Name: ____ Date: __________________

Lab Partners:____

Chemical Equilibrium

By Thomas Cahill, Arizona State University, New College of Interdisciplinary Arts and Sciences.

Chemical equilibrium is a state of balance between opposing chemical reactions. In other words, the rate at which the products form is equal to the rate at which reactants are formed from the products. In a closed system, both forward and backward reactions will reach an equilibrium state and the concentrations of reactants and products will no longer change with time.

Le Chatelier's Principle

Le Chatelier's principle states that when a system in chemical equilibrium is disturbed by a change in temperature, pressure, or concentration, the system will shift in equilibrium composition in a way that tends to counteract this change of variable. The three ways that affect this change in equilibrium include:

- **Changing concentrations** by adding or removing products or reactants to the reaction vessel.

For example, in the chemical equilibrium reaction: $2\ NO(g) + O_2(g) \rightleftharpoons 2NO_2(g)$
If you add more NO(g), the equilibrium shifts to the right producing more $NO_2(g)$
If you add more $O_2(g)$, the equilibrium shifts to the right producing more $NO_2(g)$
If you add more $NO_2(g)$, the equilibrium shifts to the left producing more NO(g) and $O_2(g)$

- **Changing partial pressure** of gaseous reactants and products. A pressure increase will cause the reaction to shift in the direction that reduces pressure, which is the side with the fewer number of gas molecules.

For example, in the equilibrium equation: $2\ SO_2(g) + O_2(g) \rightleftharpoons 2\ SO_3(g)$
An increase in pressure will cause a shift to the right producing more $SO_3(g)$

- **Changing the temperature** affects the chemical shift based on the enthalpy change for the reaction. For an endothermic reaction (positive ΔH) an increase in temperature shifts the equilibrium to the right to absorb the added heat; for an exothermic reaction (negative ΔH) an increase in temperature shifts the equilibrium to the left.

For example, in the equilibrium equation: $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3\,(g) + 91.8\ kJ$, ($\Delta H$= -91.8kJ)
An increase in the forward reaction would produce even more heat since the forward reaction is exothermic; therefore, an increase in temperature will cause a shift to the left because the reverse reaction uses the excess heat.

In this lab, you will use Le Chatelier's principle to interpret how a system at equilibrium responds to various changes in external conditions. Part A will consider changes in reactant or product concentrations, part B will study changes in temperature, and part C will study the common ion effect.

Part A – Concentration Changes

Materials

15mL test tubes, w/ caps (8) and rack	1 M $Fe(NO3)_3$	1 M KSCN Vortex
100mL graduated cylinder	0.1 M $AgNO_3$	12M HCl
10mL graduated cylinder	0.1 M Na_3PO_4	NaF
250mL beaker	0.1 M $Na_2C_2O_4$	Vortex

Procedure

Skip the grayed procedure for the online labs

Prepare an equilibrium system for the following reaction and study the response of this system to various concentration changes.

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

(deep red complex)

1. Wear gloves for this experiment!
   Go to https://www.public.asu.edu/~jhwang43/
   Click on "General Chemistry II Laboratory Exercises, By Thomas Cahill"
   Click on "Lab3: Chemical Equilibrium"
   Click on "Concentration Changes"

2. Add 100mL DI H_2O into a clean 250ml beaker, by clicking on "**Click to Add 100 mL DI H2O**"
3. Add 1mL of 1M KSCN and 1mL of 1M $Fe(NO_3)_3$ to the H_2O, by clicking on "**Click to Add 1 mL 1M KSCN**" and by clicking on "**Click to Add 1 mL 1M FE(NO3)3. Use this SOliution to fill the 8 test tubes on the right**"
4. Use a glass stirring rod to mix the solution.

When adding reagents with a dropper or pipet, be careful not to let the tip of the dropper touch the test tube or the solution inside the tube, as this will contaminate the reagent.

5. Obtain 8 test tubes and label them #1-8 with label tape. DO NOT write directly on the test tubes!
6. Add about 10mL of the prepared solution to each test tube.
7. Keep test tube #1 as a control and add the following reagents into test tubes 2 through 8:

#1 – Control test tube, click to add the equilibrium mixture by click on **"Click to Add Aqueous KSCN and FE(NO3)3 Solution Mix Prepare on the Left Column. This is the Control Don't Add Anything Else".**

#2 – Add 1mL 1M $Fe(NO_3)_3$ **"Click to Add Aqueous KSCN and FE(NO3)3 Solution Mix". Then "Click to Add 1 mL 1M Fe(NO3)3".**

#3 – Add 1mL 1M KSCN **"Click to Add Aqueous KSCN and FE(NO3)3 Solution Mix". Then "Click to Add 1 mL 1M KSCN".**

#4 – Add 20 drops 0.1M $AgNO_3$. **"Click to Add Aqueous KSCN and FE(NO3)3 Solution Mix". Then "Click to Add 20 drops 0.1M AgNO3".** The silver ions will form a AgSCN complex.

#5 – Add 1mL 12M HCl (in the HOOD). **"Click to Add Aqueous KSCN and FE(NO3)3 Solution Mix". Then "Click to Add 1 mL 12M HCl".** The chloride ions form a $FeCl_4^-$ complex.

#6 – Add 10 drops 0.1M Na_3PO_4. **"Click to Add Aqueous KSCN and FE(NO3)3 Solution Mix". Then "Click to Add 10 drops 0.1M Na3PO4".** The phosphate forms a $FePO_4$ precipitate with iron.

#7 – Add 10 drops 0.1M $Na_2C_2O_4$. **"Click to Add Aqueous KSCN and FE(NO3)3 Solution Mix". Then "Click to Add 10 drops 0.1M Na2C2O4".** The oxalate forms a $Fe(C_2O_4)_3^{3-}$ complex.

#8 – Add several crystals NaF. **"Click to Add Aqueous KSCN and FE(NO3)3 Solution Mix". Then "Click to Add several crystals NaF". T**he fluoride forms a FeF_6^{3-} complex. The NaF dissolves slowly, so mix the solution a few minutes after adding the crystals by 1) capping the test tube and using the Vortex, or 2) using a disposal pipet to pump the solution up/down to mix it in the test tube.

8. Add 10 mL of the prepared solution to a separate test tube and save for Part B of the lab.
9. Compare the color intensity of each test tube to that of the control (#1) and record your observations on the data sheet. Explain the results in terms of Le Chatelier's Principle. For example, did the reaction shift right to form more $FeSCN^{2+}$ or shift left to form more of the reactants? Explain why in terms of increasing or decreasing concentrations.
10. Explain your observations and write the net ionic equations of any reactions (complex or precipitate formation) that occurred.
11. Dispose of all chemical waste in the container in the HOOD and clean the test tubes well w/DI water. The test tubes will be reused by the next lab group.

Part B – Temperature Changes

Materials

Nitrogen dioxide equilibrium tubes
Hot water bath on hot plate in fume hood
Cobalt chloride equilibrium tubes
Ice bath in beaker in fume hood

Procedure

- Consider the following reaction: $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$
  (Colorless) (Brown)

  Go to https://www.public.asu.edu/~jhwang43/
  Click on "General Chemistry II Laboratory Exercises, By Thomas Cahill"
  Click on "Lab3: Chemical Equilibrium"
  Click on "Temperature Changes"

1. There are three nitrogen dioxide equilibrium tubes, each in a hot water bath, an ice bath, and one at room temperature set up in the fume hood.
2. One of the tubes is labeled as the room temperature control so you can compare it to the two remaining tubes. Observe the nitrogen dioxide tube in the ice bath. Use a white piece of paper, or paper towel, as the background in order to view the differences easily.
3. Next, observe the other tube in the hot water bath and record your observations on the data sheet. Use a white piece of paper as the background in order to view color differences easily.
4. Determine if the above reaction is endothermic or exothermic.

- Consider the following reaction: $Co^{2+}_{(aq)} + 4Cl^{-}_{(aq)} \rightleftharpoons CoCl_4^{2-}{}_{(aq)}$
  (Pink) (Blue)

5. Repeat steps 1-4 above, by observing the cobalt chloride test tubes.

*** DO NOT OPEN THESE TUBES***

- Consider the following reaction: $Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightleftharpoons FeSCN^{2+}_{(aq)}$
  (Deep red)

6. There is a dry bath heater set up in the hood at 90 degrees C. Place your test tube containing the solution from Part A into the dry bath heater and leave it for about 30 minutes. After about 30 minutes, return to view your solution and record your observations on the data sheet. Remove your tube with test tube tongs and let it cool in the test tube rack at your station. Once cooled, rinse the solution into the designated waste jug.
   Observe the two "Beakers" in the left-most column on the web page.

7. Determine if the reaction from Part A is an endothermic or exothermic reaction.

Part C – Common Ion Effect

The common ion effect describes the dissociation effects of two dissolved solutes that contain the same ion. For example, if both sodium acetate and acetic acid are dissolved in the same solution, they both dissociate and produce acetate ions, as shown in the following equations:

Acetic acid: $HC_2H_3O_{2(l)} \rightleftharpoons H^+_{(aq)} + C_2H_3O_2{}^-_{(aq)}$

Sodium acetate: $NaC_2H_3O_{2(s)} \rightarrow Na^+_{(aq)} + C_2H_3O_2{}^-_{(aq)}$

Sodium acetate dissociates completely, but acetic acid is a weak acid and only slightly dissociates. According to Le Chatelier's principle, the addition of acetate ions from sodium acetate will suppress the ionization of acetic acid and will shift the equilibrium to the left resulting in a decrease in the hydrogen ion concentration. The hydrogen ion concentration is inversely related to the pH of the solution, thus, a solution containing a high concentration of H^+ will have a lower pH and will be more acidic.

The rate of reaction between sodium carbonate and an acid depends on the concentration of hydrogen ions in the solution. The reaction between a carbonate and an acid is a two step process where the first reaction transfers hydrogen ions to the carbonate to form carbonic acid and the second step is the decomposition of the carbonic acid into CO_2 gas and H_2O, as shown below:

$$CO_3{}^{2-}_{(aq)} + 2\ H^+_{(aq)} \rightarrow H_2CO_{3(aq)}$$

$$H_2CO_{3(aq)} \rightleftharpoons H_2O_{(l)} + CO_{2\,(g)}$$

Therefore, acidic solutions containing a higher concentration of hydrogen ions will produce more CO_2. This part of the lab experiment will study the difference in hydrogen ion concentrations in an acetic acid/water solution and an acetic acid solution containing excess acetate ions. The reaction progress will be measured by observing the time taken for carbon dioxide to evolve in each solution as foamy bubbles. The rate at which the foam rises depends on the rate of carbon dioxide produced, which depends on the concentration of hydrogen ions in solution.

CONTINUED Part C – Common Ion Effect

Materials

Stop Watch	10M glacial acetic acid $HC_2H_3O_2$
100mL graduated cylinder	Generic hand soap
4M $NaC_2H_3O_2$	10mL graduated cylinder
Saturated $NaHCO_3$ solution	Plastic pipets

Part C Procedure

Go to https://www.public.asu.edu/~jhwang43/
Click on "General Chemistry II Laboratory Exercises, By Thomas Cahill"
Click on "Lab3: Chemical Equilibrium"
Click on "Common Ion Effect"

Trial 1 - Acetic Acid/H_2O:

1) Add 1 mL of 10M acetic acid to a clean, dry 100 mL graduated cylinder, **by click on "Click to Add 1 mL 10M Acetic Acid"**
2) Add 2 drops of soap, **by click on "Click to Add 2 drops of soap"**
3) Swirl the solution in the graduated cylinder gently to ensure the soap is distributed evenly in the acetic acid and has not settled to the bottom. Ignore any bubbles evolved at this step.
4) Add 10 mL of DI water, **by click on "Click to Add 10 mL DI wate"**
5) Again, mix the solution gently and ignore any additional bubbles that evolve.
6) Adding in the $NaHCO_3$ in the next step will cause a large amount of bubbles to rise up the graduated cylinder. The bubble formation will be timed from the moment the $NaHCO_3$ is added to the solution in the graduated cylinder to the moment that the bubbles stop progressing up the cylinder. Make sure that one group member is ready with a stopwatch to clock the amount of time it takes for the bubbles to rise to the top of the graduated cylinder.
7) Measure 4 mL of $NaHCO_3$ using a 10 mL graduated cylinder and then add it to the acid/soap solution, **by click on "Click to Add 4 mL of NaHCO3".**
   Record the time of the reaction. The reaction starts *when the $NaHCO_3$ is added* and it ends *when the column of bubbles stops rising*. This reaction will proceed rapidly.

Trial 2 - Acetic acid/Acetate solution:

8) Empty the contents of the graduated cylinder into the designated waste jug.
9) Clean and dry the graduated cylinder.
10) Repeat the above procedure, but add 10 mL of 4M $NaC_2H_3O_2$, **by click on "Click to Add 10 mL of NaC2H3O2",** instead of DI water in Step #3.
11) Record the time of the reaction on the data sheet.

Name: ______________________________ Lab Partners:_______________________________________

Chemical Equilibrium Lab Results

Part A Data

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

(Dark Red Complex)

Test tube	Reagent Added	Observed Color Change	Reaction Shift (left or right)	Explanation in terms of Le Chatelier's Principle
1	**Control**	**No Reaction**	**No Shift**	**Equilibrium State**
2				
3				
4				
5				
6				
7				
8				

______ of 3 pts

Write the net ionic equations for the reactions occurring in test tubes 4 through 8 after the addition of each reagent to the stock solution. Test tube 4 is provided as an example.

Make sure the reactions are balanced and that the charges are given for the ionic species!

4	$Ag^{+}{}_{(aq)} + SCN^{-}{}_{(aq)} \rightleftharpoons AgSCN_{(s)}$
5	
6	
7	
8	

______ of 2 pts

Part B Data

<table>
<tr><td></td><td colspan="2">$N_2O_{4(g)} \rightleftharpoons 2\ NO_{2(g)}$
Colorless Brown</td></tr>
<tr><td></td><td>Observed Color Change</td><td>Exothermic / Endothermic Reaction?</td></tr>
<tr><td>HOT</td><td></td><td rowspan="2"></td></tr>
<tr><td>COLD</td><td></td></tr>
<tr><td></td><td colspan="2">$Co^{2+}_{(aq)} + 4Cl^{-}_{(aq)} \rightleftharpoons CoCl_4^{2-}{}_{(aq)}$
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(Dark Red)</td></tr>
<tr><td></td><td>Observed Color Change</td><td>Exothermic / Endothermic Reaction?</td></tr>
<tr><td>HOT</td><td></td><td></td></tr>
</table>

______ of 6 pts

Part C Data

Trial 1 – Acetic Acid/H_2O Bubble Rising Time: ________ seconds

Trial 2 – Acetic Acid/ Acetate Bubble Rising Time: _________ seconds

Given the balanced chemical equations for the reactions that are occurring in this system, answer the following questions:

1. $CH_3COOH \Leftrightarrow CH_3COO^- + H^+$ (ionization of acetic acid)
2. $H^+ + HCO_3^- \Leftrightarrow H_2CO_3$ (protonation of carbonate)
3. $H_2CO_3 \rightarrow H_2O + CO_2$ (decomposition of carbonic acid)

1. Which of the reactions written above is the rate-limiting reaction and how do you know that it is the rate limiting reaction?

2. Using Le Chatelier's principle, explain how the common ion effect exhibited in Trial 2 affects the pH of a solution.

3. Using Le Chatelier's Principle, explain the differences in the reaction time between the Acetic acid/DI water experiment and the Acetic acid/$NaC_2H_3O_2$ experiment.

______ of 5 pts

Post Lab Questions

1. Write the equilibrium constant expression for the reaction between Fe^{3+} and SCN^{-}.

2. Write the equilibrium constant expression for the following reaction:

$$Co^{2+}_{(aq)} + 4Cl^{-}_{(aq)} \rightleftharpoons CoCl_4{}^{2-}_{(aq)}$$

In which direction will the equilibrium shift if you:

(a) Increase the concentration of Co^{2+}? ______________________________

(b) Decrease the concentration of $CoCl_4{}^{2-}$ ______________________________

3. What effect does an increase in temperature have on each of the following systems at equilibrium?

(a) $3O_{2\,(g)} \rightleftharpoons 2O_{3\,(g)}$ $\Delta H = 284kJ$ ________________________

(b) $2SO_{3\,(g)} + O_{2\,(g)} \rightleftharpoons 2SO_{3\,(g)}$ $\Delta H = -198.2kJ$ ________________________

4. Consider the following equilibrium: $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4{}^{2-}(aq)$; $\Delta H > 0$

Predict which direction will the equilibrium shift in the following scenarios. If the equilibrium does not change, write "no change" and <u>explain why this is the case</u>.

(a) H_2SO_4 is added? Why? ______________________________

(b) $BaCl_2$ is added? Why? ______________________________

(d) Heat is added? Why? ______________________________

(e) $BaSO_4(s)$ is added? Why? ______________________________

_____ of 6 pts

Total ______ of 25 pts