Determination of an Equilibrium Constant

Minneapolis Community and Technical College
Principles of Chemistry II, C1152
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I. Introduction

Equilibrium

Consider the following situation: It's rush hour and cars are entering the I-94 freeway at a rate of 30 cars per second. Obviously, if this were the only thing affecting traffic, congestion would build and soon all cars would be at a stand still. A competing process in which cars leave the freeway, reduces the total number of automobiles. These two processes, cars leaving and entering, determine the overall number of automobiles on the roadway.

The term "**equilibrium**" applies when the rates of both processes are equal. For example, if cars enter the freeway at 30 cars/second and leave the freeway at 30 cars/second, the total number of cars on the freeway never changes and we have a state of equilibrium. Traffic control engineers work to regulate traffic on and off of a freeway as they attempt to achieve total traffic volume and movement that reduces the average commute time for everyone.

Chemical equilibrium exists when the rate of the forward reaction (reactants --> products) is equal to the rate of the reverse reaction (reactants <-- products). Once equilibrium has established itself, the concentrations of product and reactant species stay constant. Thus, if the chemical system is in equilibrium, the amount of product produced will never change regardless of how long you wait.

However, should product species be physically removed from the reaction container, additional product will be made to replace the removed amount at the expense of the reactants (i.e. Le Chatelier's Principle). Eventually, a new equilibrium is achieved where upon no changes are observed until product is again removed from the container. Thus, by removing products continuously as they are made, it is possible to maximize the reaction's yield.

Now, consider the following general chemical equation:

$$x\ X\ +\ y\ Y\ +\ z\ Z\ \longleftrightarrow\ a\ A\ +\ b\ B\ +\ c\ C$$

The double arrow indicates that both forward and reverse reactions occur and that the chemical system can achieve equilibrium. The lower case letters represent the coefficients in the balanced chemical equation. Upper case letters identify the product and reactant species.
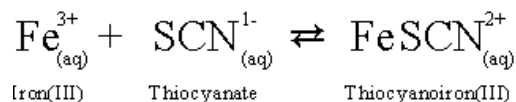
At equilibrium, the concentrations of products and reactants are related in the following way:

$$K_{eq} = \frac{[A]^a [B]^b [C]^c}{[X]^x [Y]^y [Z]^z}$$

where quantities in brackets are *molar concentrations* of products (numerator) and reactants (denominator) raised to an exponent that is the corresponding coefficient from the balanced chemical equation. K_{eq}, the equilibrium constant, remains constant from trial to trial so long as the temperature doesn't change. This expression does NOT describe a system that has yet not reached equilibrium. Only once equilibrium has been attained will the value of the expression equal the equilibrium constant, K_{eq}.

$Fe^{3+}_{(aq)}$, $SCN^-_{(aq)}$ and $FeSCN^{2+}_{(aq)}$ equilibrium

In this experiment, we will study the reaction of $Fe^{3+}_{(aq)}$ and $SCN^-_{(aq)}$ ions and the **deep red**-colored $FeSCN^{2+}_{(aq)}$ complex ions they form:

$$Fe^{3+}_{(aq)} + SCN^{1-}_{(aq)} \rightleftharpoons FeSCN^{2+}_{(aq)}$$

$$\text{Iron(III)} \qquad \text{Thiocyanate} \qquad \text{Thiocyanoiron(III)}$$

The final equilibrium concentrations of products and reactants depend on the initial amounts of reactants before the reaction occurs. However, *regardless of the initial concentrations*, the final equilibrium concentrations must satisfy the following relationship:

$$K_{eq} = \frac{[FeSCN^{2+}]}{[Fe^{3+}]\,[SCN^-]}$$

where the bracketed terms are molar equilibrium concentrations of the different species, and K_{eq} is the *temperature dependent* equilibrium constant.

Six reaction mixtures, differing in their initial reactant amounts, will be studied. The Logger Pro colorimeter will be used to determine the equilibrium *concentration* of the **deep red** product complex ion, $FeSCN^{2+}$. Calculations proceed as follows:

1. Colorimeter: Measure absorbance of solution and convert to $[FeSCN^{2+}]$
2. Use $[FeSCN^{2+}]$ to determine the number of moles of $FeSCN^{2+}$ produced.
3. Determine how many moles of Fe^{3+} and SCN^{1-} are required to produce product (use mole ratios)
4. Determine how many moles of Fe^{3+} and SCN^{1-} were initially present.
5. Determine how many moles of Fe^{3+} and SCN^{1-} remain at equilibrium.
6. Calculate the equilibrium concentrations of Fe^{3+} and SCN^{1-}.
7. Substitute the known $FeSCN^{2+}$, Fe^{3+} and SCN^{1-} *equilibrium* concentrations into the K_{eq} expression above.
8. Compare calculated values of K_{eq} from each trial. Ideally they should be constant from one trial to the next.

Colorimeter Operation

The deep red color of the equilibrium mixture is due to the presence of $FeSCN^{2+}$ complex ions that *absorb* blue light. The solution appears red because *red light is transmitted*. Thus, a solution that transmits less blue light has higher concentrations of $FeSCN^{2+}$ than a solution that transmits more blue light.

A two point calibration curve (figure at right) is used to convert measured absorbances (via colorimeter) to $FeSCN^{2+}$ concentrations.

Calibration point #1 is determined by using a solution that contains no $FeSCN^{2+}$. This solution should have zero absorbance.

Calibration point #2 is determined using a **standard** solution that is initially 100x more concentrated in Fe^{3+} than SCN^-. Such large amounts of Fe^{3+} force the equilibrium in this case far in favor of the products. Thus, it can be assumed that approximately all of the SCN^- ions have reacted and have been converted into product. Consequently, the concentration of $FeSCN^{2+}$ in the equilibrium mixture is approximately equal to the original SCN^- concentration before the reaction occurred.

The graph and trendline analysis is used to determine $FeSCN^{2+}$ concentrations from absorbance measurements performed on all other equilibrium mixtures.
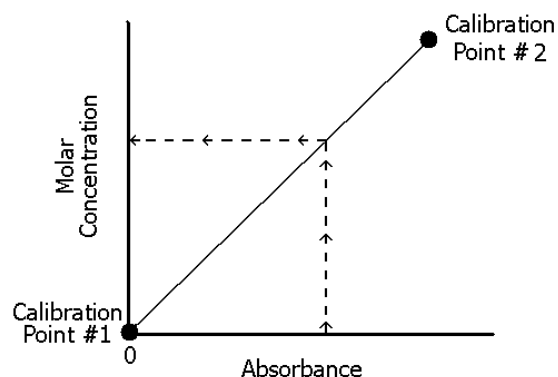
II. MSDS: Chemical Information

Potassium Thiocyanate (0.02 % solution)
WARNING! HARMFUL IF SWALLOWED OR INHALED. CAUSES IRRITATION TO SKIN, EYES AND RESPIRATORY TRACT.
Health Rating: 2 - Moderate
Flammability Rating: 0 - None
Reactivity Rating: 1 - Slight
Contact Rating: 1 - Slight
Lab Protective Equip: GOGGLES; LAB COAT
Storage Color Code: Orange (General Storage)
Potential Health Effects
Inhalation: Causes irritation to the respiratory tract. Symptoms may include coughing, shortness of breath.
Ingestion: May cause vomiting, disorientation, weakness, low blood pressure, convulsions and death which may be delayed. The probable lethal dose is between 15-30 grams.
Skin Contact: Causes irritation to skin. Symptoms include redness, itching, and pain.
Eye Contact: Causes irritation, redness, and pain.
Chronic Exposure: Prolonged or repeated skin exposure may cause dermatitis. Repeated ingestion of small amounts may cause hives, abnormal bleeding, weight loss, mental effects, and an enlarged thyroid.
Aggravation of Pre -existing Conditions: No information found.

Iron nitrate solution
Potential Health Effects
Eye: May cause eye irritation.
Skin: May cause skin irritation.
Ingestion: May cause irritation of the digestive tract.
Inhalation: May cause respiratory tract irritation.
Chronic: No information found.

III. Procedure

*You will be working in pairs today.

Solutions:

- Obtain *seven* vials with screw-on lids and number them 1 through 7.
- Prepare the following solutions using two burettes provided at your station.
- Be sure to thoroughly mix the contents of each of the seven vials before proceeding to the analysis steps.
- On your bench top, line up the solutions 1, 2, …7 and observe how the color intensity changes. Record your observations in your notebook.

Colorimeter:

The colorimeter used in today's experiment is shown above. **Blue light** will be used since it is readily absorbed by the $FeSCN^{2+}$ complex ion. As the concentration of $FeSCN^{2+}$ in the sample increases, the amount of blue light that emerges from the sample and is detected decreases. Observe the following precautions when using the colorimeter:

- Handle the cuvettes by the ribbed sides. Fingerprints on the smooth sides will adversely affect your results.
- Wipe the cuvette's smooth sides with a KimWipe if necessary.
- Orient the cuvette in the colorimeter such that the light beam travels through the smooth sides.
- From trial to trial, position the cuvette in the colorimeter in exactly the same way. You can mark the bottom of the cuvette to help with this.
- When making the absorbance measurement, close the lid on the colorimeter.
- Don't spill samples in the calorimeter. If you do, please alert the instructor.
- When done for the day, remove all cuvettes/samples from the colorimeter.

Vial Number	0.00200 M Fe(NO$_3$)$_3$ (mL)	0.00200 M KSCN (mL)
1	1.0	9.0
2	2.0	8.0
3	4.0	6.0
4	5.0	5.0
5	6.0	4.0
6	8.0	2.0
	0.200 M	0.00200 M
7 (Standard)	9.0	1.0

A. Colorimeter calibration

- *All cuvettes should be wiped clean and dry on the outside with a tissue.*

- *Handle cuvettes only by the top edge of the ribbed sides.*

- **All solutions should be free of bubbles.** Gently tap the cuvette to eliminate bubbles clinging to the inside surfaces (especially the smooth sides!)

  Prepare a "blank" by filling a clean cuvette 3/4 full with distilled water. Open the colorimeter door and place the water filled blank cuvette inside. Make sure the cuvette's smooth, transparent windows are positioned correctly. Close the colorimeter door.

  Use the colorimeter's arrow keys to select the **470 nm (blue)** light source.

  Press and hold the "CAL" button for 1 second and release. When the red light on the colorimeter stops flashing, it is ready for use and the computer display should read close to 100% T.

  If after calibration Logger Pro indicates something other than 100% (+/- 0.5%), alert the instructor who will then supply you with a new cuvette. Repeat the calibration procedure with the new cuvette.

  Use the same cuvette for all of the subsequent measurements.

B. Absorbance Measurements

The colorimeters will display values of %T and not absorbance. Convert these values to absorbance using the following formula:

Absorbance = -log (%T/100)

Insert the cuvette containing solution #1 (¾ full) into the colorimeter, *close the lid* and record the %T reading.

Remove the cuvette and carefully immerse it in an ice/water bath. Monitor the solution's temperature (in the cuvette) with a thermometer. When the temperature reaches 8°C remove the cuvette and QUICKLY dry it with a tissue.

Place the cooled cuvette into the colorimeter and record the %T.

> ** Don't delay. Condensation forming on the exterior of the cold cuvette will cause %T measurements to drop. Your goal is to get a good %T measurement before condensation becomes a significant problem.*

Dispose of the solution in a waste beaker and rinse the cuvette with ~ 1mL of the next solution to be tested. Only solutions 1, 3 an 5 are tested at both room temperature and at 8°C.

> ** Wipe the thermometer off with a KimWipe between trials to avoid contamination.*

Cleanup: Place your used solutions in the containers marked "Student Products" at the sides of the lab. Remove your cuvette from the colorimeter before putting the colorimeter away. Nitric acid, present in the samples, will severely damage the colorimeter if a cuvette is left in the sample compartment! Rinse the cuvette several times with distilled water and set aside, inverted, to dry.

Data Table I:

	Warm Trials		Cooled Trials	
	Temp (°C)	**%T / Abs.**	**Temp (°C)**	**%T / Abs.**
Vial #1			8.0 °C	
Vial #2				
Vial #3			8.0 °C	
Vial #4				
Vial #5			8.0 °C	
Vial #6				
Vial #7 (standard)				

Data Analysis Table II:

		Vial #1		Vial #2		Vial #3		Vial #4		Vial #5		Vial #6	
		Warm	Cold	Warm	Cold	Warm	Cold	Warm	Cold	Warm	Cold	Warm	Cold
$FeSCN^{2+}$	Absorbance												
	Concentration												
	Moles												
Fe^{3+}	Initial Concentration												
	Initial moles												
	Final Moles												
	Equilibrium Concentration												
SCN^{-}	Initial Concentration												
	Initial moles												
	Final Moles												
	Equilibrium Concentration												
K_{eq}													

Data Analysis

Point Calibration Curve

1. Determine the $FeSCN^{2+}$ concentration for vial #7
   a. Calculate the number of moles of SCN^- originally present in vial #7. Assume this is the same number of moles of $FeSCN^{2+}$ produced.
   b. Calculate the $FeSCN^{2+}$ final concentration by dividing the number of moles by the solution's *total volume*.
2. Use Excel to construct a 2 point calibration curve (concentration vs. absorbance) using the absorbance and concentration of the standard (from preceding step), and the point (0,0).

3. Perform a linear trendline analysis and record the trendline equation Display a minimum of 8 significant figures for both the slope and the y intercept.)

Calculations: (reported in the data tables above)

The following calculations can be GREATLY simplified by using an EXCEL spreadsheet.
Please ask if you would like help doing this.

1. Use the trendline equation from the 2 point absorbance calibration curve to determine the concentrations of $FeSCN^{2+}$ in the 6 unknown equilibrium mixtures (vials #1 - #6) at both high and low temperatures.

2. Use each solution's total volume and measured $FeSCN^{2+}$ concentration to calculate the number of moles of $FeSCN^{2+}$ present at equilibrium in each of the trials.

3. Calculate the number of moles of Fe^{3+} and SCN^- that were *initially present* for in each of the 6 vials at both temperatures.

4. Subtract the number of moles of $FeSCN^{2+}$ present at equilibrium (step 2) from each of the initial mole amounts (step 3) to determine the number of moles of each reactant left over when equilibrium was reached. (This works so simply because all mole ratios are 1:1)

5. Calculate the equilibrium concentrations of Fe^{3+} and SCN^- by dividing their residual amounts (results of step 4) by the solution's total volume.

6. Use the equilibrium concentrations to calculate equilibrium constants for each of the trials. (Equation is provided in Introduction section)

7. Calculate the average K_{eq} for high and low temperatures.

V. Team Report

Page 1:

- **Upper right corner:** Your name, Your lab section number, Date of experiment

- **Calibration Graph:**
  Copy and paste our Excel calibration graph on the page.
  Include trendline and trendline equation.

Page 2:

- **Data tables I and II :**
  Obtain a copy of the two data tables from the lab-handout web site
  and fill in your values.

Page 3:

Answers to the following questions:

1. Use your calculated K_{eq} values to determine :
   a. the average K_{eq} for room temperature. (Show work)
   b. the average K_{eq} for colder temperatures. (Show work)

2. Compare the two average values from question #1 and determine if the equilibrium reaction is endothermic or exothermic. Explain your answer in *ridiculous* detail.

3. Refer back to your observations of the seven solutions and explain, in chemical terms, why the color intensity was greatest for the middle solutions and faintest for solutions 1 and 6.