Experiment 5
Stress on Equilibrium System

I. General Introduction

Any chemical reaction tends to proceed until the rate of the forward reaction becomes equal to the rate of the reverse reaction. The reaction then is said to be at equilibrium. Adding or removing a component, in an equilibrium system, will disturb the dynamic balance between two rates by forcing the forward and reverse reaction rates to become unequal. In order for the chemical system to reestablish equilibrium the concentration of all components must change. One way of predicting these concentration shifts is through the use of Le Chatelier's principle: When a stress is applied to a system at equilibrium, the system will in a direction to reduce the stress and reestablish equilibrium.

In this experiment, you will look at different equilibria, observe how addition or removal of components affects those equilibria and see if the results are consistent with Le Chatelier's principle.

II. Saturated Solution Equilibria

Suppose we have a solution that has been saturated with a solute: This means that the solution has already dissolved as much solute as possible. If we try to dissolve additional solute, no more will dissolve, because the saturated solution is in equilibrium with the solute:

$$\text{Solute} + \text{Solvent} \leftrightarrow \text{Solution}$$

Le Chatelier's principle is most easily seen when an ionic solute is used: Suppose we have a saturated solution of sodium chloride, NaCl. Then

$$NaCl_{(s)} \leftrightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)}$$

will describe the equilibrium that exists. The rate ions leave the solid and go into the solution is just equal to the rate ions from the solution combine and precipitate. If Na^+ or Cl^- is added to a solution saturated in $NaCl_{(s)}$, the rate at which ions combine to form a solid becomes greater than the rate at which ions dissolve and $NaCl_{(s)}$ precipitates until the rates are again equal.

III. Complex Ion Equilibria

Often, dissolved transition metal ions will react with certain molecules or ions to produce brightly colored species called complex ions. For example, if a thiocyanate (SCN^-) salt is added to a solution containing Fe^{3+}, a bright red complex ion is formed.

$$Fe^{3+} + SCN^{-} \leftrightarrow Fe(SCN)^{2+}$$

This is an equilibrium process that is easy to study, because we can monitor the bright red color of [$Fe(NCS)^{2+}$] as an indication of the position of the equilibrium: If the solution is very red, there is a lot of [$Fe(NCS)^{2+}$] present: if the solution is not very red, then there must be very little [$Fe(NCS)^{2+}$) present.

Using this equilibrium, we can try adding more Fe^{3+} or SCN^- to see what effect this has on the red color according to Le Chatelier's principle.

IV. Acid/Base Equilibria

Many acids and bases exist in solution in equilibrium with their ions: This is particularly true for weak acids and bases. As an example, the weak base ammonia is involved in an equilibrium in aqueous solution

$$NH_{3(aq)} + H^+_{(aq)} \leftrightarrow NH_4{}^+_{(aq)}$$

Once again, we will use Le Chatelier's principle to play around with this equilibrium. We will try adding more ammonium ion or hydrogen ion to see what happens. Since none of the components of this system is itself colored, we will be adding an acid/base indicator that changes color with hydrogen ion concentration or pH, to have an index of the position of the ammonia equilibrium.

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V Experimental Procedure

A. Solubility Equilibria and Common Ion Effects

1. Obtain 5 mL of saturated sodium chloride solution in a test tube. This solution was repaired by adding solid NaCl to water until no more would dissolve. Then the clear solution was filtered from any undissolved solid NaCl. Concentrated (12M) HCl is 12 M in Cl^- and 12 M in H^+. Predict what should happen if 5 mL of saturated NaCl is treated with 10-20 drops of concentrated HCl. Try it. Examine the test tube carefully. In your notebook and on the report form, describe what happens in terms of Le Chatelier's principle.

Tube	1
sat $NaCl_{(aq)}$	5 mL
Addition	HCl

2 (a). Obtain 2 mL of 1.0 M K_2Cr0_4 solution in a test tube. Add 2 mL of distilled water and mix vigorously. Now add 6.0 M HCl drop wise (about one mL) and stir. Record your observations. The react ion you are observing is the format ion of the dichromate anion according to the following equilibrium:

$$2CrO_4^{2-}{}_{(aq)} + 2H^+{}_{(aq)} \leftrightarrow Cr_2O_7^{2-}{}_{(aq)} + H_2O$$

Predict what would happen if you added an equal number of drops of 6.0 M NaOH. Try it. Record and explain your observations in terms of Le Chatelier's principle.

Tube	1	2
K_2Cr0_4 solution	4 mL	4 mL
Addition	HCl	NaOH

(b) Form some $BaCrO_4$ precipitate by adding a few drops of 1.0 M K_2CrO_4 to 3 mL of a 0.10 M $BaCl_2$. Now add a few mL of 6.0 M HCl drop wise with stirring. Record your observations and describe what happens in terms of Le Chatelier's principle.

Tube	1
$BaCrO_{4(ppt)}$	3 mL
Addition	HCl

B. Complex Ion Equilibria and Common Ion Effects

Prepare a stock sample of the bright red complex ion $[Fe(NCS)^{2+}]$ by mixing 1 mL of

0.20 M iron(III) chloride and 2 mL of 0.10 M KSCN solutions. The color of this mixture is too intense to use as is, so dilute this mixture to 50 mL by adding about 47 mL of water.

Pour about 5 mL of the diluted red stock solution into each of five test tubes. Label the test tubes 1, 2… thru 5. Test tube 1 will be used as a standard to compare color with what will be happening in the other test tubes.

To test tube 2, add about 0.5 mL of 0.20 M $FeCl_3$ solution and stir.

To test tube 3, add about 1 mL of 0.10 M KSCN solution and stir.

To test tube 4, add several drops of 6.0M NaOH and stir (any precipitate is $Fe(OH)_3$.

To test tube 5, add 0.10M $AgNO_3$ solution drop wise until a change becomes evident. Ag^+ ion removes SCN^- ion from solution as a solid (silver thiocynate).

Tube	1	2	3	4	5
Stock Solution	5 mL	5 mL	5 mL	5 mL	5 mL
Addition	None	$FeCl_3$	KSCN	NaOH	$AgNO_3$

Describe the intensification or fading of the red color in each test tube in terms of Le Chatelier's principal.

C. Acid/Base Equilibria

Under the fume hood, prepare a dilute ammonia solution by adding 4 drops of concentrated ammonia to 100 mL of water.

Add 3 drops of phenolpthalein to the dilute ammonia solution, which will turn pink.

Place about 5 mL each of the pink dilute ammonia solution into two test tubes.

To one of the test tubes, add several small crystals of ammonium chloride.

To the other test tube, add a few drops of 12M HCl.

Tube	1	2
Stock Solution	5 mL	5 mL
Addition	NH_4Cl	HCl

Describe what happens to the pink color in terms of how Le Chatelier's principal is affecting the equilibrium system.

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Name:____________________________
Partner: __________________________

Stresses on Equilibrium Systems
Report Form

A. Solubility Equilibria and Common Ion Effects

1. Observation when concentrated HCl is added to a saturated solution of NaCl.

   Write out pertinent equilibrium and explain in terms of Le Chatelier's principle.

Equation:	☐	$\rightleftharpoons$	☐	+	☐
Stress:					
Shift:					
New Equilibrium: (Increased or decreased)	☐	$\rightleftharpoons$	☐	+	☐

2.(a) Observation when HCl is added to the K_2CrO_4 solution

Observation when NaOH is added to K_2CrO_4/HCl solution

Write out pertinent equilibrium and explain in terms of Le Chatelier's principle what happens when HCl is added to the K_2CrO_4 solution:

Equation:	☐	+	☐	$\rightleftharpoons$	☐	+	☐
Stress:							
Shift:							
New Equilibrium: (increased or decreased)	☐	+	☐	$\rightleftharpoons$	☐	+	☐

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Write out pertinent equilibrium and explain in terms of Le Chatelier's principle what happens NaOH is added to the K_2CrO_4 solution.

Equation:		+		$\rightleftharpoons$		+	
Stress:							
Shift:							
New Equilibrium: (increased or decreased)		+		$\rightleftharpoons$		+	

2.(b) Observation when 6 M HCl is added to the saturated solution of $BaCrO_4$

Write out pertinent equilibrium and explain in terms of Le Chatelier's principle.

Before the addition of HCl, the following solubility equilibrium exists:

(s)	$\rightleftharpoons$	**(aq)**	+	**(aq)**
(yellow ppt)				**(yellow solution)**

The addition of H^+ (from the strong acid HCl) will combine with one of the products in the equation above:

(aq)	**+ 2 H^+(aq)**	$\rightleftharpoons$	**(aq)**	+	**(l)**
yellow			**orange**		

This will have two consequences:

1. As the concentration of the $[CrO_4^{2-}]$ is _____________, the solubility equilibrium shifts to the _____________ and some (or all) of the _____________ precipitate dissolves

Equation:	**(s)**	$\rightleftharpoons$	**(aq)**	+	**(aq)**
Stress:					
Shift:					

New Equilibrium: (increased or decreased		$\rightleftarrows$		

2. The addition of H^+ ions to the yellow solution of CrO_4^{2-} (chromate)will shift the second equilibrium to the ___________ with the formation of the orange _________________

Equation:	**(aq)** yellow	+ **(aq)**	$\rightleftarrows$	**(aq)** orange	+ **(l)**
Stress:					
Shift:					
New Equilibrium: (increased or decreased)			$\rightleftarrows$		

B. Complex Ion Equilibria and Common Ion Effects

Observation when Fe^{3+} is added to $[Fe(SCN)^{2+}]$:

The following equilibrium exists in solution:

	+		$\rightleftarrows$	**bright red**

An increase in the concentration of $[Fe^{3+}]$ shifts the equilibrium to the _________ toward the formation of the _________________. As a result, the color ______________ (fades or intensifies).

Equation:	+	$\rightleftarrows$	**bright red**
Stress:			
Shift:			
New Equilibrium: (increased or decreased)			

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Observation when SCN^- is added:

Explanation in terms of Le Chatelier's Principle:
An increase in the concentration of [SCN^-] ions shifts the equilibrium to the ________ toward the formation of the ____________________. As a result, the color ____________.

Equation:	$\rightleftharpoons$ **bright red**
Stress:	
Shift:	
New Equilibrium:	

Observation when NaOH is added:

<u>Summary:</u>
Adding SCN^- ____________(increases, decreases) the number of moles of colored complex **and consumes _____**. Adding Fe^{3+} ____________(increases, decreases) the number of moles of colored complex and consumes _______ . Adding OH^- _____________(increases, decreases) the number of moles of colored complex by consuming ______to give __________**(formula)**

Observation when Ag^+ is added to [$FeSCN^{2+}$]:
Equation:
Ag^+(aq) + _______**(aq)** $\longrightarrow$ ___________**(s)**

Since the concentration of the SCN^- is ___________, the equilibrium reaction in which the colored complex is present _______________ (formula) shifts to the __________ and as such the number of moles of colored complex is ____________ (increased, decreased).

Equation: $\rightleftharpoons$

Stress:	
Shift:	
New Equilibrium:	$\rightleftharpoons$

C. Acid Base Equilibria

Observation when NH_4^+ is added to the solution:

Explanation in terms of LeChatelier's principle

The following equilibrium exists in an aqueous solution of ammonia:

The presence of the ______ ions make the solution turn pink when phenolphthalein is added.
The addition of NH_4Cl, a soluble salt [$NH_4Cl(aq) \longrightarrow NH_4^+(aq) + Cl^-(aq)$]
_______________ (increases, decreases) the concentration of the ______ ions in the equilibrium system.
This causes the equilibrium to shift to the ________ , which in turn decreases the concentration of the ______ ions. As a result the solution is no longer pink.

Equation:	**(aq)**	+	**(l)**	$\rightleftharpoons$	**(aq)**	+	**(aq)**	
Stress:								
Shift:								
New Equilibrium:				$\rightleftharpoons$				

Observation when HCl is added to solution:

Explanation in terms of Le Chatelier's principle:

The addition of _____ ions (from HCl) ___________ (increases, decreases) the concentration of the OH^- ions, since it reacts with them to form water as illustrated in the Net ionic Equation below:

$\longrightarrow$

The decrease in the concentration of the OH^-, ions shifts the equilibrium to the _________ .
However, the concentration of OH^- ions formed in the new equilibrium is ________ (more, less) than that in the original equilibrium.

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Equation:	$\rightleftharpoons$
Stress:	
Shift	
New Equilibrium:	$\rightleftharpoons$