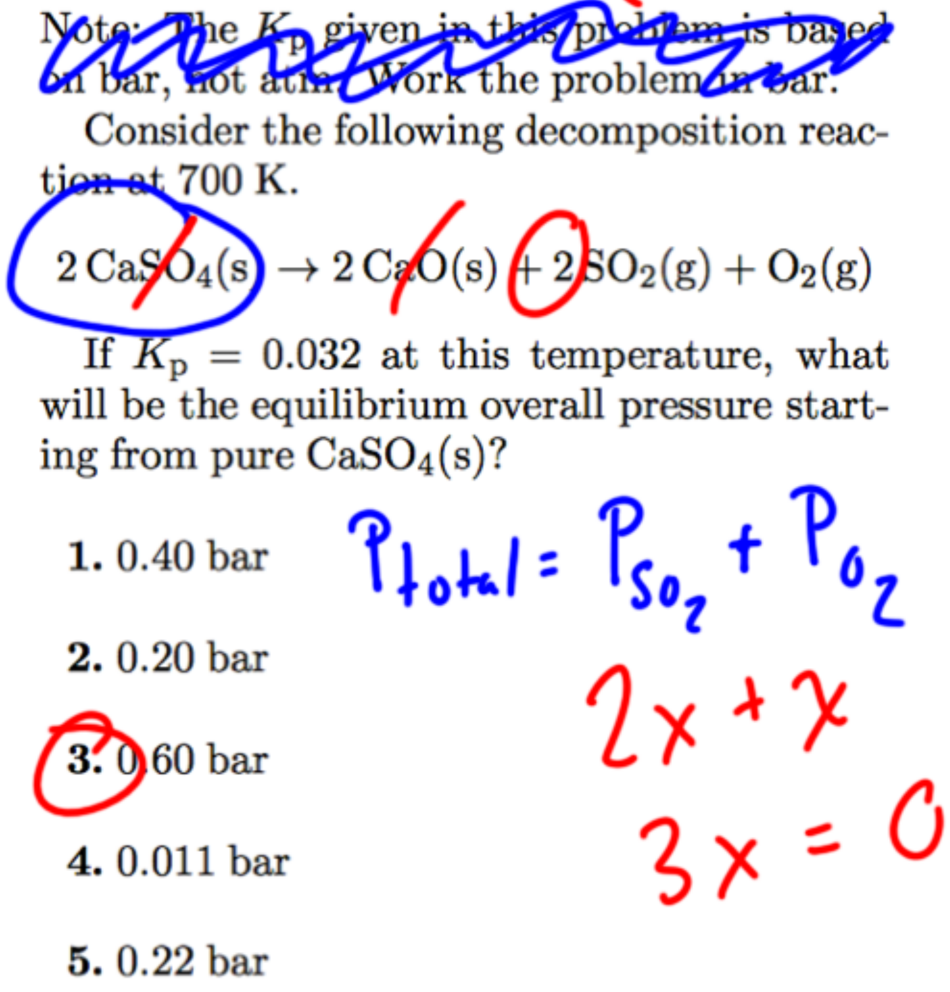
# Q vs K: RICE Tables

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

$$K_p = 0.032 = P_{SO_2}^{2} \cdot P_{O_2}$$

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

$$x = 0.2$$



~~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.

$$2\,\cancel{\mathrm{CaSO_4(s)}} \rightarrow 2\,\cancel{\mathrm{CaO(s)}} + 2\,\mathrm{SO_2(g)} + \mathrm{O_2(g)}$$

If $K_p = 0.032$ at this temperature, what will be the equilibrium overall pressure starting from pure $CaSO_4(s)$?

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

$$P_{total} = P_{SO_2} + P_{O_2}$$

$$2x + x$$

$$3x = 0.6$$

| R | $2CaSO_4$ | $\rightarrow$ | $2CaO$ | + | $2SO_2$ | + | $O_2$ |
|---|---|---|---|---|---|---|---|
| I | a lot | | 0 | | 0 | | 0 |
| C | $-2x$ | | $+2x$ | | $+2x$ | | $+x$ |
| E | a lot $-2x$ | | $2x$ | | $\boxed{2x}$ | | $\boxed{x}$ |

# 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 ; increasing T shifts toward products

pH ↑ "acidity" ↓ $[H^+]$ ↓

# Quantifying Acids and Bases

- The standard units of measurement for acids and bases are pH and pOH

$$\mathrm{pH} = -\log[H^+] \quad \mathrm{pOH} = -\log[OH^-]$$

- **In a strong acid or strong base solution, we can use this relationship:**

$$\mathrm{pH} = -\log[C_A] \qquad \mathrm{pOH} = -\log[C_B]^{*}$$

- pH and pOH can be interconverted using the relationship based on $pK_w$ (14):

$$\boxed{\mathrm{pH} = 14 - pOH} \quad \boxed{\mathrm{pOH} = 14 - pH}$$

# Quantifying Weak Acids and Bases

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

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

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

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

$$\begin{tikzcd} & \underline{\frac{K_w}{K_a} = K_b} \\ \underline{K_w = K_aK_b} \arrow[ur] \arrow[dr] & \\ & \underline{\frac{K_w}{K_b} = K_a} \end{tikzcd}$$

Important
NOT on
formula
sheet

# Quick Concept Check

weak base, expect very low % ionization

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

product

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

acid —— base

$$CH_3NH_2 + H_2O \rightleftharpoons CH_3NH_3^+ + OH^-$$

weak base barely does anything ~1.5M

conj. acid very small

# Neutralization Reactions

strong base

You mix 10 mL of 3M LiOH with 10 mL of 3M $HNO_2$ . The final solution will be

weak acid

Acid, Neutral, or Basic?

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

EXTRA: What is the pH of the final solution? $K_a$ for $HNO_2$ is $5.6 \times 10^{-4}$

100% neutralization

↳ $LiNO_2$

$14 - pOH = pH$

8.71

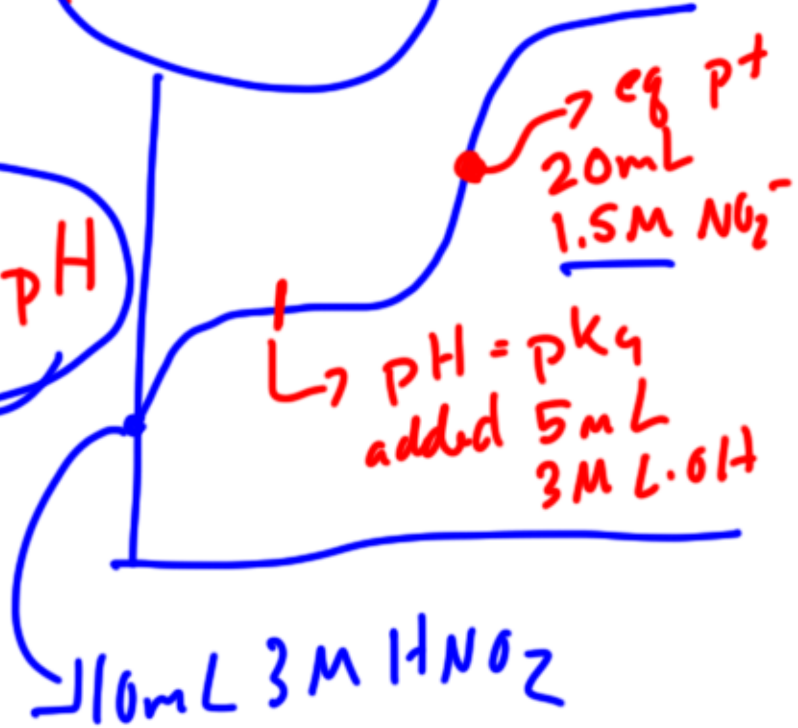
pOH

$[OH^-] = \sqrt{K_b \cdot C_b}$

1.5

-log

$[OH^-] = \sqrt{\left(\frac{10^{-14}}{5.6\times10^{-4}}\right)(1.5)}$



$C_5H_5N$ p$K_a$ = 5.26
$C_6H_5NH_2$ p$K_a$ = 4.63

# Buffer Big Picture

Mixing the contents of which two solutions will result in an ideal buffer at pH = 5.26?

**1.** 40 mL 0.2 M HCl and 160 mL 0.1 M $C_6H_5NH_2$

**2.** 180 mL 0.3 M HCl and 60 mL 0.1 M $C_5H_5N$

**3.** 60 mL 0.3 M HCl and 180 mL 0.1 M $C_5H_5N$

**4.** 30 mL 0.3 M HCl and 180 mL 0.1 M $C_5H_5N$

**5.** 50 mL 0.3 M HCl and 150 mL 0.1 M $C_6H_5NH_2$

Ideal Buffer

1:1 HA : $A^-$
2:1 HA : NaOH

- **By definition, a buffer is made of:**
  - A weak acid and its salt (conjugate base)
  - A weak base and its salt (conjugate acid)
- **By definition, a buffer is made from:**
  - A weak acid + strong base
  - A weak base + strong acid

$\underbrace{\text{moles HCl}}_{\text{eq pt}}$ = moles $C_5H_5N$

moles $C_5H_5NH^+$ = moles $C_5H_5N$

# 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 ($CH_3NH_3Cl$) 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?

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

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

$$-\log K_a = pK_a$$

$$pH = pK_a + \log \frac{A}{HA}$$

10.64

$$CH_3NH_2 = 0.4 - 0.1 = \boxed{0.3}$$

$$CH_3NH_3^+ = 0.4 + 0.1 = \boxed{0.5}$$

10.42

Acid + Base ⇌ Salt + Water

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| R | $HBr$ | + | $B$ | ⇌ | $B^+Br^-$ | + | $H_2O$ |
| I | 0.1 | | 0.4 | | 0.4 | | |
| C | -0.1 | | -0.1 | | +0.1 | | |
| E | 0 | | 0.3 | | 0.5 | | |
| | | | ↓ | | ↓ | | |
| | | | A | | HA | | |

$$pH = pKa + \log\left(\frac{0.3}{0.5}\right)$$

# Solubility Equilibria, $K_{sp}$

$K_{SP}$ IS A UNIQUE FORM OF EQUILIBRIUM THAT QUANTIFIES THE DISSOLUTION OF A SOLID SALT INTO ITS AQUEOUS PRODUCTS.

WE MOSTLY FOCUS ON SPARINGLY SOLUBLE SALTS

# $K_{sp}$ Question Types

**There are three main scenarios of solubility equilibria:**

1. **You add a chunk of a sparingly soluble salt to deionized water and calculate the molar solubility from the $K_{sp}$ and stoichiometry (or vice versa).**
   - $K_{sp} = [Pb^{2+}][I^-]^2 = (x)(2x)^2 = 4x^3$
   - x is your molar solubility; x and 2x are your ion concentrations here (NOT x and $(2x)^2$)
2. **You add a chunk of a sparingly soluble salt to a a solution with a common ion already in solution**
   - $K_{sp} = [Pb^{2+}][I^-]^2 = (x)(0.05M - 2x)^2 = 4x^3$
   - x is still your molar solubility, but much lower than in the previous example
   - Hint: the math is always easier when you ignore the variable subtracted from the given concentration (the 2x in this example)
3. **You mix two aqueous solutions to perform a double displacement precipitation reaction**
   - $Q_{sp} = [Pb^{2+}][I^-]^2$
   - If Q > K, a precipitate forms
   - You can use stoichiometry to determine how much precipitate forms (For small Ksp values, you can assume 100% precipitation to solve for the mass of ppt)

# $K_{sp}$ to Molar Solubility

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

| | | | |
|---|---|---|---|
| R | $Li_3PO_4 \rightarrow$ | $3Li^+ +$ | $PO_4^{3-}$ |
| I | a lot | 0 | 0 |
| C | $-x$ | $+3x$ | $+x$ |
| E | | $3x$ | $x$ |

$$\underbrace{3x \quad x}$$

$$(3x)^3 x = K$$

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

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

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

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

$K_{sp}$ 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

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.

# $K_{sp}$ 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 x $10^{-9}$.

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

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

$K_{sp}$ 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.

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

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

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

✓

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

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

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

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

$$Q_{sp} > K_{sp}$$ , ppt forms

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

# $K_{sp}$ 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 $8.9 \times 10^{-19}$.

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

no exponent

$$Ag_3PO_4 \rightarrow 3Ag^+ + PO_4^{3-}$$

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

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

$K_{sp}$ 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

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

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

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

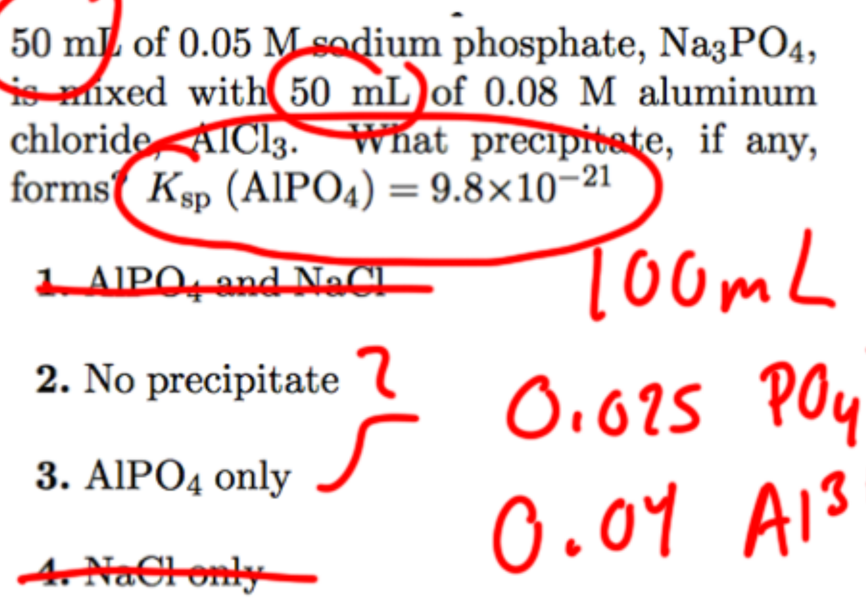
x represents the "Molar Solubility," which is a direct measurement of solubility. Molar solubility is the concentration of a solute that dissolves in molarity (M) for a reaction.

# 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**

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 $Q_{sp} = K_{sp}$

$$\cancel{Na_3}PO_4 + Al\cancel{Cl_3} \rightarrow 3\cancel{NaCl} + AlPO_4$$



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? $K_{sp}\,(AlPO_4) = 9.8\times10^{-21}$

1. ~~$AlPO_4$ and NaCl~~
2. No precipitate ?
3. $AlPO_4$ only
4. ~~NaCl only~~

100mL

$0.025\ PO_4^{3-}$

$0.04\ Al^{3+}$

$$9.8\times10^{-21} = K_{sp} = [Al^{3+}][PO_4^{3-}]$$

$$Q = (0.025)(0.04)$$

$Q_{sp} >>> k_{sp}$

Follow-up: What's the mass of this ppt?

# $K_{sp}$ Solubility Comparison

Which of the following salts is more soluble?

↳ must solve for $x$, can't rely on $K_{sp}$ alone

$Li_3PO_4$ ($K_{sp} = 3.2 \times 10^{-9}$) or $Fe(OH)_2$ ($K_{sp} = 8 \times 10^{-16}$)

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

$$\sqrt[4]{\frac{3.2\times10^{-9}}{27}} = x$$

$$3.3\times10^{-3} = x$$

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

$$\sqrt[3]{\frac{8\times10^{-16}}{4}} = x$$

$$5.8\times10^{-6} = x$$

Common Ion ⟹ solubility goes down when common ion is present

# $K_{sp}$ Solubility Comparison II

In which of the following solutions is your $\underbrace{Li_3}\underbrace{PO_4}$ **least** soluble?

**$Li_3PO_4$ ($K_{sp} = 3.2 \times 10^{-9}$)**

[✓ I)] 0.5 M NaCl

II) 0.25 M LiCl 0.25 M Li

III) 0.25 M $Na_3PO_4$ 0.25 M $PO_4^{3-}$

[✓ IV)] 0.25 M $\underbrace{Li_2}CO_3$ $0.25 M \times 2 = 0.5 M\ Li^+$

In which of these is your $Li_3PO_4$ **most** soluble?

# Unit Four: Kinetics

# Introduction to Kinetics

**There are four types of kinetics calculations that we have discussed in this class:**

1. **Relative rates of a reaction (think stoichiometry)**: If you can measure the rate of formation for a product, you can use stoichiometry to determine the rates for all other products and reactants
2. **Rate Laws**: The rate law is a fundamental equation used to calculate the rate of a reaction from the rate constant, *k*, and the concentrations of the reactants raised to the power of their "order". The overall reaction order is the sum of the orders of the reactants.
3. **Empirical Rate Law:** Because the order of reactants are not necessarily based on stoichiometry, you must run an experiment to measure this value based on the initial rate of reaction at different starting concentrations

These work well for initial rates

4. **Integrated Rate Law:** Knowing the order of a reaction, you can determine the rate or concentrations of a reactant at any given point in time (calculus is necessary here because if the rate is dependent on concentration, the rate is changes as the reaction proceeds)

Takes into account the fact that the rate can change over time

# 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)
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. How much your rate changes as a factor of concentration is based on the order of that reactant.

Increase the rate without changing the rate constant

3. **Temperature**
   - Higher temperature, higher rate **always** (in this class)
   - Increases the rate based on the fact that the **rate constant** in temperature dependent
4. **Catalysts**
   - Catalysts decrease the **activation energy**, which increases the rate based on the Arrhenius Equation
   - The activation energy is decreased by modifying the substrate orientation
   - Increases the rate based on the fact that the rate constant is proportional to the **negative activation energy**

Increase the rate by increasing the rate constant

$NO + \frac{1}{2}O_2 \rightarrow NO_2$

# Big Picture Exam Questions

A mechanism for the endothermic gas phase oxidation of NO to $NO_2$ is proposed to be:

Step 1: $2NO \rightleftharpoons N_2O_2$ (Fast)
Step 2: $O_2 + N_2O_2 \rightarrow 2NO_2$ (Slow)

Which of the following reaction profiles best fit this data?

What is the rate law of the overall reaction?

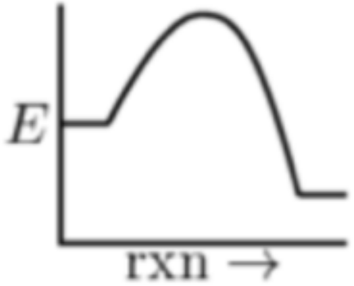
intermediate

$k_2[O_2][N_2O_2]$

$\left(\frac{k_1[NO]^2}{k_{-1}}\right) = \frac{k_{-1}}{k_{-1}}[N_2O_2]$

$\boxed{\frac{k_2k_1}{k_{-1}}[O_2][NO]^2}$

1.



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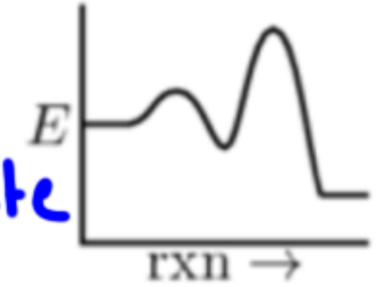

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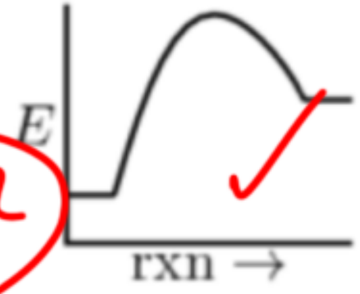

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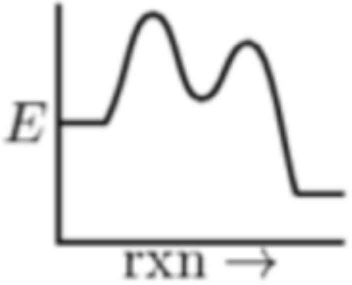
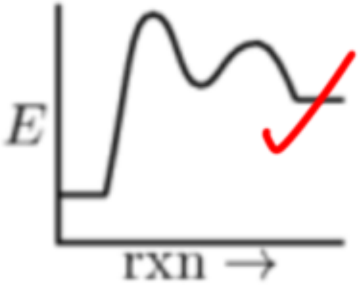


5.



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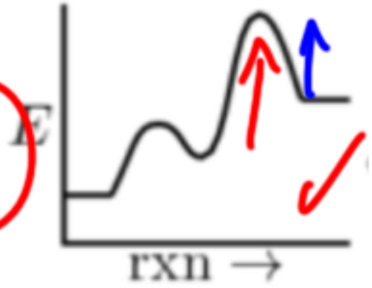

$$K = \frac{[N_2O_2]}{[NO]^2}$$

# Big Picture Exam Questions

A mechanism for the endothermic gas phase oxidation of NO to $NO_2$ is proposed to be:

Step 1: $2NO \rightleftharpoons N_2O_2$ (Fast)

Step 2: $O_2 + N_2O_2 \rightarrow 2NO_2$ (Slow)

Which of the following reaction profiles best fit this data?

What is the relationship between the rate constant and the equilibrium constant?

$$k_1[NO]^2 = k_{-1}[N_2O_2]$$

$$\frac{k_1}{k_{-1}} = \frac{[N_2O_2]}{[NO]^2} = \boxed{K = \frac{k_f}{k_r}}$$

big K

McCord

# Unit Five: Electrochemistry

# Unit 5 Outline: Electrochemistry

I. Understand fundamental redox reactions
  - Balancing redox reactions
  - Assigning oxidation numbers
  - Identifying the roles of the different species in the reaction

II. Combine half-reactions into standard cells (voltaic and electrolytic)
  - Important: Electrolytic applications (electrolysis and electroplating)

III. Apply the concepts of electrochemical cells to non-standard conditions
  - Concentration Cells
  - Nernst Potential

IV. Complete the storylines of thermodynamics and equilibrium by converting electrical potential into K and $\Delta G$.

V. Common applications of batteries
  - Primary and secondary cells
  - Fuel Cells
  - Lead-Acid (car) Batteries

# Unit 5 Equations

1. Electrochemical Cell Potential $$\mathcal{E}^{\circ}_{cell} = \mathcal{E}^{\circ}_{cathode} - \mathcal{E}^{\circ}_{anode}$$
2. Faraday's Law, plating a metal, electrolysis $$\frac{I \cdot t}{n \cdot F} = \text{moles created}$$
3. Convert between electrical potential (ε) and free energy/ maximum electrical work (ΔG) $$\Delta G = -nF\mathcal{E} \qquad \Delta G^{\circ} = -nF\mathcal{E}^{\circ}$$
4. Convert between electrical potential (ε) and the equilibrium constant (K) $$\mathcal{E}^{\circ} = \frac{RT}{nF}\ln K \qquad \mathcal{E}^{\circ} = \frac{0.05916}{n}\log K$$
5. Non-standard Cell Potential $$\mathcal{E} = \mathcal{E}^{\circ} - \frac{RT}{nF}\ln Q$$ AND: $$\mathcal{E} = \mathcal{E}^{\circ} - \frac{0.05916}{n}\log Q$$

# Electrochemistry Definitions

1. **Redox Reaction**: a chemical reaction that involves the transfer of electrons from one species to another, resulting in a change in oxidation state. A redox reaction involves one species undergoing reduction and another undergoing oxidation.
2. **Reduction**: a species gains electrons in a half-reaction, resulting in a lower oxidation state
3. **Oxidation**: a species loses electrons in a half-reaction, resulting in a higher oxidation state
4. **Oxidizing Agent:** the species that drives the oxidation of another species in a redox reaction **; the oxidizing agent is always the species undergoing reduction as a reactant**
5. **Reducing Agent:** the species that drives the reduction of another species in a redox reaction **; the reducing agent is always the species undergoing oxidation as a reactant**

$$3Cu^{2+} + 2Al \rightarrow 3Cu + 2Al^{3+}$$

$$Cu^{2+} + 2e^{-} \rightarrow Cu$$

$$Al \rightarrow Al^{3+} + 3e^{-}$$

LEO says GER
OIL RIG

# Electrochemical Cell Definitions

1. **Anode**: the site of oxidation (An Ox) ; gives electrons to the wire
2. **Cathode**: the site of reduction (Red Cat) ; takes in electrons from the wire
3. Voltage: the difference in potential per unit charge (J/C or V); a measurement of the "pulling power" on the electrons
4. **Voltaic Cell (Galvanic Cell)**: an electrochemical cell with a positive standard cell potential ; the redox reaction of the cell occurs without an external power source (spontaneous) ; $\varepsilon^\circ_{cathode} > \varepsilon^\circ_{anode}$ (reduction potentials)
5. **Electrolytic Cell:** an electrochemical cell with a negative standard cell potential ; the redox reaction of the cell relies on an external power source (non-spontaneous) $\varepsilon^\circ_{cathode} < \varepsilon^\circ_{anode}$ (reduction potentials)

# Electrochemical Cells

| | Voltaic Cells | Electrolytic Cells |
|---|---|---|
| Cathode (rxn and charge) | Reduction, + | Reduction, - |
| Anode (rxn and charge) | Oxidation, - | Oxidation, + |
| Direction of $e^-$ flow | Anode to cathode | Anode to cathode |
| Direction of current flow | Cathode to anode | Cathode to anode |
| $\varepsilon°$ | + | - |
| $\Delta G$ | - | + |
| K | >1 | <1 |
| Work | - (by system) | + (on system) |
| Flow of anions | Anode | Anode |
| Flow of cations | Cathode | Cathode |

# Equilibrium Constant Problem

$\mathcal{E}° = \frac{0.05916}{\boxed{n}} \log K$

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

$3Cu + 2Bi^{3+} \rightleftharpoons 3Cu^{2+} + 2Bi$

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

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

1. $4.3 \times 10^{-3}$
2. $8.0 \times 10^{-8}$
3. $\boxed{6.3} \times 10^{-15}$
4. $1.8 \times 10^{-5}$
5. ~~$1.3 \times 10^{7}$~~
6. ~~$1.6 \times 10^{14}$~~

$(Bi^{3+} + 3e^- \rightarrow Bi) \times 2$

$(Cu \rightarrow Cu^{2+} + 2e^-) \times 3$

$n = \boxed{6e^-}$

$\mathcal{E}°_{cath} - \mathcal{E}°_{anode}$

$0.20 - 0.34$

$\boxed{= -0.14}$

$\Delta G > 0$

$K < 1$

$-0.14\,V = \frac{0.05916}{6} \log K$

$K = 10^{\frac{\mathcal{E}° \cdot n}{0.05916}}$

$k = 10$

# Equilibrium Constant Problem

What is the volume of $H_2$ produced through the electrolysis of water at 300 K and 2.1 atm after a total charge of $5.28 \times 10^4$ C is applied?

1. 2.41 L
[✓ 2.] 3.21 L
3. 4.01 L
4. 1.60 L
5. 2.92 L

$$\frac{52800}{2\cdot 96485} \qquad \frac{cl\cdot t}{n\cdot F} = \text{moles } H_2$$

$cl\cdot t$ → charge applied

$n\cdot F$ → charge required per mol

$$2H^+ + 2e^- \rightarrow H_2$$

$= n$

$$PV = nRT \qquad V = \frac{nRT}{P}$$

$R$ → $0.08206 \frac{L\,atm}{mol\,K}$

$T$ → 300K

$P$ → 2.1 atm

# Exam 5 Nernst Problem

Consider the following voltaic cell:

$$\mathrm{Pt}\,\left|\,\underline{\underset{(0.050\ \mathrm{M})}{Sn^{2+}},\ \underset{(0.50\ \mathrm{M})}{Sn^{4+}}}\,\right|\left|\,\underset{(0.010\ \mathrm{M})}{Ag^{+}}\,\right|\,\mathrm{Ag}$$

E° = 0.65 V

The experimental cell potential for the cell is closest to

1. 0.561 V
2. 0.798 V
3. 0.650 V
4. 0.502 V
5. 0.354 V
6. 0.946 V
7. 0.739 V

$$Sn^{2+} \rightarrow Sn^{4+} + 2e^-$$

$$(Ag^+ + e^- \rightarrow Ag) \times 2$$

$$Sn^{2+} + 2Ag^+ \rightarrow Sn^{4+} + \cancel{2Ag}$$

$$n = 2, \quad Q = \frac{[Sn^{4+}]}{[Sn^{2+}][Ag^+]^2}$$

$$\mathcal{E} = 0.65 - \frac{0.05916}{2}\log Q$$

$$= 0.502\,\mathrm{V}$$

$$\frac{0.50}{(0.050)(0.010)^2}$$