Lab 2: Properties of Systems in Chemical Equilibrium

The two key purposes of this lab are:

1) To observe how systems in equilibrium respond to stress by: increasing or decreasing the concentration of one component; increasing the volume of a solution; or changing the temperature of the system; and
2) To experimentally determine K_{sp} for $PbCl_2$, and whether the equilibrium reaction: $PbCl_2(s) \leftrightarrows Pb^{2+}(aq) + 2Cl^-(aq)$ is endothermic or exothermic.

Observations of the effect of temperature on systems in equilibrium will allow you to determine whether the reaction is endothermic or exothermic.

Parts A-C of this lab require only qualitative observations (change of color and/or visible amount of precipitate) which allow you to determine the direction of a shift in equilibrium, while part D requires you to measure exact amounts of each component to calculate K_{sp} for $PbCl_2$.

Five separate equilibrium systems will be studied: two with color changes that clearly indicate a shift in equilibrium and three systems involving solubility of an ionic compound where appearance (or disappearance) of a precipitate indicates a shift in equilibrium. The reactions are as follows, where the color of soluble components is listed beneath the species:

$$\underset{\text{(yellow)}}{\mathbf{HMV}(aq)} \leftrightarrows \mathbf{H^+}(aq) + \underset{\text{(violet)}}{\mathbf{MV^-}(aq)} \quad \textbf{(HMV = protonated methyl violet)}$$

$$\underset{\text{(pink)}}{\mathbf{[Co(H_2O)_6]^{2+}}(aq)} + \mathbf{4Cl^-}(aq) \leftrightarrows \underset{\text{(blue)}}{\mathbf{[CoCl_4]^{2-}}(aq)} + \mathbf{6H_2O}$$

$$\mathbf{Zn(OH)_2}(s) \rightleftarrows \mathbf{Zn^{2+}}(aq) + \mathbf{2OH^-}(aq)$$

$$\mathbf{Mg(OH)_2}(s) \rightleftarrows \mathbf{Mg^{2+}}(aq) + \mathbf{2OH^-}(aq)$$

$$\mathbf{PbCl_2}(s) \rightleftarrows \mathbf{Pb^{2+}}(aq) + \mathbf{2Cl^-}(aq)$$

<u>Part A</u>: Methyl violet: Effect of adding and/or removing a reagent

Methyl violet, HMV, is an acid-base indicator which changes color when it dissociates into H^+ ions and MV^- ions. It is not a strong acid, thus does not dissociate 100% in solution. The amount of dissociation is dependent on Kc for the reaction:

$$\underset{\text{(yellow)}}{\mathbf{HMV}(aq)} \leftrightarrows \mathbf{H^+}(aq) + \underset{\text{(violet)}}{\mathbf{MV^-}(aq)} \qquad \mathbf{K_c} = \frac{[\mathbf{H^+}][\mathbf{MV^-}]}{[\mathbf{HMV}]}$$

A difference in color allows you to visually observe the equilibrium undergoing a shift from higher concentration of HMV to higher concentrations of MV^- and the reverse.

You will alter the concentration of H^+ ion through addition of strong acid (HCl); and through addition of strong base (NaOH). Addition of strong base will effectively remove H^+ from solution because OH^- ions react with H^+ ions to form H_2O, leaving fewer H^+ ions in solution, while addition of strong acid of course adds H^+ ions to the system.

Procedure for Part A:

You will need: 3 test tubes, two disposable pipets with bulbs and a test tube rack, or large beaker to hold the test tubes upright.

Add a small amount (~3 mL) of 6M HCl into one of the test tubes and a similar amount of 6M NaOH into another test tube. Label each tube according to its contents (otherwise it's hard to tell the difference between them, unless you have litmus paper handy!). Place a disposable pipette (with bulb) into each test tube, and use the contents of these tubes to add HCl and NaOH to your reaction tube as described below:

Add about 5 mL distilled water to the third test tube, and then add a few drops of methyl violet, and swirl the tube. Observe and record the color. If it is not violet, add a few drops of 6M NaOH until the color is violet.

Add a few drops of 6M HCl to the violet solution, and swirl until you see a color change and record the color change observed.

Add a few drops of NaOH to the solution and swirl until you see a color change and record the color change observed.

In the post lab questions you will be asked to use Le Chatelier's theory to explain your observations, remembering that addition of NaOH results in the removal of H^+ ions.

<u>Part B</u>: Complex ion: Effect of increasing solution volume, and of changing temperature

You will prepare a solution containing $[Co(H_2O)_6]^{2+}$ and $[CoCl_4]^{2-}$ ions from crystals of $[Co(H_2O)_6]Cl_2$ and observe shifting in equilibrium below (by noting changes of color) when:

1) The volume of solution is increased by addition of water, and
2) The solution is heated.

$$\underset{\textbf{(pink)}}{[Co(H_2O)_6]^{2+}(aq)} + 4Cl^-(aq) \leftrightarrows \underset{\textbf{(blue)}}{[CoCl_4]^{2-}(aq)} + 6H_2O$$

Procedure for Part B:

Perform this part of your experiment in a fume hood.
You will need: one test tube, a hand-held test tube holder, a 5 mL graduated cylinder, distilled water and a hot water bath.

Place a small amount (~0.10 g) of $CoCl_2 \cdot 6H_2O$ a test tube. Pour ~ 2mL of 12 M HCl into the graduated cylinder and add it to the test tube with the $CoCl_2 \cdot 6H_2O$. Observe and record the color.

Add ~ 2 mL distilled water and observe, noting whether you see a change in color. Continue adding H_2O, ~ 1 ml at a time until you see a change in color. Record your observations.

Hold the test tube in a warm water bath and record any color change you observe.

Post lab questions will ask you to use Le Chatelier's theory to explain your observations, and to use these results to establish whether the reaction is exothermic or endothermic.

Part C: Solubility: effect of addition and/or removal of ions:

$$\mathbf{Zn(OH)_2}(\boldsymbol{s}) \rightleftarrows \mathbf{Zn^{2+}}(\boldsymbol{aq}) + \mathbf{2OH^-}(\boldsymbol{aq})$$

$$\mathbf{Mg(OH)_2}(\boldsymbol{s}) \rightleftarrows \mathbf{Mg^{2+}}(\boldsymbol{aq}) + \mathbf{2OH^-}(\boldsymbol{aq})$$

Many metal hydroxides exhibit low solubility in pure water. Addition of H^+ ions (by adding strong acid) effectively removes OH^- ions from solution (by forming H_2O).

Adding NaOH to a saturated solution of metal hydroxide increases the concentration of OH^- ions. Addition of NH_3 results in a reaction of NH_3 with water to generate NH_4^+ and OH^- which also increases concentration of OH^- ions:

$$NH_3(aq) + H_2O(l) \rightarrow NH_4^+(aq) + OH^-(aq)$$

However, addition of a large excess of NaOH can result in the formation of a complex ion where OH^- ions act as ligands involved in coordinate covalent bonds with the metal. Also addition of a large excess of NH_3 can result in formation of a complex ion where NH_3 ions act as ligands involved in coordinate covalent bond with the metal.

Both types of complex ions are soluble in water, and thus their formation serves to effectively remove a non-complex metal ion from solution.

Not all metals form soluble complex ions. You will observe one that does and one that does not.

The direction of equilibrium shift in response to addition of H^+ and OH^- (and excess OH^-) can be observed by watching solid appear and/or disappear.

Procedure for Part C:

You will need 6 test tubes, a 5 mL graduated cylinder, 3 small beakers and 3 disposable pipets.

Place a small amount (~5 mL) of 6M NaOH in one of the beakers, a small amount (~5mL) of 6M NH_3 in another and a small amount (~5 mL) of HCl in the third. Label each of the beakers and designate a separate disposable pipet for each of them to transfer the reagents to your reaction tube.

Label three test tubes A, B, and C add about 2 mL of 0.1M $Zn(NO_3)_2$ and one drop of 6 molar NaOH, and stir. Record your observations.

Add 6M HCl to the contents of test tube A and swirl. Continue adding HCl <u>one drop at a time</u> until you see a definite change in amount of precipitate. Record your observations.

Add several drops of 6 M NaOH, one drop at a time, to the contents of tube B. Record your initial observations and then record observations after several drops of NaOH have been added (keep adding until you see a distinct change in the amount of precipitate).

Add several drops of 6 M NH_3, one drop at a time, to the contents of tube C. Record your initial observations and then record observations after several drops of NH_3 have been added (keep adding until you see a distinct change in the amount of precipitate).

Label the remaining three test tubes D,E and F and add about 2 mL 0.10 M $Mg(NO_3)_2$ and 1 drop of 6 M NaOH to each of them. Repeat the steps above, and record the effects of adding HCl and NaOH (both immediately and in excess) and NH_3 (both immediately and in excess).

Post lab questions will ask you to use Le Chatelier's theory to explain your observations,

<u>Part D</u>: Solubility: effect of temperature, and experimental determination of K_{sp}:

You will study the process:

$$\mathbf{PbCl_2(\mathit{s}) \leftrightarrows Pb^{2+}(\mathit{aq}) + 2Cl^-(\mathit{aq})}$$

To determine Ksp of $PbCl_2$ at room temperature and establish whether this process is exo- or endo- thermic in the direction it is written above.

Procedure for Part D:

You will need a hot water bath, a LARGE test tube, a 5 mL graduated cylinder, a 5 mL graduated pipet, a two small beakers, and a test tube rack or a large beaker to stand the test tube upright, as well as a test tube clamp to hold the test tube in the hot water bath.

Place <u>precisely</u> 5 mL 0.30 M $Pb(NO_3)_2$ into the test tube. Add <u>precisely</u> 1 mL 0.30 M HCl to the tube and stir. Record your observations.

Continue adding 2 additional mL of 0.30 M HCl, on mL at a time, recording your observations. The measurements of HCl must be precise.

After addition of a total of 3 mL of HCl, hold the test tube in the hot water bath for several minutes and record your observations.

Allow the tube to cool to room temperature. Once the tube has reached room temperature add 1 mL of water at a time (carefully measured) to the test tube and swirl. Stop adding water as soon as the precipitate has completely disappeared. Record the volume of water required to dissolve all precipitate.

Calculate the concentration of both Pb^{+} and Cl^{-} ions in the saturated solution (just after enough water had been added to dissolve all precipitate). Use these concentrations to determine Ksp. Use the observations you made by placing the tube in a hot bath to establish whether this reaction is exothermic or endothermic.

Observations:

Part A:

$$\underset{\text{(yellow)}}{HMV(aq)} \rightleftarrows H^{+}(aq) + \underset{\text{(violet)}}{MV^{-}(aq)}$$

Action	Color Observed
Add HCl	
Add NaOH	

Part B:

$$[Co(H_2O)_6]^{2+}(aq) + 4Cl^{-}(aq) \rightleftarrows [CoCl_4]^{2-}(aq) + 6H_2O(l)$$

Action	Observation
Add HCl	
Add water	
heat	
cool	

Part C:

$Zn(OH)_2(s) \rightleftarrows Zn^{2+}(aq) + 2OH^-(aq)$

Action	Observation
Add HCl	
Add NaOH	
Add EXCESS NaOH	
Add NH_3	
Add EXCESS NH_3	

$Mg(OH)_2(s) \rightleftarrows Mg^{2+}(aq) + 2OH^-(aq)$

Action	Observation
Add HCl	
Add NaOH	
Add EXCESS NaOH	
Add NH_3	
Add EXCESS NH_3	

Part D:

$PbCl_2(s) \rightleftarrows Pb^{2+}(aq) + 2Cl^-(aq)$

Action	Observation
Heat tube with $PbCl_2$ ppt	
Cool previous tube	

Data table for Ksp determination

	Conc. (M)	V (in Liters)	moles	Final M (after addition of H_2O)
Pb^{2+}				
Cl^-				
H_2O				
Total V of saturated solution with no ppt				

Show calculations all calculations, including the final product to determine Ksp of $PbCl_2$.

Lab 2 Post-lab questions:

1. a. Re-write the equation for the equilibrium reaction studied in part A of this experiment.

b. Based on the color change you observed, the concentration of what form of methyl violet (HMV or MV^-) was increased as a result of the addition of H^+?

c. The concentration of what form of methyl violet was increased as a result of the addition of OH^-?

d. Explain these observations using Le Chatelier's principle:

2. a. Re-write the equation for the equilibrium reaction studied in part B of this experiment.

b. What direction did the reaction shift in response to increasing the volume of solvent?

c. Explain this observation using Le Chatelier's principle.

d. What direction did the reaction shift in response to heating the reaction tube?

e. Does this indicate the reaction is endothermic or exothermic?

3. a. Rewrite the equation for the equilibrium reactions studied in part C of this experiment.

b. What direction did the each of these reactions shift as a result of addition of H^+? Why is this observation consistent with Le Chatelier's principle?

c. What direction did each of these reactions shift upon addition of a small amount of OH^- AND upon addition of a small amount of NH_3? Why are these observations consistent with Le Chatelier's principle?

d. Which metal hydroxide became more soluble after the addition of a large excess of OH^- AND after the addition of a large excess of NH_3? Why is this result also consistent with Le Chatelier's principle?

4. a. Rewrite the equation for the dissociation of $PbCl_2$

b. Based on your observations, is this process endothermic or exothermic?

c. Why does $PbCl_2$ not appear as a solid after only one mL of HCl was added to Pb^{2+} solution?

d. Compare your calculated value of Ksp with the accepted literature value.

Lab 2 Pre-lab questions:

1.) The organic solvent phenol, C_6H_5OH dissociates to a small extent in water according to the following equilibrium equation:

$$C_6H_5OH(aq) \rightleftarrows C_6H_5O^-(aq) + H^+(aq)$$

Use Le Chatelier's principle to predict which form of phenol (C_6H_5OH or $C_6H_5O^-$) will increase in concentration as a result of the addition of HCl.

Which form of phenol will increase in concentration as a result of the addition of NaOH? Why?

2.) Use Le Chatelier's principle to predict the direction of equilibrium shift when you increase the volume of the solution in the following "generic" reaction:

$$A^{2+}(aq) + 4B^-(aq) \rightleftarrows AB^{2-}(aq)$$

3.) Oxalic acid forms a stable transition metal complex with Fe^{3+}(aq). Use Le Chatelier's principle to explain why the addition of oxalic acid to a solution which could be described by the equilibrium reaction below results in a distinct change in color of the solution from bright reddish orange to very pale yellow.

$$\underset{\text{(pale yellow)}}{Fe^{3+}(aq)} + \underset{\text{(colorless)}}{SCN^-(aq)} \rightleftarrows \underset{\text{(reddish orange)}}{[FeSCN]^{2+}(aq)}$$

4.) I carefully measured 3.0 mL of 0.045M $Ca(NO_3)_2$ and placed it in a test tube with 5.0 mL of 0.045 M NaF. The formula for the resulting precipitate is: __________________.

I added warm water to the mixture above until the precipitate disappeared. The amount of water required to dissolve all precipitate was 13.0 mL. What is the experimentally determined value for Ksp the precipitate based on these results?

The literature value of Ksp for this particular ionic compound is 1.8×10^{-7}. What factors in my experiment could explain the difference between the literature value and the experimentally determined value for Ksp above (Hint: recall that I added WARM water)?