Lab [20 pts]   Name _____

Le Châtelier's Principle   Lab Partner(s) _____

                                                Period _____Date_____
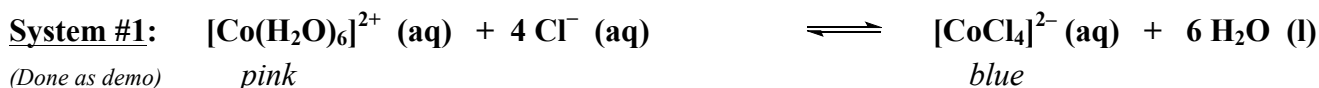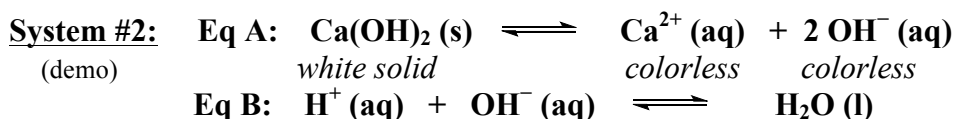
Purpose: To do four equilibrium reactions and observe how the equilibrium position shifts due to added
        "stress" on the system. You will see Le Châtelier's Principle in action.

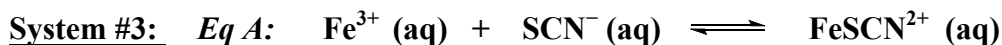***Write-up:*** Fill in all charts and answer the post lab questions.
  KEY PHRASES for Explanations: *"Shifted... to consume added..."   or   " shifted ... to replenish depleted..."*
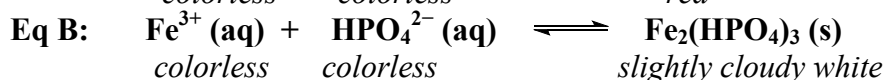
System #1: $[Co(H_2O)_6]^{2+}$ (aq) + 4 Cl⁻ (aq)   ⇌ $[CoCl_4]^{2-}$ (aq) + 6 H₂O (l)

(Done as demo)   *pink*   *blue*

	Color? ppt forms? ppt gone?	Equilibrium position shifted to the...	Explanation for shift in equilibrium position
a) Put a dropper-full of 0.1 M $[Co(H_2O)_6]Cl_2$ into a small tt			
b) Add drops of 12 M HCl until a color change occurs.			
c) Add drops of water until a color change occurs.			
d) Observe the specified test tube at **room temp**.			
e) Observe the test tube after **heating**.			
f) Observe the test tube after **cooling**.			

System #2:   Eq A: $Ca(OH)_2$ (s) ⇌ Ca^{2+} (aq) + 2 OH⁻ (aq)

  (demo)   *white solid*   *colorless*   *colorless*

           Eq B: H⁺ (aq) + OH⁻ (aq)   ⇌   H₂O (l)

	Color? ppt forms? ppt gone?	Equilibrium position shifted to the..	Explanation for shift (s) in equilibrium position
a) Put a dropper-full of saturated solution of $Ca(OH)_2$ in a small tt.			
b) Add drops of 1 M NaOH(aq) until a change is observed.	Eq.A	Eq A:	Eq A:
c) Add drops of 3 M HNO₃ (aq) until a change is observed. *(Stopper test tube and shake.)*	*Eq B: can't see change* ---------- *Eq. A:*	Eq B: ---------------- Eq A:	Eq B: *This shift in Eq. B causes _____ to be depleted.* Eq A:

System #3:   *Eq A:* Fe^{3+} (aq) + SCN^- (aq) ⇌ $FeSCN^{2+}$ (aq)
                     colorless   colorless   red
         Eq B: Fe^{3+} (aq) + HPO_4^{2-} (aq) ⇌ $Fe_2(HPO_4)_3$ (s)
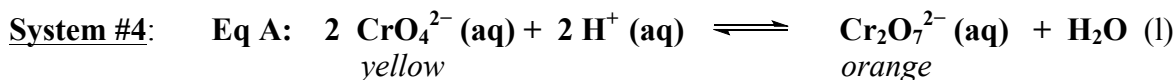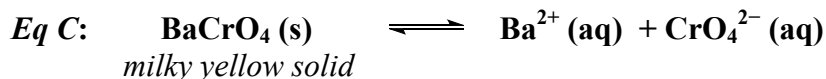   *colorless   colorless   slightly cloudy white*

1) Put about 10 mL of 0.0020 M KSCN and 10 mL of distilled water into a 100 mL beaker.
2) Add 3-4 drops of 0.2 M $Fe(NO_3)_3$ solution into the beaker. (source of Fe^{+3})
3) Pour equal amounts of the solution from the beaker into four small test tubes. (about ½ full each). These will be the test tubes #1-#4. Follow directions in chart to know what to do to each test tube.

	Color? ppt forms? ppt gone?	Eq position shifted to the...	Explanation for shift(s) in equilibrium position
tt #1 Do nothing . This is *Reference solution*			
tt #2 Add a pea-sized amount of solid KSCN to this tt.	Eq A	Eq A:	Eq A:
tt #3 Add 5 drops of 0.2 M $Fe(NO_3)_3$. Insert stopper. Shake.	Eq A	Eq A:	Eq A:
tt #4 Add a pea-sized amount of Na_2HPO_4 (s). Shake if needed	Eq. B ------------- Eq. A	Eq B: ----------------- Eq A:	Eq B: *This shift in Eq. B causes_____ to be depleted.* Eq A:

System #4:   **Eq A: 2 CrO_4^{2-} (aq) + 2 H^+ (aq) ⇌ $Cr_2O_7^{2-}$ (aq) + H_2O (l)**
                     yellow   orange
         Eq B: H^+ (aq) + OH^- (aq) ⇌ H_2O (l)

         Eq C: $BaCrO_4$ (s) ⇌ Ba^{2+} (aq) + CrO_4^{2-} (aq)
                     milky yellow solid

	Color? ppt forms? ppt gone?	Eq. position shifted to the ..	Explanation for shift(s) in equilibrium position.
a) Put on dropper-full of 0.1 M K_2CrO_4 into a small tt.			
b) Add drops of 3 M HNO_3 until a color change is seen.	*Eq A*	Eq A:	*Eq A:*
c) Add a dropper-full of 1 M NaOH (aq). A color change should be observed.	*Eq B: can't see change* -------------- Eq A:	Eq B: ---------------- Eq A:	Eq B: *Shift in Eq. B causes _____ to be depleted.* Eq A:
d) Add drops of 0.1 M $BaCl_2$ (aq) until a change is observed.	*Eq C*	Eq C:	Eq C:
e) Add drops of 3M HNO_3 Stopper test tube and shake. A change should be observed.	Eq A: orange-eventually --------------- Eq. C:	Eq A: ---------------- Eq C:	Eq A: *Shift in Eq. A, causes _____ to be depleted.* Eq C:

Post Lab Questions: [15 pts total]   *Write all answers on a separate sheet of paper.*

1) **[3 pts] Analysis of system #4: CrO_4-Cr_2O_7**

Eq A: $2\ CrO_4^{2-}$ (aq) + $2\ H^+$ (aq) $\rightleftharpoons$ $Cr_2O_7^{2-}$ (aq) + H_2O (l)
       yellow   *orange*
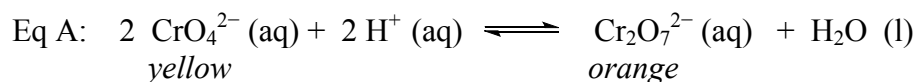
Explain how and why this system shifted when HNO_3 (aq) was added by answering the following questions:
  a) Write the K_{eq} expression for Equation A. (no numbers)

  b) At the instant the HNO_3 is added, the system is temporarily not at equilibrium. *(It has not shifted yet to compensate for the disturbance.)* At this instance, one could calculate the "Q" value. Would this "Q" value be higher or lower than the K_{eq} for this reaction? Explain reasoning.

  c) Then, the reaction shifts to return the system to equilibrium by changing the "Q" value back into the K_{eq}. In which direction does the reaction shift and how does this shift change the Q value back into the K_{eq}? *(Include whether the Q has to increase or decrease to get back to K_{eq})*
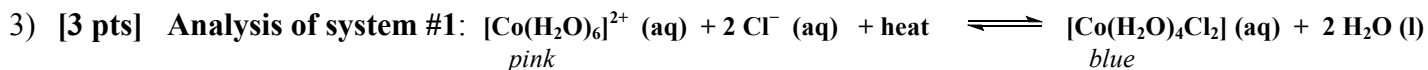
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2) **[4 pts] Analysis of system #4: CrO_4-Cr_2O_7**

Eq C: $BaCrO_4$ (s) $\rightleftharpoons$ Ba^{2+} (aq) + CrO_4^{2-} (aq)
        milky yellow solid
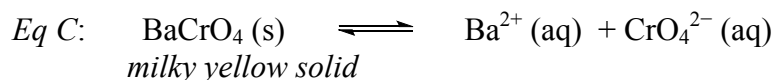
In step d) for System #4, $BaCl_2$ (aq) was added. This shifted Eq. C and caused a milky yellow solid to form. **Discuss this phenomenon** by answering the following questions.

  a) Write the K_{sp} expression for $BaCrO_4$ (Equation C).

  b) At that instant that $BaCl_2$ was added, the system was not at equilibrium. Thus, a "Q" value could be calculated. Would this "Q" value be higher or lower than the K_{sp}? Explain reasoning.

  c) To get back to equilibrium, the reaction shifts to return the "Q" back to the K_{sp}. When the reaction shifts to return to equilibrium, solid is formed. Why does forming solid return the "Q" back to the K_{sp}? *(Include whether the Q has to increase or decrease to get back to the K_{sp})*

  d) Assume that the concentration of CrO_4^{2-} was 0.1 M when the solid precipitated. Determine the lowest concentration of Ba^{+2} needed to get the solid to precipitate. K_{sp} of $BaCrO_4 = 2.0 \times 10^{-10}$ *(NOTE: Since this is a complex system, the $[Ba^{2+}]$ does not have to equal $[CrO_2^{2-}]$)*

  e) K_{sp} values are a measure of how soluble solids are in water. Look at the K_{sp} values for $BaCrO_4$ and $CaCO_3$ given below. Which substance is more soluble in water? Explain your reasoning.
        K_{sp} for $BaCrO_4 =$ 2.0×10^{-10} K_{sp} for $CaCO_3 = 8.7 \times 10^{-9}$

3) **[3 pts]   Analysis of system #1**: $[Co(H_2O)_6]^{2+}$ (aq) + 2 Cl^- (aq) + heat $\rightleftharpoons$ $[Co(H_2O)_4Cl_2]$ (aq) + 2 H_2O (l)
                        pink   *blue*

     As we discussed in the first question above, when concentrations are increased or decreased, the equilibrium system is disturbed and is temporarily at a "Q" value. To come back to equilibrium, the reaction must shift so that the "Q" value returns to the K_{eq}.
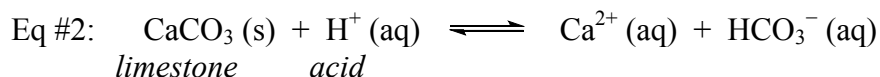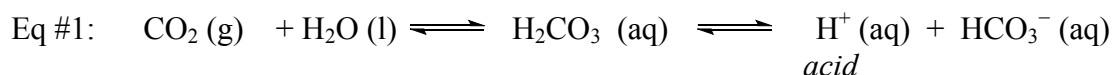
     When one changes the temperature, we noticed that the equilibrium is disturbed and the reaction compensates by shifting towards reactants or products. In class, we explained this shift by considering "heat" as a reactant or as a product. Thus, when heat is added/removed, this would disturb the equilibrium.

     However, "heat" is not really a reactant or product. Thus, "heat" is not written in the Keq expression. So, how is it possible to get to a "Q" value when one is not changing a reactant or product concentration?

Let's figure it out by understanding the "real" reason for why system #1 shifts to the right when the temperature is increased. To do so, answer the following questions about system #1:

a) Is the forward reaction favorable in terms of enthalpy? Justify your answer.
b) Is the forward reaction favorable in terms of entropy? Justify your answer.
     HINT: $[Co(H_2O)_4Cl_2]$ (aq) is more disordered than $[Co(H_2O)_6]^{2+}$ (aq)
c) Since one driving force is favorable and the other is not, the spontaneity of the forward reaction depends on the temperature. When temperature is increased, does the value of ΔG^o (for forward reaction) increase or decrease? Explain by discussing $\Delta G^o = \Delta H^o - T\Delta S^o$
d) Thus, changing the temperature changes the ΔG^o. This means that the spontaneity of the forward reaction changes. (The energy diagram changes.) Thus, the K_{eq} value actually changes when temperature changes. When the temperature increases in system #1, restate what happens to the ΔG^o and then determine whether the K_{eq} value increases or decreases. Justify.
e) At the instant that the temperature increases, system #1 is temporarily not at equilibrium because there is now a new K_{eq}. The system is now at a "Q" value. Is this "Q" value higher or lower than the new K_{eq}? Why does the reaction have to shift to the right to get back to equilibrium?

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4) [1 pt] Stalactites and Stalagmites are the results of this complex equilibrium system in action:

Eq #1: CO_2 (g) + H_2O (l) $\rightleftharpoons$ H_2CO_3 (aq) $\rightleftharpoons$ H^+ (aq) + HCO_3^- (aq)
                                                          acid

Eq #2: $CaCO_3$ (s) + H^+ (aq) $\rightleftharpoons$ Ca^{2+} (aq) + HCO_3^- (aq)
     limestone   *acid*

a) If the concentration of CO_2 (g) increases, the Eq. #1 will shift to the ......
b) This causes the H^+ (aq) concentration to ......
c) Thus, Eq #2. will shift to the .....
d) What effect does this have on the solubility of $CaCO_3$ solid? (Does the solid dissolve more or less?)

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5) **[4 pts]   Read the Chem Matters Article**, "Underground Sculpture." As you read the article, also look at Eq #1 and Eq #2 (above in question #4). These equations are the same reactions that are discussed in the article.

a) How do caves get formed? *Hints: State what conditions are needed to form caves. Then, explain how eq. #1 and eq. #2 (the ones written in question #4 above) shift when those conditions exist.*

b) Why do Stalactites and Stalagmites form in caves? *Hints: State what conditions are needed to form stalactites and stalagmites. Then, explain how eq. #1 and eq.#2 (the ones written in question #4 above) shift when those conditions exist.*