

## LeChatlier's Principle – Disturbing Chemical Equilibria

*Before beginning, for each system, prepare a table like the one below in your lab notebook with your predictions about the effect of each addition in each test tube.*

### *System #\_\_ Data Table*

Equilibrium System: <i>Write the primary reaction studied for the system.</i>				
Test Tube	Addition	Predicted Outcome	Observation	Explanation*

\* Leave a lot of room to write in the explanation. This will be where you will discuss:

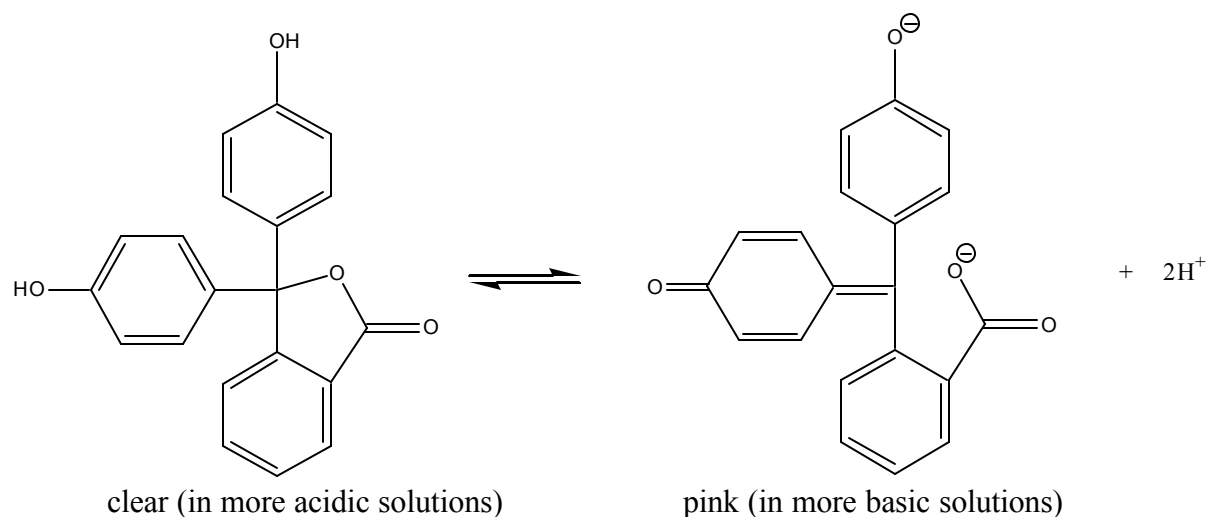
- Whether what you have done results in the addition *or* removal of a reactant *or* product.
- How competing equilibria interact.
- If other factors are affecting the equilibrium.

## System 1: Acid / Base Equilibria and the pH indicator Methyl Violet

### *Background*

Acid-Base indicators are chemical compounds that have one form under more acidic conditions, and a different form under more basic conditions. The two forms of the indicator have different colors. Consider the familiar acid-base indicator, phenolphthalein. In its “protonated” form – which is dominant in acidic or neutral solution, it is clear. However, in basic solution, its pink “deprotonated” form dominates.

The reaction between the protonated and deprotonated forms is an equilibrium. In solution, the phenolphthalein is never fully protonated or deprotonated. Let’s consider the reaction as follows:

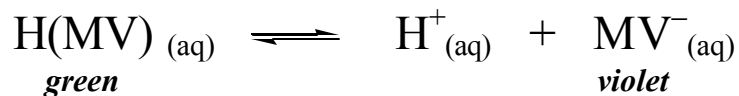


This equilibrium shifts to the right or the left, based on the concentration of  $H^+$  in the solution it is in. If the system is at equilibrium under basic conditions and significant  $H^+$  is added, the reaction will shift to the left to use up the extra  $H^+$  that was added to the solution and establish a new equilibrium condition. If enough  $H^+$  is added, then most of the phenolphthalein will be converted to its protonated form, and the pink color of the anion form will no longer be noticeable because it will be at such a low concentration.

This shift is not permanent. If base ( $OH^-$ ) ions are added to the solution, the free  $H^+$  on the product side of the reaction will be used up by an acid-base neutralization reaction – the above reaction will shift to the right to replace the  $H^+$  ions, and the pink form will dominate again. By adding acid or base, we can push this equilibrium back and forth indefinitely.

## *Methyl Violet*

We have observed phenolphthalein in the laboratory many times. In this experiment, you will investigate the reaction equilibrium of the indicator methyl violet. Its equilibrium is described by the equation:



### Procedure:

Prepare the test solution by adding 1-2 drops of indicator solution to about 20 mL of deionized water. Divide the solution evenly into two test tubes. Save one as a reference. Note the color.

**Test Tube #1 (control):** Add nothing

**Test Tube #2:**

**Addition #1:** Add the 6.0 M HCl solution dropwise until further addition results in no significant change. Describe the change.

**Addition #2:** Add the 6.0 M NaOH solution dropwise until further addition results in no color change. Describe the change.

**Addition #3:** Again add the 6.0 M HCl solution dropwise until further addition results in no significant change. Describe the change.

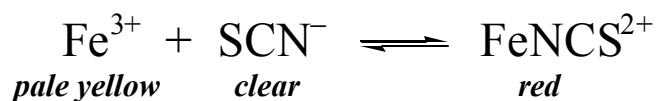
### *System #1 Data Table*

Equilibrium System: $\text{H(MV)}_{(\text{aq})} \rightleftharpoons \text{H}^+_{(\text{aq})} + \text{MV}^-_{(\text{aq})}$				
Test Tube	Addition	Predicted Outcome	Observation	Explanation
1	None (control)	No changes.	<i>Note color</i>	
2	6.0 M HCl	Solution expected to turn green.	<i>Note color</i>	Addition of the HCl pushes the reaction toward reactant side by creating an excess of $\text{H}^+$ ions, a product. The equilibrium shifts to reduce the new stress on the system.
2	6.0 M NaOH			
2	6.0 M HCl			

*Note that some boxes are filled in as an example.*

## System #2: Complex ion formation

Many transition metal ions make highly colored complexes with certain anions or molecules in solution. Iron(III) ions react with thiocyanate ions in solution to make a deep red complex:



### Procedure:

In a small beaker, mix 10.0 mL of 0.01 M  $\text{Fe}(\text{NO}_3)_3$  solution with 10.0 mL of 0.01 M NaSCN. Add 50 mL of deionized water to the mixture. Divide the solution equally among 6 similarly-sized test tubes (#1-6).

**Test tube #1 (control):** Add nothing.

**Test tube #2:** Add 2 mL of 0.01 M  $\text{Fe}(\text{NO}_3)_3$  to the solution. Describe the change.

**Test tube #3:** Add 2 mL of 0.01 M NaSCN to the solution. Describe the change.

**Test tube #4:** Add 5-10 drops of 6.0 M NaOH to the solution. *The addition of NaOH will result in the formation of insoluble  $\text{Fe}(\text{OH})_3$ .* Describe the change in the solution.

**Test tube #5:** Cool the test tube in an ice bath.

**Test tube #6:** Heat the test tube in a hot water bath. Compare the intensity of the color in test tubes #1 (control – room temperature), #5 (cold), and #6 (hot).

### *Additional system #2 Question:*

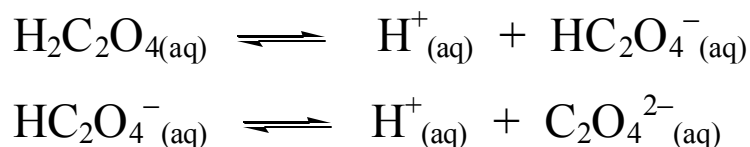
1. *Is the reaction exothermic or endothermic? Explain.*

### System #3: Equilibria involving a precipitate

Calcium chloride is a very soluble salt. When we put it into water, we can dissolve a reasonably large quantity per liter. Until we reach saturation, the dissolution and dissociation of  $\text{CaCl}_2$  is essentially 100%. Sodium oxalate is also quite soluble and ionizes completely in water: Because we will not have saturated solutions, we assume the following reactions go to completion:

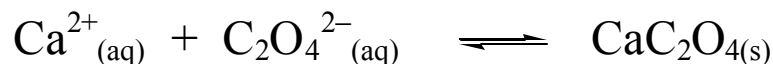


Dissolving acids and some other ionic compounds in water is a more complex process characterized by a step-wise dissociation that is in equilibrium at each step. Consider the diprotic acid, oxalic acid:



These equilibria are both reactant-favored and so only produce a small amount of product relative to reactants.

The compound calcium oxalate ( $\text{CaC}_2\text{O}_4$ ) is not very soluble in water. When calcium and oxalate ions are in the same solution, even at low concentration, we expect a precipitate that forms by the following reaction:



The above reaction is highly product-favored. All three of the equilibria described interact with the other two equilibrium reactions. A change that affects any one of the equilibria will affect all three. We will mix different combinations of compounds containing calcium ions, oxalate ions, and  $\text{H}^{+}$  ions to study and manipulate these equilibria.

#### Procedure:

Put approximately 5.0 mL of 0.05 M  $\text{CaCl}_2$  into each of two test tubes labeled #1 and #2.

**Test Tube #1:** Add 1.0 mL of 0.1 M  $\text{Na}_2\text{C}_2\text{O}_4$ . Describe the change.

#### **Test Tube #2:**

**Addition #1:** Add 1.0 mL of 0.10 M  $\text{H}_2\text{C}_2\text{O}_4$  solution. Describe the change, comparing to test tube #1.

**Addition #2:** Add 10 drops of 6.0 M  $\text{HCl}$ . Describe the change.

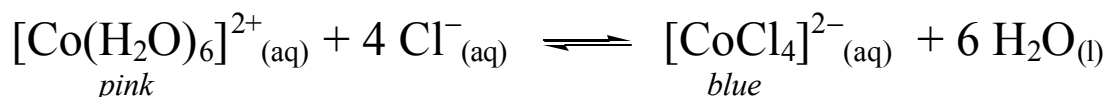
**Note:**  $\text{HCl}$  is fully dissociated into  $\text{H}^{+}$  ions and  $\text{Cl}^{-}$  ions.

**Addition #3:** Add 10 drops of 6.0 M  $\text{NH}_4\text{OH}$ . Describe the change.

## System #4: Heat and equilibria

Most reactions either release heat or consume heat. Many reaction processes in solution release or consume heat, but because of the large heat capacity of water, we do not notice the energy transfer in many reactions we study. Complex ion formation is an example of such a process. In this experiment, we will determine whether a specific complex ion formation is endothermic (heat acts as a reactant) or exothermic (heat acts as a product).

In aqueous solution, cobalt ions are solvated by six water molecules to make a light pink complex ion:  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ . If an excess of chloride is added to the solution, the blue cobalt-chloride complex forms:  $[\text{CoCl}_4]^{2-}$ .



Based on the directions that the addition of heat (hot water bath) and removal of heat (cold water bath) push the reaction, you can determine whether the reaction is endothermic or exothermic.

### Procedure:

In a small container, put 2-3 mL (1 pipette) of 0.1 M  $\text{CoCl}_2$ . Though chloride ions are present in this solution, water is in significant excess; therefore, nearly all of the cobalt (II) ions are in the  $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$  form.

**Under the fume hood:** add concentrated HCl dropwise until the solution turns a purple-violet color. If it turns a deep blue, too much chloride is present – you should properly discard the solution and start again.

When the solution is purple there is a significant quantity of both complex ions. Divide the solution equally into three test tubes and label #1-3.

**Test Tube #1 (control):** Maintain at room temperature.

**Test Tube #2:** Place in a hot water bath ( $\sim 50^\circ\text{C}$ ). Describe the change.

**Test Tube #3:** Place in an ice-water bath ( $\sim 3^\circ\text{C}$ ). Describe the change.

*Switch test tubes 2 & 3.* Describe the change. Allow them both to come to room temperature. Compare to the control.

### **Additional System #4 Question:**

1. *Is the reaction exothermic or endothermic? Explain.*

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## POST-LAB QUESTIONS

Name: \_\_\_\_\_

- In system #2, if the solution is diluted, the concentration of the product, and both reactants all go decrease.
  - Write the equilibrium (K) expression.
  - At the point the solution is diluted, will Q be  $<$ ,  $=$ , or  $>$  K? Justify your answer.
  - Based on LeChatlier's principle, will the reaction shift to the right or to the left?
- For system #3, write the equilibrium expression for the *precipitation* reaction being studied.
- For system #4, write the equilibrium (K) expression for the reaction being studied.
- For system #4, does is the K value larger or smaller at higher temperature? Explain this in terms of whether the reaction is endothermic or exothermic.