

CHEM 1112: Chemical Equilibrium

modified by K.Stone and J. Burt 10/10/96

I. A Qualitative Study of LeChatelier's Principle and the Common Ion Effect

Introduction:

In today's experiments we will consider chemical equilibrium and the reversibility of chemical reactions. As part of our study of equilibrium we have learned that equilibrium is reached when the rate of the forward and reverse reactions are equal. For the generalized reaction below:



The equilibrium constant expression is

$$K_{eq} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

We have also studied the principle of Le Chatelier, stating that if a stress is placed upon a system in equilibrium, the equilibrium will shift in such a manner to relieve the stress.

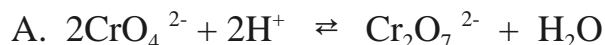
The object of the experiments in Part I is to illustrate how chemical equilibria shift when stresses

are placed on the equilibrium system. Your interpretations should include chemical reactions describing the observed changes, particularly with respect to the "common ion effect."

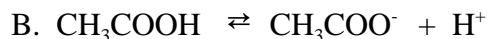
Procedure:

Note: The solutions used in this section contain heavy metals. Dispose of excess reagents and waste in the **Aqueous Waste** container.

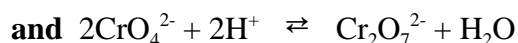
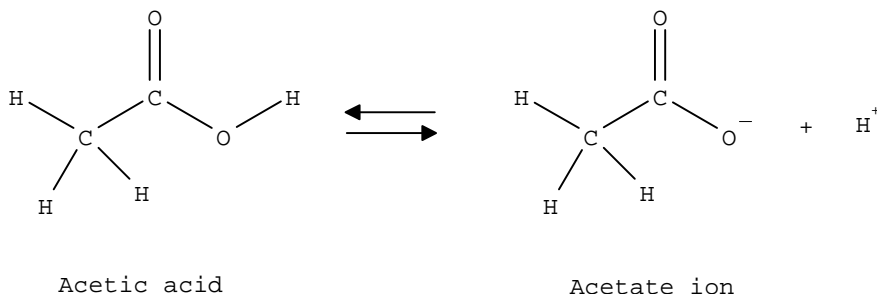
For each equation below, you will study the effects of adding or removing reactants or products. Please write the results that you observe for each reaction in your notebook as you do the experiments. Then, in your **well organized conclusion**, rewrite each of the equilibrium reactions and explain your observations. Remember Le Chatelier!



1. Place approximately 5 ml of 1 M K_2CrO_4 (potassium chromate) in a test tube. Note the color. Add 3 M H_2SO_4 (sulfuric acid) to the K_2CrO_4 solution until you observe a change in color. Describe the change in your notebook with respect to the reaction given below.
2. To the solution from step 1 add 6M NaOH until you observe another color change. Describe the change in your notebook, again with respect to the given reaction.
3. To the solution from step 2 add H_2SO_4 until the same color you previously observed in step 1 appears.



1. Add approximately 5 ml of 0.1 M acetic acid (CH_3COOH) to a test tube and include 2 to 3 drops of methyl orange pH indicator. (Note color.)
2. Next add 1 M $\text{Na}(\text{CH}_3\text{COO})$ (sodium acetate) solution until a color transition is observed. (Wastes: the chemicals in this section can be washed down the drain).



1. Place approximately 5 ml of 0.1 M BaCl_2 (barium chloride) solution in a test tube. (Note color.) Add several drops of 1 M K_2CrO_4 and note the result. (Wastes: the heavy metal solutions should be put in the **Aqueous Waste** container).
2. Add 6 M HCl until you observe a significant change in the above solution.

Be sure to account for the observed changes in your conclusion.

II. A Quantitative Study of the Equilibrium between Iron(III) and Thiocyanate Ion

The ions Fe^{+++} (ferric ion) and SCN^- (thiocyanate) react in solution to form a blood-red substance, the composition of which has been a subject of some controversy among chemists. Two possible equilibrium equations for this reaction are:



Our goal is to determine which of the above equations is correct.

Each equilibrium equation, 1 and 2, gives a different expression for the equilibrium constant. For equation 1 the equilibrium constant is:

$$K_1 = \frac{[\text{Fe}(\text{SCN})^{2+}]}{[\text{Fe}^{3+}][\text{SCN}^-]} \quad (3)$$

For equation 2 the equilibrium constant is:

$$K_2 = \frac{[\text{Fe}(\text{SCN})_3]}{[\text{Fe}^{3+}][\text{SCN}^-]^3} \quad (4)$$

Since the value for an equilibrium constant is independent of the relative concentrations of the reactants, we can distinguish between reactions (1) and (2). This is done by varying the relative concentrations of Fe^{3+} and SCN^- . For each variation of the relative concentrations the values for K_1 and K_2 are calculated. Only the expression for the equilibrium constant derived from the proper equilibrium reaction will actually remain constant (or at least it will be more constant than the one derived from the incorrect reaction).

In order to evaluate the equilibrium constants, the equilibrium concentrations of Fe^{3+} , of SCN^- , and of the reaction product $[\text{Fe}(\text{SCN})^{2+}]$ or $[\text{Fe}(\text{SCN})_3]$ must be determined. The concentration of the reaction product is determined by measuring the absorbance for color intensity of its red color with a spectrophotometer. The absorbance is directly proportional to the concentration of the colored species. Beer's law states that the amount of light energy absorbed is directly proportional to the concentration of the absorbing species, as shown in equation 5.

$$A = \epsilon bc$$

A is absorbance, b is the path length of the measuring tube, ϵ is the molar absorptivity and c is the concentration of the absorbing species. In our experiment will use the value: C1 or C2 for the molar absorptivity and b is 1 cm for our instrument. Therefore, once the absorbance has been measured, you can calculate the concentration from the equation:

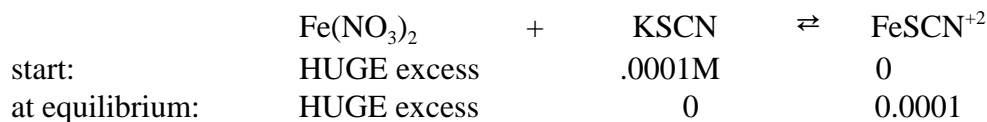
$$\text{Absorbance} = C1 [\text{Fe}(\text{SCN})^{2+}] \quad (6)$$

If $[\text{Fe}(\text{SCN})_3]$ is the red complex, you may calculate its concentration from the equation:

$$\text{Absorbance} = C2 [\text{Fe}(\text{SCN})_3] \quad (7)$$

At this point you should realize that you can measure A, but you do not know C1, C2 or the concentrations of $[\text{Fe}(\text{SCN})^{2+}]$ and $[\text{Fe}(\text{SCN})_3]$. You have two equations and four unknowns. Even the most wonderful mathematician won't be able to solve these equations. So, we are going to make some approximations and pull a few tricks out of our experimental design bag.

We will use a very concentrated solution of $\text{Fe}(\text{NO}_3)_3$ and a small concentration of KSCN in our first test tube. In this situation the $\text{Fe}(\text{NO}_3)_3$ will be in an overwhelming excess and this will force the equilibrium as far to the right as possible. The limit to the amount of iron thiocyanate formed will be the concentration of the thiocyanate ion.



Now we know the concentration of FeSCN^{+2} at equilibrium. We can solve equation 6 for the value of C1.

$$A_{(\text{tube } 1)} = C1[.0001]$$

measure calculate

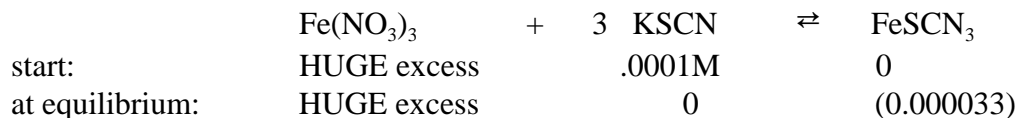
Since C1 is a constant, you can use this value for all of the other concentrations of $\text{Fe}(\text{NO}_3)_3$ that are added to a constant amount of KSCN. Thus for each solution, you will know A (absorbance) b(1 cm) and C1.

For all other tubes:

$$A(\text{tube } 2, 3, 4, \text{ or } 5) = C1 [\text{FeSCN}^{+2}]$$

measure known calculate

For the other possible reaction:



Note: it took 3 moles of thiocyanate ion to combine to form 1 mole of the iron thiocyanate complex. Therefore, the equilibrium concentration of the complex is:

$$(0.0001/3) = 0.000033 \text{ or } 3.3 \times 10^{-5}.$$

Use the procedure above to determine C2, and all of the equilibrium concentration values for FeSCN_3 .

The equilibrium concentrations of Fe^{+++} and SCN^- are calculated as follows:

Assuming that equation (1) is the correct reaction, we have:

$$[\text{Fe}^{3+}]_{\text{eq}} = [\text{Fe}^{3+}]_{\text{i}} - [\text{Fe}(\text{SCN}^{++})]_{\text{eq}}$$

$$[\text{SCN}^-]_{\text{eq}} = [\text{SCN}^-]_{\text{i}} - [\text{Fe}(\text{SCN}^{++})]_{\text{eq}}$$

Assuming that equation (2) is the correct reaction, we have:

$$[\text{Fe}^{3+}]_{\text{eq}} = [\text{Fe}^{3+}]_{\text{i}} - [\text{Fe}(\text{SCN})_3]_{\text{eq}}$$

$$[\text{SCN}^-]_{\text{eq}} = [\text{SCN}^-]_{\text{i}} - 3[\text{Fe}(\text{SCN})_3]_{\text{eq}}$$

(Note: In all the expressions such as $[\text{Fe}^{3+}]_i$, the i refers to the initial concentration.)

Now that all of the equilibrium concentrations have been determined, you can calculate the equilibrium constants for each possible reaction.

From the equilibrium constant values, you can now decide which reaction, (1) or (2), is actually occurring. The correct equilibrium constant will change relatively little as the concentrations of reactants and products are varied.

Do all of your calculations using Excel. You include a table of values and a table with your formulas. Be sure to use parentheses correctly. To raise a number to the third power, use the '^' symbol. Here is an example:

$$(3*4)/(4*5^3) = .024$$

Conclusion: Compare K_1 and K_2 with respect to their constancy. According to your data which value of K has more constant values? Based on this observation, which is the correct chemical reaction, equation 1 or equation 2? In your conclusion state which complex is formed, and support your conclusion with a restatement of the values that you obtained for the equilibrium constants.

Procedure

Read everything before embarking on this adventure. Some solutions will need to be used as soon as they are made, so you will need to plan your work accordingly.

Check out from the stockroom: 2 - 10 ml pipettes

2 - cuvettes (do not use these as test tubes)

1 - pipette bulb

10 - test tubes

1 - 100 ml volumetric flask

Standardization of Spectrophotometer:

Use the **same** spectrophotometer for all of your measurements. Make sure that the wavelength is set at 480 nm (nanometers). Turn on the instrument and allow it to warm up for 15 minutes.

Standardize the instrument as follows:

1. With the sample holder completely empty and the sample holder cover closed, set the meter to infinite (∞) absorbance using the knob at the bottom **left-hand** side of the instrument.
2. Fill the cuvette with distilled water. [Caution: keep your fingers off the bottom part of the cuvette. Finger prints will cause an erroneous absorbance to be observed]. Place it in the spectrophotometer, verify proper alignment and adjust the meter to zero absorbance with the knob at the lower **right-hand** side of the instrument. The instrument is now ready to use.

Preparation of $\text{Fe}(\text{NO}_3)_3$ solutions:

You will be using the $M_1V_1 = M_2V_2$ equation. M is molarity and V is volume for solution 1

(concentrated) and solution 2 (dilute). For example, if you need a 100 ml of a 0.1 molar solution of NaOH and there is only a 1M solution on the bench, you would take 10 ml of the 1 M solution and add enough water to make 100 ml

$$\begin{aligned}M_1 &= 1 \text{ M} \\V_1 &= 10 \text{ ml} \\M_2 &= 0.1 \text{ M} \\V_2 &= 100 \text{ ml}\end{aligned}$$

MAKING THE STANDARDS

Starting with the stock 0.20 M $\text{Fe}(\text{NO}_3)_3$ you are going to make 4 dilutions.
The results will be:

Test tube A: 0.20M $\text{Fe}(\text{NO}_3)_3$ standard
Test tube B: 0.020M $\text{Fe}(\text{NO}_3)_3$ standard
Test tube C: 0.010M $\text{Fe}(\text{NO}_3)_3$ standard
Test tube D: 0.0050M $\text{Fe}(\text{NO}_3)_3$ standard
Test tube E: 0.0025M $\text{Fe}(\text{NO}_3)_3$ standard.

1. Label five clean dry 18 mm x 150 mm test tubes A, B, C, D, and E. Also, it will be useful to put the concentration of each solution on the label, ie: A, 0.2M $\text{Fe}(\text{NO}_3)_3$.
2. Fill test tube A with 0.20 M $\text{Fe}(\text{NO}_3)_3$ from the stock bottle.
3. Carefully pipet 10.0 ml of the 0.20 M $\text{Fe}(\text{NO}_3)_3$ from test tube A into your 100 ml volumetric flask. Dilute with deionized water to 100.0 ml. Cover the top and mix by inverting several times. Fill test tube B with this solution.
3. Pipet 10.0 ml of deionized water into test tubes C, D, and E.
4. Pipet 10.0 ml of the 0.020M $\text{Fe}(\text{NO}_3)_3$ from test tube B into test tube C and mix thoroughly.
5. Pipet 10.0 ml of the 0.010M $\text{Fe}(\text{NO}_3)_3$ from test tube C into test tube D and mix thoroughly.
6. Pipet 10.0 ml of your 0.0050M $\text{Fe}(\text{NO}_3)_3$ from test tube D into test tube E and mix thoroughly.

MIXING THE ABSORBANCE SOLUTIONS

1. Label five clean dry 18x150 test tubes 1 to 5.
2. Pour about 40 ml of 0.0002 M KSCN from the stock bottle into a clean dry 100 ml beaker.
3. Carefully pipet 5.0 ml of 0.0002 M KSCN into each tube.

4. Pipet 5.0 ml 0.20M $\text{Fe}(\text{NO}_3)_3$ into test tube 1 . Mix well and measure the absorbance immediately.
5. Repeat this procedure with test tubes 2 through 5 using the amounts of the $\text{Fe}(\text{NO}_3)_3$ solutions indicated below.
 - Test tube 2: add 5.0 ml of 0.020M $\text{Fe}(\text{NO}_3)_3$
 - Test tube 3: add 5.0 ml of 0.010M $\text{Fe}(\text{NO}_3)_3$
 - Test tube 4: add 5.0 ml of 0.0050M $\text{Fe}(\text{NO}_3)_3$
 - Test tube 5: add 5.0 ml of 0.0025M $\text{Fe}(\text{NO}_3)_3$.

You will need to calculate the actual molarity to get the initial concentration of Fe^{+3} and SCN^- of these solutions. Use the $M_1V_1 = M_2V_2$ equation to do this.

It is important to measure the absorbance immediately after mixing since the color of the red complex fades with time. Record your absorbance readings in your notebook.

Note: Pour the $\text{Fe}(\text{NO}_3)_3$ and KSCN solutions down the drain and rinse the test tubes, beakers, pipets, and cylinders with deionized water **three times**.

Your report should include the following:

Title

Purpose (in your own words)

Results and observations obtained in the lab (with your instructor's signature)

Calculations:

Excel table containing the values for K1

Excel table containing the values for K2

Excel table containing the formulas for K1

Excel table containing the formulas for K2

Sample calculation for the molarity of Fe^{+3} in tube 5

Conclusion:

This should include a well organized discussion of the effects of stress on the three equilibrium systems in part I with explanations for all of the observations. A restatement of the observations would enhance this discussion. The results from part two should be summarized. Use these K values to rationalize which of the two complexes is formed.