I. Introduction

Equilibrium

Consider the following situation: It is 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. However, cars also leave the freeway and this 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 a situation that reduces the average commute time for everyone.

Chemical equilibrium exists when the rate of the forward reaction converting reactants to products is equal to the rate of the reverse reaction which converts products into reactants.

\[ \text{Rate}_{\text{forward \ reaction}} = \text{Rate}_{\text{reverse \ reaction}} \]

Once chemical equilibrium has been established, the levels of products and reactants remain constant. Thus, if the system is in equilibrium, no further changes will be observed. Note however that on a molecular/atomic scale, both forward and reverse reactions still occur.

Now, consider the following general chemical equation:

\[ x \ X + y \ Y + z \ Z \leftrightarrow a \ A + b \ B + c \ C \]

The double arrow (\( \leftrightarrow \)) indicates that both forward and reverse reactions occur and that this is a chemical equilibrium situation. The lower case letters are the coefficients in the balanced chemical equation and the upper case letters identify the product and reactant species.

Because equilibrium concentrations of products and reactants don’t change, their ratio is constant:

\[ \frac{[\text{Products}_{\text{eq}}]}{[\text{Reactants}_{\text{eq}}]} = \frac{[A]_\text{eq}^a [B]_\text{eq}^b [C]_\text{eq}^c}{[X]_\text{eq}^x [Y]_\text{eq}^y [Z]_\text{eq}^z} = \text{constant} = K_c \]

This constant is known as the concentration based equilibrium constant \( K_c \) and is calculated using equilibrium concentrations of reactants and products. These molar concentration values for each species appear in brackets raised to an exponent that is the coefficient from the balanced chemical equation. This value of \( K_c \) remains constant from trial to trial as long as the temperature is constant.

The 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 product they form; deep red/orange-colored FeSCN\(^{2+}\) (aq) complex ions:

\[
\begin{align*}
\text{Colorless} & \quad \text{Colorless} & \quad \text{Orange} \\
\text{Fe}^{3+} \text{(aq)} & + & \text{SCN}^- \text{(aq)} & \leftrightarrow & \text{FeSCN}^{2+} \text{(aq)} \\
\text{Iron(III)} & & \text{Thiocyanate} & & \text{Thiocyanatoiron (III)}
\end{align*}
\]

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:
\[ K_c = \frac{[\text{FeSCN}^2+]_{\text{eq}}}{[\text{Fe}^{3+}]_{\text{eq}} [\text{SCN}^-]_{\text{eq}}} \]  

(Equation 1)

whereas described previously, brackets denote equilibrium molar concentrations of products & reactants.

Our goal in this experiment is to determine the equilibrium constant, \( K_c \). To do so, we’ll need equilibrium concentrations we can substitute into the equation above. Because the FeSCN\(^{2+}\) is the only colored species (red/orange), its equilibrium concentration can be measured directly using the LoggerPro colorimeter. The equilibrium concentrations of the reactants Fe\(^{3+}\) and SCN\(^-\) can be then determined by subtracting the product amounts from the initial reactant concentrations.

Six reaction mixtures with different initial reactant amounts will be analyzed at constant temperature to verify \( K_c \) values are constant. Ideally, \( K_c \) would be the same in all trials as long as the temperature doesn’t change.

Additionally, three trials will be performed at lower temperatures to determine the effect on \( K_c \). Remember that since \( K_c \) is the product to reactant ratio, an increase in \( K_c \) means there are more products and less reactants. Conversely, a decrease in \( K_c \) means there are fewer products and more reactants in the equilibrium mixture.

**Equilibrium: The I.C.E. method**

The method used to solve equilibrium problems is referred to as **I.C.E.**, which is an abbreviation for **I**nitial, **C**hange and **E**quilibrium:

1. **Initial concentrations**: pre-equilibrium concentrations of all reactants and products
   a. Usually require dilution calculations and are not “bottle label” concentrations
   b. Solids and liquids are not included in this step as their molar concentrations are constant.

2. **Change**: The changes to the initial concentrations that are required to reach equilibrium.
   a. Includes a variable “X”
   b. Uses stoichiometric coefficients from the balanced chemical equation
   c. “-” denotes decreases and “+” denotes increases
   d. May require a \( Q \) vs. \( K_c \) comparison to determine the direction of the equilibrium change.

3. **Equilibrium**: The new concentration levels reached after equilibrium is reached.

The application of the I.C.E. method to this experiment’s equilibrium is diagramed below. Application of the dilution equation \( M_1V_1 = M_2V_2 \) is required to calculate the initial concentrations of Fe\(^{3+}\) and SCN\(^-\) for each of the six trials. Initially we assume there is no product present.

The initial product and reactant concentrations for Trial #1 are shown below. You will be asked to verify these results for Trial #1 and determine the initial concentrations for the remaining five trials as a prelab exercise.

\[
\begin{align*}
\text{Initial (Dilution)} & \quad 2.00 \times 10^{-4} \text{ M} & 1.80 \times 10^{-3} \text{ M} & 0.000 \text{ M} \\
\text{Change} & \quad -X & -X & +X \\
\text{Equilibrium} & \quad 2.00 \times 10^{-4} - X & 1.80 \times 10^{-3} - X & 0.000 + X
\end{align*}
\]

**Initial**: Inspection of the initial concentrations shows us that we have we have reactants but no product. However, for there to be equilibrium there must be non-zero concentrations of all reactants and products. This reaction will “shift right” to make product while at the same time consuming reactants.

**Change**: Because of the 1:1:1 mole ratio, making “X” amount of product requires “X” amount of both reactants. Reactants are consumed hence their changes are negative (-X). Product is produced and so its change is positive (+X).

**Equilibrium**: The “Equilibrium” line represents the final equilibrium concentrations for products and reactants after the change “X” is applied to the initial concentrations.
The equilibrium values are used to calculate the value of $K_c$:

$$K_c = \frac{[\text{FeSCN}^{2+}]_{\text{eq}}}{[\text{Fe}^{3+}]_{\text{eq}} [\text{SCN}^{-}]_{\text{eq}}} \quad \frac{(0.000 + X)}{(2.00 \times 10^{-4} - X) (1.80 \times 10^{-3} - X)}$$

(Equation 2)

Obviously, if we knew the value of “X” for this trial (#1), we could substitute it into Equation 2 and we’d have a value for $K_c$.

But how do we find “X”? Since X is really just the equilibrium FeSCN$^{2+}$ concentration, all we need to do is experimentally measure $[\text{FeSCN}^{2+}]_{\text{eq}}$ and we have our value for “X”. We’ll do that with the Logger Pro colorimeter and a calibration curve.

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$^{2+}$. We can assume this solution also has zero absorbance.

Calibration point #2 is determined using Vial #7. Note that this vial is only used to obtain the second calibration point and cannot be used to determine another $K_c$.

Vial #7 is prepared by mixing 9.00 mL of 0.200 M Fe$^{3+}$ with 1.00 mL of 0.00200 M SCN$^{-}$. Clearly the Fe$^{3+}$ is in excess for two reasons: i) volume is larger and ii) the concentration is 100X larger. Such large amounts of Fe$^{3+}$ force the equilibrium in this case far in favor of the products completely consuming the available SCN$^{-}$. 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. This concentration can be determined to be $2.00 \times 10^{-4}$ M. Once Vial #7’s absorbance has been measured, the second calibration point can be plotted.

The graph and trendline analysis is used to determine FeSCN$^{2+}$ concentrations (“X”) for Vials #1 – #6.

Spreadsheet Calculations

The calculations required to determine equilibrium constants in this experiment involve many steps. While it is possible to manually perform these calculations, it requires a lot of time. To save you time, you’ll be using an Excel spreadsheet to determine $K_c$ values. Spreadsheet calculations also have the advantage that they never round results. This eliminates rounding errors in calculations.

When you have finished your experimental measurements and cleanup, you should obtain a computer and download a copy of the Excel spreadsheet template found on the laboratory handout website. You’ll be entering data and performing all calculations on the spreadsheet. A printout of the spreadsheet is part of the lab report for this lab.

1. Excel review:
   a. All equations begin with the “=” sign
   b. Use appropriate cell coordinates (e.g. A1 B5, etc.) in your equations.
   c. Once an equation is done correctly once, you can copy and paste it into subsequent cells. Cell references will change automatically.
2. Use the dilution equation using the values in columns D and E to determine the initial concentrations in H, I and J.

3. Enter your %T values in column F and write an equation that converts %T into absorbance for all trials in column G.
   
   … Absorbance = -\log (\%T/100)....

4. Use your Vial #7 absorbance and the known FeSCN$^{2+}$ concentration from Trial #7 to construct a calibration curve.
   
   a. Enter your Trial #7 absorbance in the small data table (shown at right). Now enter the known FeSCN$^{2+}$ concentration.
   
   b. Select the data table values and construct a scatter plot.
   
   c. Perform a linear trendline analysis and increase the number of displayed decimal digits to at least 8.

5. Use the trendline equation and the absorbances in column G to determine FeSCN$^{2+}$ equilibrium concentrations for column K. These values are the same as “X” in our calculations.

6. Use the value of “X” in column K and the initial concentrations in columns H, I and J to determine equilibrium concentrations of Fe$^{3+}$ and SCN$^{-}$ and FeSCN$^{2+}$ in columns L, M and N.

7. Write an equation that calculates $K_c$ from all equilibrium concentrations in column O (See equation #1). Room temperature $K_c$ values are usually in the 160 – 180 range.

II. PRELAB EXERCISE

Clearly answer these questions in INK in your lab notebook before coming to lab.

1. Determine the $K_c$ expression (see Equation 1) for the three chemical equilibria shown at right.

   a. $\text{CH}_3\text{COOH}_{(aq)} + \text{H}_2\text{O}_{(l)} \rightleftharpoons \text{H}_3\text{O}^{+}_{(aq)} + \text{CH}_3\text{COO}^{-}_{(aq)}$

   b. $4 \text{NH}_3_{(g)} + 7 \text{O}_2_{(g)} \rightleftharpoons 4\text{NO}_2_{(g)} + 6 \text{H}_2\text{O}_{(g)}$

   c. $\text{CaCO}_3_{(s)} \rightleftharpoons \text{CaO}_{(s)} + \text{CO}_2_{(g)}$

2. Verify the dilution calculations referred to above for Vial #1 and determine the initial concentrations for the five remaining solutions. Show your calculations

3. In the reaction below there is initially no NH$_3$ product. Why is it the reaction cannot shift right to make product?

   \[
   \text{N}_2_{(g)} + 3\text{H}_2_{(g)} \rightleftharpoons 2 \text{NH}_3_{(g)}
   \]

   Initial $\quad 1.0 \text{ M} \quad 0.0 \text{ M} \quad 0.0 \text{ M}$
III. Word Processed Report

Page 1: *Upper right hand corner Name, Lab section number and date*

**Answers to the following questions (Calculations may be hand written):**

1. Use your calculated Kc values to determine:
   a. the average Kc for the six room temperature trials. (Show work)
   b. the average Kc for the three 8°C temperatures. (Show work)

2. Exothermic reactions shift left and create more reactants when heated. Endothermic reactions shift right and create more products when heated. Compare the two average values from question #1 and determine whether this reaction is exothermic or endothermic.

3. Refer back to your observations of the first six solutions (not vial #7) and explain in chemical terms why the color intensity was greatest for the middle solutions and faintest for solutions 1 and 6.

4. Set up a complete ICE table for the following problem:

   4.00 mL of 0.0040 M Fe(NO₃)₃ solution is mixed with 16.00 mL of 0.0040 M KSCN.

   a. Use dilution calculations to determine the initial concentrations of all species.

   b. Use “X” as your variable to denote all changes (watch the sign)

   c. Write out the Kc expression (Equation #2) using the initial concentrations you determined above in step “a”.

   d. Use your value of the room temperature Kc to determine the equilibrium concentrations of all species. This will likely require an application of the quadratic equation to solve for “X”.

Page 2: Data table: A printout of your Excel spreadsheet. Be sure all numbers are visible on a SINGLE page.

Page 3: Calibration Graph. Include trendline, trendline equation (8 decimal places), title, and axis labels.
IV. Procedure

*You will be working with a partner 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 - 6 and observe how the color intensity changes. Record your observations in your notebook.

<table>
<thead>
<tr>
<th>Vial Number</th>
<th>0.00200 M Fe(NO₃)₃ (mL)</th>
<th>0.00200 M KSCN (mL)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.0</td>
<td>9.0</td>
</tr>
<tr>
<td>2</td>
<td>2.0</td>
<td>8.0</td>
</tr>
<tr>
<td>3</td>
<td>4.0</td>
<td>6.0</td>
</tr>
<tr>
<td>4</td>
<td>5.0</td>
<td>5.0</td>
</tr>
<tr>
<td>5</td>
<td>6.0</td>
<td>4.0</td>
</tr>
<tr>
<td>6</td>
<td>8.0</td>
<td>2.0</td>
</tr>
<tr>
<td>7 (Calibration)</td>
<td>9.0</td>
<td>1.0</td>
</tr>
</tbody>
</table>

A. Colorimeter calibration

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. This step is performed only ONCE.

NOTE:

Do not press “CAL” before any other measurements.

If after calibration Logger Pro indicates something other than 100% (+/- 0.5%), alert the instructor.

Use the same cuvette for all subsequent measurements.

Absorbances MUST change from vial to vial or there is something wrong.
B. %T Measurements

The colorimeters will display values of %T.

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.

Quickly 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, and 5 are tested at both room temperature and at 8°C.

* Wipe the thermometer off with a tissue 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.