Experiment 5
Equilibrium Systems

PURPOSE

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.

PRINCIPLES

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 shift in the direction that reduces the stress and a new equilibrium is established.

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.

I. 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:

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

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

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

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 $Na^{+}(aq)$ or $Cl^{-}(aq)$ 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. The net result is that $NaCl_{(s)}$ precipitates until the rates are again equal.

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II. 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:

$$\mathbf{Fe^{3+}(aq) + SCN^-(aq) \rightleftharpoons Fe(SCN)^{2+}(aq)}$$

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

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

III. 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

$$NH_3(aq) + H^+(aq) \rightleftharpoons NH_4^+(aq)$$

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. The change in color will provide us with valuable information related to the position of the ammonia equilibrium.

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PROCEDURE

I. Solubility Equilibria and Common Ion Effects

1. Obtain 5 mL of **saturated sodium chloride solution** in a test tube. This solution was prepared by adding solid NaCl to water until no more would dissolve. Then the clear solution was filtered from any undissolved solid NaCl.
   Add 10-20 drops of concentrated HCL to the 5 mL solution of saturated NaCl solution.
   Note: Concentrated (12M) HCl is 12 M in Cl^- and 12 M in H^+)

Tube	1
sat $NaCl_{(aq)}$	5 mL
Addition of HCl 12 M	10 -20 drops

Examine the test tube carefully. In your notebook and on the report form, describe what happens in terms of Le Chatelier's principle.

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.

K_2Cr0_4 1.0 M solution	Distilled Water	HCL 6.0 M solution
2 mL	2 mL	1 mL

The reaction you are observing is the formation of the dichromate anion according to the following equilibrium:

$$2CrO_4^{2-}(aq) + 2H^+(aq) \rightleftharpoons Cr_2O_7^{2-}(aq) + H_2O(l)$$

Chromate ion — dichromate ion

Yellow — **Orange**

Now add about 1 mL of 6.0 M NaOH to the test tube containing the orange solution. Record and explain your observations in terms of Le Chatelier's principle.

K_2Cr0_4 1.0 M solution	Distilled Water	HCL 6.0 M solution	NaOH 6.0 M NaoH
2 mL	2 mL	1 mL	1 mL

(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 $BaCl_2$.

$BaCl_2(aq)$	+	$K_2CrO_4(aq)$	$\rightleftharpoons$	**$BaCrO_4(s)$**	+	$2\ KCl(aq)$
3 mL 0.10 M		few drops 1.0 M yellow solution		**yellow precipitate**		

Total Ionic Equation is:

$$Ba^{2+}(aq) + \cancel{2\ Cl^-(aq)} + \cancel{2K^+(aq)} + CrO_4^{2-}(aq) \rightleftharpoons \mathbf{BaCrO_4(s)} + \cancel{2\ K^+(aq)} + \cancel{2\ Cl^-(aq)}$$

The Net Ionic Equation illustrating the formation of the **$BaCrO_4(s)$** precipitate is obtained by canceling out the spectator ions.

Net Ionic Equation is:

$Ba^{2+}(aq)$ + $CrO_4^{2-}(aq)$	$\rightleftharpoons$	**$BaCrO_4(s)$**
yellow solution		yellow precipitate

Now add a few mL of 6.0 M HCl drop wise with stirring to the test tube containing the yellow precipitate of $BaCrO_4$ .Record your observations and describe what happens in terms of Le Chatelier's principle.

II. Complex Ion Equilibria and Common Ion Effects

Prepare a stock sample of the bright red complex ion $[Fe(SCN)^{2+}]$ by mixing 1 mL of 0.20 M iron(III) chloride and 2 mL of 0.10 M KSCN solutions.

$Fe^{3+}(aq)$	**+**	**$SCN^-(aq)$**	$\rightleftharpoons$	**$Fe(SCN)^{2+}(aq)$**
1 mL 0.20 M		2 mL 0.10		bright red solution

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.

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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 6.0 M NaOH and stir.
The precipitate that forms is $Fe(OH)_3$.
To test tube 5, add 0.10M $AgNO_3$ solution drop wise until a change becomes evident.
Note: Ag^+ ion removes SCN^- ion from solution as a solid (silver thiocynate).

$$Ag^+(aq) + SCN^-(aq) \longrightarrow AgSCN(s)$$

Tube	1	2	3	4	5
Stock Solution	5 mL	5 mL	5 mL	5 mL	5 mL
Addition	None	0.5 mL $FeCl_3$ 0.20 M	1 mL KSCN 0.10 M	few drops NaOH 6.0 M	few drops $AgNO_3$ 0.10 M

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

III. 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	A few Small crystals of NH_4Cl	A few drops of HCl 12 M

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

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Name:_____
Partner: _____

Stresses on Equilibrium Systems
Report Form

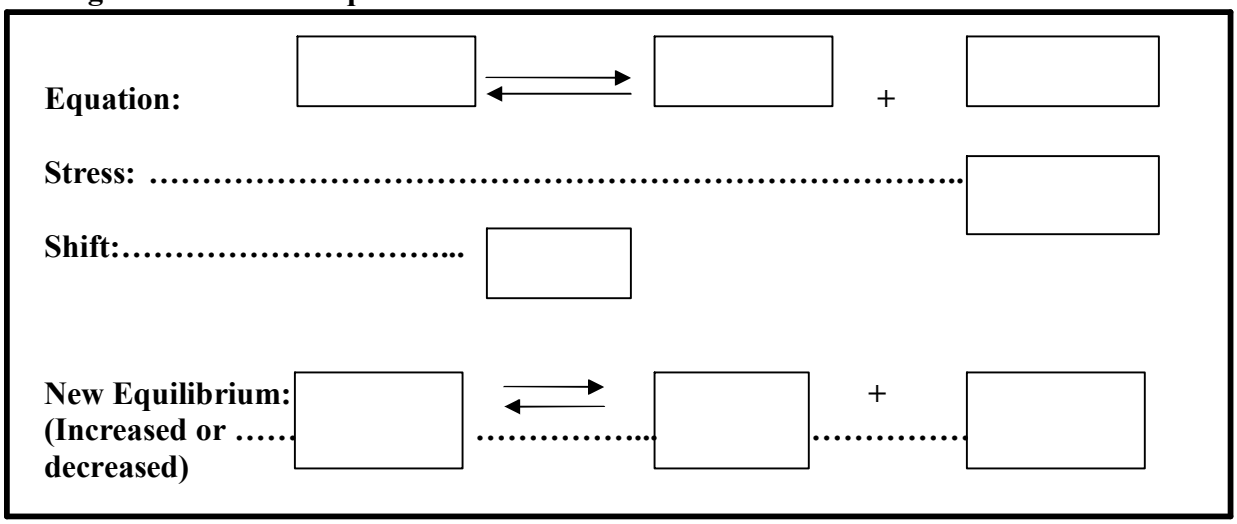
I. Solubility Equilibria and Common Ion Effects

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

_____

_____

Indicate the stress applied, the shift in equilibrium and the concentration changes of all reagents in the new equilibrium:



Account for your observation(s) by explaining it/them in terms of Le Chatelier's principle:

_____

_____

_____

_____

_____

_____

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

_____

_____

Write out pertinent equilibrium that illustrates what happens when HCl is added to the K_2CrO_4 solution.
Indicate the stress applied, the shift in equilibrium and the concentration changes of all reagents in the new equilibrium:

Equation: [ ] + [ ] ⇌ [ ] + [ ]
Yellow **Orange**

Stress: …… [ ]

Shift:……..... [ ]

New Equilibrium: (Increased or decreased [ ] [ ] ⇌ [ ] [ ]

Account for what you have observed when HCl was added to the K_2CrO_4 solution, by providing an explanation in terms of Le Chatelier's principle :

_____

_____

_____

_____

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Observation when NaOH is added to K_2CrO_4/HCl solution

_____

_____

Write out pertinent equilibrium that illustrates what happens when NaOH is added to the acidic solution of K_2CrO_4.

Indicate the stress applied, the shift in equilibrium and the concentration changes of all reagents in the new equilibrium:

Equation: ☐ + ☐ ⇌ ☐ + ☐

Yellow **Orange**

Stress: …… ☐

Shift:……..... ☐

New Equilibrium: (Increased or decreased ☐ + ☐ ⇌ ☐ + ☐

Account for what you have observed when NaOH was added to the acidic solution of K_2CrO_4 solution, by providing an explanation in terms of Le Chatelier's principle:

_____

_____

_____

_____

_____

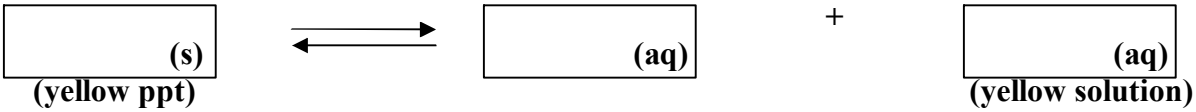
2.(b) Observation when 6 M HCl is added to the saturated solution of $BaCrO_4$
Note what happens to the precipitate and note any change in the color of the solution.

_____

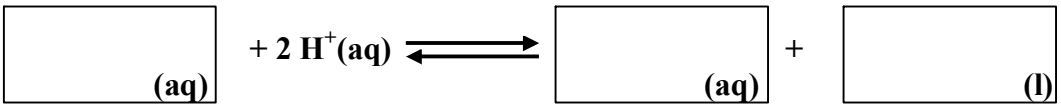
_____

_____

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



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

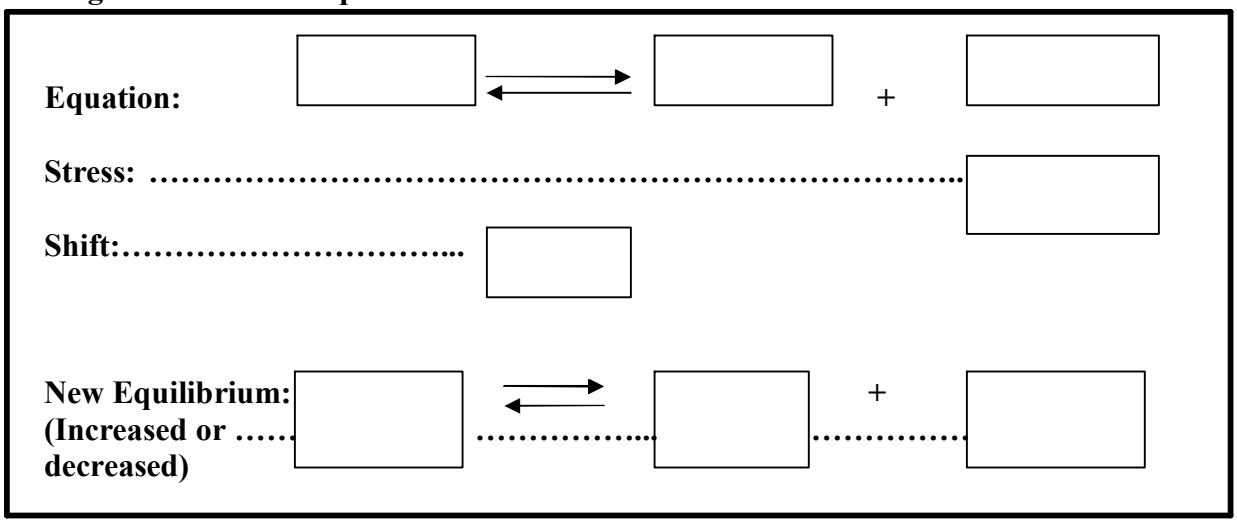


This will have two consequences:

A. <u>It will shift the solubility equilibrium of the $BaCrO_4$</u>

Write out pertinent equilibrium that illustrates what happens when HCl is added to the solution containing the $BaCrO_4$ precipitate.

Indicate the stress applied, the shift in equilibrium and the concentration changes of all reagents in the new equilibrium:



Explain by completing the blanks:

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

(formula)

B. <u>It will shift the equilibrium containing the yellow CrO_4^{2-} ions and the orange $Cr_2O_7^{2-}$ ions</u>
Write out pertinent equilibrium that illustrates what happens when HCl is added to the solution containing the **yellow CrO_4^{2-} ions and the orange $Cr_2O_7^{2-}$ ions**
Indicate the stress applied, the shift in equilibrium and the concentration changes of all reagents in the new equilibrium:

Equation: [ ] + [ ] ⇌ [ ] + [ ]
Yellow **Orange**

Stress: …… [ ]

Shift:……..... [ ]

New Equilibrium: (Increased or decreased [ ] + [ ] ⇌ [ ] + [ ]

Explain by completing the blanks:
The addition of H^+ ions to the yellow solution of CrO_4^{2-} (chromate)will shift the equilibrium to the _____ with the formation of the orange _____

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II. Complex Ion Equilibria and Common Ion Effects

Observation when Fe^{3+} is added to $[Fe(SCN)^{2+}]$ solution containing the $[Fe(SCN)^{2+}]$ in equilibrium with the Fe^{3+} and the SCN^{-} ions (Test Tube # 2)

_____

Write out the pertinent equilibrium.

Indicate the stress applied, the shift in equilibrium and the concentration changes of all reagents in the new equilibrium:

Equation: [ ] + [ ] ⇌ [ ]

Bright Red

Stress: [ ]

Shift:……..... [ ]

New Equilibrium: (Increased or decreased [ ] + [ ] ⇌ [ ]

Explain by completing the blanks:

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).

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Observation when SCN^- is added to $[Fe(SCN)^{2+}]$ solution containing the $[Fe(SCN)^{2+}]$ in equilibrium with the Fe^{3+} and the SCN^- ions (Test Tube # 3)

_____

Write out the pertinent equilibrium by completing the boxes below.

Indicate the stress applied, the shift in equilibrium and the concentration changes of all reagents in the new equilibrium:

Equation: [ ] + [ ] ⇌ [ ]

Bright Red

Stress:……. [ ]

Shift:……. [ ]

New Equilibrium: (Increased or decreased [ ] + [ ] ⇌ [ ]

Explain by completing the blanks:

An increase in the concentration of $[SCN^-]$ ions shifts the equilibrium to the _____ toward the formation of the _____. As a result, the color _____.

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Observation when OH^- is added to $[Fe(SCN)^{2+}]$ solution containing the $[Fe(SCN)^{2+}]$ in equilibrium with the Fe^{3+} and the SCN^- ions (Test Tube # 3)

Write out the pertinent equilibrium by completing the boxes below.
Indicate the stress applied, the shift in equilibrium and the concentration changes of all reagents in the new equilibrium:

Equation: [ ] + [ ] ⇌ [ ]
Bright Red

Stress:…….. [ ]

Shift:……..... [ ]

New Equilibrium: (Increased or decreased [ ] + [ ] ⇌ [ ]

Explain by completing the blanks:

Adding OH^- _____(increases, decreases) the number of moles of colored complex by

consuming _____to give _____(formula)

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Observation when Ag^+ is added to $[Fe(SCN)^{2+}]$ solution containing the $[Fe(SCN)^{2+}]$ in equilibrium with the Fe^{3+} and the SCN^- ions (Test Tube # 5)

Write out the pertinent equilibrium by completing the boxes below.
Indicate the stress applied, the shift in equilibrium and the concentration changes of all reagents in the new equilibrium:

Equation: ☐ + ☐ ⇌ ☐
Bright Red

Stress:…….. ☐

Shift:……..... ☐

New Equilibrium: (Increased or decreased ☐ + ☐ ⇌ ☐

Explain by completing the blanks:
Equation:
Ag^+(aq) + **_____(aq)** ⟶ **_____(s)**

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

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III. Acid Base Equilibria

Observation when a few crystals of NH_4Cl are added to the pink NH_3 solution containing phenolphtalein.

_____

Write out the pertinent equilibrium.

Indicate the stress applied, the shift in equilibrium and the concentration changes of all reagents in the new equilibrium:

Equation: ☐ + ☐ ⇌ ☐ + ☐

Stress:…… ☐

Shift:……..... ☐

New Equilibrium: (Increased or decreased ☐ + ☐ ☐ + ☐

Explain by completing the blanks:

The presence of the _____ ions make the aqueous solution of NH_3 turn pink when phenolphthalein is added. The addition of NH_4Cl, a soluble salt, _____ (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.

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Observation when HCl is added to the pink NH_3 solution containing phenolphtalein.

_____

Write out the pertinent equilibrium.

Indicate the stress applied, the shift in equilibrium and the concentration changes of all reagents in the new equilibrium:

Equation: [ ] + [ ] ⇌ [ ] + [ ]

Stress:…… [ ]

Shift:……..... [ ]

New Equilibrium: (Increased or decreased [ ] + [ ] [ ] + [ ]

Explain by completing the blanks:

The addition of _____ ions (from HCl) _____ (increases, decreases) the concentration of the OH^- ions, since they react forming water as illustrated by the Net ionic Equation below:

[ ] ⟶

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