Chemical Equilibria, LeChatelier's Principle
v010714

You are encouraged to carefully read the following sections in Tro (2^{nd} ed.) to prepare for this experiment: Sec 14.9 (LeChatelier's principle), pp 740 – 3 (indicators).

The effect of equilibrium is everywhere in the physical world. You have lots of experience with systems either at equilibrium (a state of very low potential energy) or not at equilibrium but one that desires to get there. Unburned gasoline surrounded by oxygen in a car is an example of this latter case.

$$\text{Gasoline } (C_xH_y) + O_2 \leftrightarrows CO_2 + H_2O$$

From experience, you know that such a system will react, consuming gasoline and oxygen, until the vast majority of this fuel has become CO_2 and H_2O; little apparent gasoline remains. As a result, you must continuously buy more gas. All chemical systems will always fall in one of the following categories:

1. **At equilibrium already**
2. **not at equilibrium,**
    a) **because of the presence of too much reactant and not enough product, or**
    b) **because of too much product and not enough reactant.**

A system at equilibrium appears to be undergoing no net change. Products and reactants are exchanging and reforming at equal rates. You can't outwardly tell anything is happening. Quite boring. This would describe the solution of $NaHSO_4$(aq) sitting in front of you on the lab bench. It's important to appreciate that many chemical systems fall in an "in between" equilibrium condition. Unlike gasoline and oxygen burning, many chemical systems are at equilibrium only when observable amounts of *both reactants and products* are *present at the same time* in the same mixture.

LeChatelier's principle proscribes the changes expected when a chemical system is not at equilibrium (cases 2a and 2b above). The system will shift (reaction occurs), causing reactants to make products or causing products to make reactants, such that the correct amounts of reactants and products are achieved, satisfying the equilibrium condition for that reaction at that temperature. The equilibrium constant, K, numerically specifies the equilibrium condition for a reaction, and K is temperature dependent.

All of the three reactions you study today will initially be at equilibrium. You will apply one of the following four possible stresses, causing it to momentarily not be at equilibrium, and then you will observe the changes that result as the system again reestablishes equilibrium.
The

Table 1. Possible stresses and responses in equilibrium conditions

Stress	**Problem(s) for a particular situation**	**Remedy, LeChatelier shift**
I. Remove Reactant	not enough R, too much P	Shift to R; [P] decrease, [R] increase
II. Add Product		
III. Remove Product	not enough P, too much R	Shift to P; [R] decrease, [P] increase
IV. Add Reactant		

combustion of gasoline example illustrates Stress example IV. Having lots of gasoline and O_2 relative to the possible CO_2 and H_2O means this system has too much Reactant and not enough Product to be at equilibrium. Gasoline burns, oxygen is consumed, and lots of CO_2 and H_2O form; the systems shifts to make lots of product to reach equilibrium. Throughout the experiment today, you will be asked to continuously categorize the type of stress applied. Every example will fall in one of the four categories (I – IV) summarized above.

Adding reactant or product

The concept of *adding* reactant or product is straightforward. You will know when you are adding reactant or adding product because of formula written on the label. Keep in mind that labels describe the complete compound formula, so that consideration of dissociation of ionic compounds, spectators ions, etc. is required to see that a particular reagent is a source of reactant or product. For example, adding solid $NaHSO_4$ to the following equilibrium, delivers the HSO_4^- ion to the mixture (due to the dissolution and dissociation of the salt), causing stress IV. You would expect to observe a change, a chemical reaction shift, to remedy this problem.

$$HSO_4^-(aq) + H_2O(l) \leftrightarrows SO_4^{2-}(aq) + H_3O^+(aq)$$

Sometimes, as in this present equilibrium case, all reactants and products are colorless. Even if there was a shift, you couldn't see the change with your eye. For this reason acid/base indicators will be added to two of the reactions. These indicators are brightly colored compounds whose color varies depending on $[H_3O^+]$ or $[OH^-]$. The two indicators we will be using today are summarized in Table 2.

Table 2. Acid / base indicators used in this experiment.

Indicator	**Color when $[H_3O^+]$ decreases, when $[OH^-]$ increases**	**Color when $[H_3O^+]$ increases, when $[OH^-]$ decreases**
Thymol blue	more peach colored	more purple/fuchsia colored
Phenolphthalein	more pink colored	less pink (sometimes colorless if $[OH^-]$ low enough)

Removing reactant or product

The concept of *removing* reactant or product sometimes involves physically removing the material. An example of this is a gaseous product escaping a mixture. More common for solutions and complex mixtures is the case that this effect is achieved by adding another reagent, one that specifically *reacts to remove* a particular reactant or product. Some examples of this today include the addition of HCl, an acid source of H_3O^+ and $EDTA^{4-}$. $EDTA^{4-}$ is an aggressive binder of metals ions like Mg^{2+} and Ca^{2+}. It is commonly added to soap to combat problems with hard water that reduce a soap's effectiveness. It is also added to test-tubes used to collect blood samples to reduce the amount of free $Ca^{2+}(aq)$, an ion that triggers blood coagulation and would otherwise cause the blood sample to clump together in the tube.

Remember, if a reagent is added and causes a shift in an equilibrium, it must be causing one of the four stresses summarized in Table 1. Your instructor may offer additional insights into the roles of the reagents used in this experiment.

Heat as a reactant or product, the temperature dependence of equilibria

Nearly every chemical reaction fits one of two categories: endothermic (ΔH is +, heat a reactant) or exothermic (ΔH is -, heat a product). The three equilibria studied today are examples of this. Generally heat is added by warming a reaction mixture. This added heat is either a reactant or a product, so that necessarily the effect causes a shift in response (Table 1). Generally heat is removed by cooling a reaction mixture, causing the opposite effect as when heat was added.

There is a difference between adding/removing heat vs adding/removing chemical reagents. Temperature changes cause the equilibrium condition (value of K) to change, and the system shifts, concentrations change, to meet this new value of K. Reagents added at constant temperature do not change the value of K, but this does cause the concentrations to momentarily not satisfy K. These concentrations readjust during the shift so that the same value of K is again reached.

Table 3. Reagents to be used in this experiment

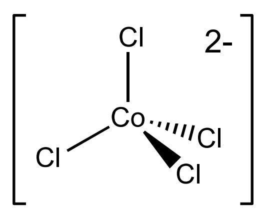
Reaction A	Reaction B	Reaction C
0.1 M $NaHSO_4$(aq) 0.1 M Na_2SO_4(aq) $NaHSO_4$(s) thymol blue indicator	0.1 M $MgCl_2$(aq) 0.1 M NaOH(aq) 0.1 M N_4EDTA(aq) concentrated HCl(aq) phenolphthalein indicator	0.1 M $CoCl_2$(in alcohol) 0.1 M $AgNO_3$(aq) concentrated HCl(aq)

General procedural notes:

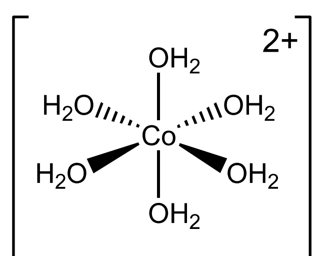
1. All solution reagents are in dropper bottles and are ready to be added directly.
2. Reactions will be conducted in a plastic well plate.
3. Table 4 outlines the experiment. Headings refer to well locations in the plate and numbers in parentheses represent the number of drops to be added.|
4. The contents of Reactions B and C should be placed in the appropriate waste container. Reaction A may be discarded down the drain.

Table 4. An outline for the experiment; each cell represents a well in a clear plastic well plate. Numbers in parentheses represent numbers of drops of solution to add.

	1	2	3	4	5
A	(10) $NaHSO_4$(aq) (1) thymol blue Na_2SO_4(aq)	(10) $NaHSO_4$(aq) (1) thymol blue	(10) $NaHSO_4$(aq) (1) thymol blue $NaHSO_4$(s)	(20) $NaHSO_4$(aq) (1) thymol blue hot/cold	(20) $NaHSO_4$(aq) (1) thymol blue cold/hot
B	(20) $MgCl_2$(aq) (10) NaOH(aq) HCl(aq)	(20) $MgCl_2$(aq) (10) NaOH(aq) Na_4EDTA(aq)	(20) $MgCl_2$(aq) (10) NaOH(aq) (1) phenolphthalein hot/cold/hot…		
	look for changes in the ppt				
C	(20) $CoCl_2$(eth) (1) H_2O HCl(aq) $AgNO_3$(aq)	(20) $CoCl_2$(eth) (1) H_2O hot/cold…			



blue



pink

A : $HSO_4^-(aq) + H_2O(l) \rightleftarrows H_3O^+(aq) + SO_4^{2-}(aq)$

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

C: $CoCl_4^{2-}(aq) + 6H_2O(l) \rightleftarrows Co(OH_2)_6^{2+}(aq) + 4Cl^-(aq)$

Procedural Steps, Results and Observations

A1, A2, A3

- Add 10 drops of $NaHSO_4(aq)$ to wells A1, A2, and A3.
- To each of these wells also add one drop of thymol blue.

1. Describe the color of thymol blue in the $NaHSO_4$ solution.

A1

Add $Na_2SO_4(aq)$ dropwise to well A1 until you see a color change.

2. (a) Describe the color of well A1 (relative to A2, the control) after the addition of Na_2SO_4.

(b) Is the addition of Na_2SO_4 predicted to cause equilibrium A to shift left or right? Explain.

A3

Add small crystals (rice size) of $NaHSO_4(s)$ to well A3 until you see a color change. Stir the mixture thoroughly with a toothpick after each addition of solid.

3. (a) Describe the color of well A3 (relative to A2, the control) after the addition of solid $NaHSO_4$.

(b) Is the addition of $NaHSO_4$ predicted to cause equilibrium A to shift left or right? Explain.

A4, A5

In wells A4 and A5 prepare identical mixtures of $NaHSO_4(aq)$ and thymol blue using the amounts in Table 4. Draw each mixture up into its own plastic pipet. Place the solution-filled bulb of pipet A4 in a hot water bath, leave it long enough until the color stops changing. Do the same with pipet A5 in a cold water bath.

4. (a) Describe the color of well A4 after the mixture is warmed. Does this heated mixture look more like well A1 or A3?

(b) Describe the color of well A5 after the mixture is cooled. Does this cooled mixture look more like well A1 or A3?

(c) Based on your description above, is reaction A predicted to be endothermic or exothermic?

B1, B2
Prepare identical mixtures of $MgCl_2$ and NaOH in wells B1 and B2 using the amounts in Table 4.

5. (a) Consult your text (p. 149). Explain your initial observations in these wells as the mixtures are formed in light of information found on p. 149.

(b) Consider equilibrium B, which of the stresses (I – IV of Table 1) is the reason for the observations you saw?

B1
To the mixture in well B1, add concentrated HCl(aq) dropwise, stirring with each drop, until you notice a change.
6. (a) Describe the effect observed on the B1 mixture when HCl is added.

(b) Is HCl added here a reactant or a product in reaction B? Did it's addition cause a change in equilibrium B? Explain.

(c) Which direction is equilibrium B predicted to shift with the addition of HCl(aq)? Why?

(d) Did the observed shift match your predictions? Explain.

B2
To the mixture in well B2, add Na_4EDTA(aq) dropwise, stirring with each drop, until you notice a change.
7. (a) Describe the effect observed on the B1 mixture when Na_4EDTA is added.

(b) Consider the role $EDTA^{4-}$ in commercial soaps and preserved-blood samples. What was the predicted effect of adding EDTA-solution to the mixture in B2?

(c) Did your observations for well B2 match your predictions? Explain.

B3

Prepare the mixture of $MgCl_2$, NaOH, and phenolphthalein in well B3 using the amounts in Table 4. Draw up the mixture in a plastic pipet and place the solution-filled bulb in a hot water bath. Leave it there until the mixture stops changing.

8. (a) Describe the effects of adding heat to the mixture in B3.

(b) Predict the effect of *removing heat* from the mixture in B3.

(c) Test your prediction in (b). Did it match your predictions? Explain.

(d) Based on your description above, is reaction B predicted to be endothermic or exothermic?

C1,C2

It is important that your wells be completely dry initially when studying equilibrium C. Add ethanolic solution of $CoCl_2$ to well C1. Add 1 drop of water to this mixture.

9. (a) Describe the effect of adding water to the original ethanolic $CoCl_2$ solution in well C1.

(b) Is the addition of water an example of stress I, II, III, or IV (Table 1)? Explain.

(c) Add concentrated HCl(aq) dropwise, with continuous stirring, to the mixture in C1 until you see a change. Describe the change you observed.

(d) Is the addition of HCl an example of stress I, II, III, or IV (Table 1)? Explain.

(c) Add $AgNO_3$(aq) dropwise, with continuous stirring, to the mixture in C1 until you see a change. Describe the change you observed.

(d) Is the addition of $AgNO_3$ an example of stress I, II, III, or IV (Table 1) (Hint: see p. 149)? Explain.

C2

Prepare the mixture of ethanolic $CoCl_2$ and *one drop* of water in C2 using the amounts in Table 4. Draw up the mixture in a plastic pipet and place the solution-filled bulb in a hot water bath. Leave it there until the mixture stops changing.

10. (a) Describe the effects of adding heat to the mixture in C2.

(b) Predict the effect of *removing heat* from the mixture in C2

(c) Test your prediction in (b). Did it match your predictions? Explain.

(d) Based on your description above, is reaction C predicted to be endothermic or exothermic?

Postlab Questions

1.What would have been the effect of adding $KHSO_4(s)$ to the mixture in A3 instead of the $NaHSO_4(s)$ that was added? Explain.

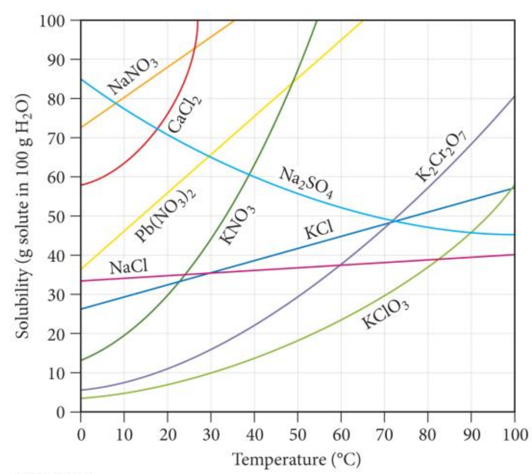
2. Potassium ion has the same charge as silver ion. In this case (C1) would the same effect have been observed if $KNO_3(aq)$ was added instead of $AgNO_3(aq)$? Explain.

3. (a) Most solids are more soluble in hot water. Does $Mg(OH)_2$ fit this pattern? Explain.

(b) Figure 12.11 (from Tro, shown at right) summarizes the temperature dependent water solubilities of nine different compounds.

i) Identify one solid from this figure whose water solubility trend is the same as $Mg(OH)_2$.

ii) Identify one solid from this figure whose water solubility trend is opposite of $Mg(OH)_2$.



4. Equilibrium C is an example of a reaction used as a moisture indicator in a commercial desiccant called Drierite, mostly anhydrous $CaSO_4$.

(a) The image at right shows Drierite with (blue) and without (white) the cobalt(II) chloride indicator. What color is expected when the material has absorbed as much moisture as possible?

(b) The spent desiccant in (a) can be regenerated by heating (dehydrating the hydrated calcium sulfate). What color change should be observed in the indicator and why?

Prelab Questions

1. Copper makes beautifully colored compounds and polyatomic ions. One such example is summarized below

$$Cu(OH_2)_6^{2+}(aq) \ + \ 4Br^-(aq) \leftrightarrows CuBr_4^{2-}(aq) \ + \ 6H_2O(l)$$

(a) Grey anhydrous $CuSO_4$ dissolved in water gives a blue solution. Explain.

(b) The addition of AgBr(s) to the mixture above causes no change. However, when NaBr(s) is added a noticeable color change occurs. Predict the color change and explain it in terms of LeChatelier's principle.

(c) Why did the two different solids added in (b) have two different effects?

2. Cave formations like Blanchard Springs Caverns (Fifty-six, AR) are very sensitive to atmospheric CO_2 levels. The pertinent reaction is

$$CaCO_3(s) \ + \ CO_2(g) \ + \ H_2O(l) \ \leftrightarrows \ Ca^{2+}(aq) \ + \ 2HCO_3^-(aq)$$

(a) If atmospheric CO_2 levels begin to fall, what effect is this predicted to have on the rock formations in these caves?

(b) Use appropriate enthalpies from your text appendices, determine the enthalpy change for the top reaction. Under what conditions hot or cold are the cave formations presumed to be more soluble?

3. Consult the Figure 14.12 of Tro. p 647.

(a) Sketch a Lewis dot structure for the NO_2 molecule. Refer to your dot structure, and use it to explain why two NO_2 molecules dimerize to make N_2O_4.

(b) Bond formation *always* releases energy. Is the information on p. 647 about the reaction $N_2O_4 \rightarrow 2NO_2(g)$ consistent with this statement? Explain.

(c) When it's *really cold* in Little Rock, the sky can look clear and blue. The same sky in July might look brown and gross. In both cases the many cars in the city are producing significant amounts of nitrogen oxides. Describe these observations in terms of LeChatelier's principle.