**The Determination of *Keq* for FeSCN2+**

**Introduction:**

For any reversible chemical reaction at equilibrium, the concentrations of all reactants and products are constant or stable. There is no further net change in the amounts of reactants and products unless the reaction mixture is disturbed in some way. The equilibrium constant provides a mathematical description of the position of equilibrium for any reversible chemical reaction. What is the equilibrium constant and how can it be determined?

# Concepts: Chemical equilibrium Equilibrium constant Complex-ion reaction Colorimetry

# Background:

Any reversible reaction eventually reaches a position of *chemical equilibrium*. In some cases, equilibrium favors products and it appears that the reaction proceeds essentially to completion. The amount of reactants remaining under these conditions is very small. In other cases, equilibrium favors reactants and it appears that the reaction occurs only to a slight extent. Under these conditions, the amount of products present at equilibrium is very small. These ideas can be expressed mathematically in the form of the equilibrium constant. Consider the following general equation for a reversible chemical reaction:

*a*A + *b*B  *c*C + *d*D *Equation 1*

The *equilibrium constant K*eq for this general reaction is [C]*c*[D]*d*

given by Equation 2, where the square brackets refer to the *K*eq = [A]*a*[B]*b* *Equation 2*

molar concentrations of the reactants and products at equilibrium .

The equilibrium constant gets its name from the fact that for any reversible chemical reaction, the value of *K*eq is a constant at a particular temperature. The concentrations of reactants and products at equilibrium vary, depending on the initial amounts of materials present. The special ratio of reactants and products described by *K*eq is always the same, however, as long as the system has reached equilibrium and the temperature does not change. The value of *K*eq can be calculated if the concentrations of reactants and products at equilibrium are known.

The reversible chemical reaction of iron(III) ions (Fe3+ ) with thiocyanate ions (SCN–) provides a convenient example for determining the equilibrium constant of a reaction. As shown in Equation 3, Fe3+ and SCN– ions combine to form a special type of combined or “complex” ion having the formula FeSCN 2+ .

Fe3+(*aq*) + SCN–(*aq*) FeSCN2+(*aq*) *Equation 3*

*Pale yellow Colorless Blood-red*

The equilibrium constant expression for the reaction is Keq = [FeSCN2+] *Equation 4*

[Fe3+][SCN-]

The value of *K*eq can be determined experimentally by mixing known concentrations of Fe3+ and SCN– ions and measuring the concentration of FeSCN 2+ ions at equilibrium. As noted in Equation 3, the reactant ions are pale yellow and colorless, respectively, while the product ions are blood - red. The concentration of FeSCN 2+ complex ions at equilibrium is proportional to the intensity of the red color.

A special sensor or instrument called a *colorimeter (or spectrophotometer)* can be used to measure the absorbance of light by the red ions. The more intense the red color, the greater the absorbance. The wavelength of light absorbed by the red ions is about 450 nm. None of the other ions present in solution absorb light at this wavelength. As long as the same size container is used to measure the absorbance of each solution, the absorbance is directly proportional to the concentration of FeSCN 2+ ions.

***Experiment Overview***

The purpose of this experiment is to calculate the equilibrium constant for the reaction of iron (III) ions with thiocyanate ions. The reaction is tested under different conditions to determine if the equilibrium constant always has the same numerical value. There are two parts to the experiment.

In **Part A**, a series of reference solutions and test solutions are prepared. The reference solutions are prepared by mixing a large excess of Fe3+ ions with known amounts of SCN– ions. According to LeChâtelier’s Principle, the large excess of iron(III) ions should effectively convert all of the thiocyanate ions to the blood - red

FeSCN 2+ complex ions. The concentration of FeSCN 2+ complex ions in the reference solutions is essentially equal to the initial concentration of SCN– ions. The test solutions are prepared by mixing a constant amount of Fe3+ ions with different amounts of SCN– ions. These solutions contain unknown concentrations of FeSCN2+ ions at equilibrium.

In **Part B**, the absorbances of both the reference solutions and the test solutions are measured by colorimetry. A calibration curve is constructed from the absorption values of the reference solutions. The unknown concentrations of FeSCN2+ in the test solutions are calculated by comparing their absorbance readings to the absorbance values of the calibration curve.

**Pre-Lab Calculations**

1. The five reference solutions in Part A are prepared by mixing the 0.200 M Fe(NO3)3 solution and

the 0.00020 M KSCN solution in the amounts listed in the following table .

|  |  |  |
| --- | --- | --- |
|  | **Volume of 0.200 M** | **Volume of 0.00020 M** |
| **St a n d a r d** | **Fe(NO3)3 Solution** | **KSCN Solution** |
| Reference solution #1 | 4.0 mL | 1.0 mL |
| Reference solution #2 | 3.5 mL | 1.5 mL |
| Reference solution #3 | 3.0 mL | 2.0 mL |
| Reference solution #4 | 2.5 mL | 2.5 mL |
| Reference solution #5 | 2.0 mL | 3.0 mL |

The concentration of Fe3+ ions in the first reference solution (*M*2) before any reaction occurs can be calculated using the so-called “dilution equation”, as shown below.

*M*1*V*1 = *M*2*V*2 *Dilution Equation*

*M*1 = concentration of solution before mixing = 0.200 M Fe(NO3)3

*V*1 = volume of solution before mixing = 4.0 mL

*V*2 = final volume of reference solution after mixing = 4.0 + 1.0 mL = 5.0 mL

*M*2 = *M*1*V*1 = (0.200 M)(4.0 mL) = 0.16 M

*V*2 (5.0 mL)

Use the dilution equation to ***calculate the*** ***concentration of SCN– ions*** in the five ***Reference*** solutions before any reaction occurs. Enter these values in the Reference Solutions Data Table as **[FeSCN2+]**. R*emember*

*“According to Le Châtelier’s Principle, the large excess of iron(III) ions should effectively convert all of the thiocyanate ions to the blood - red FeSCN 2+ complex ions. The concentration of FeSCN 2+ complex ions in the reference solutions is essentially equal to the initial concentration of SCN– ions.”*

2. The following table summarizes the volumes of Fe3+ and SCN– stock solutions that will be mixed together to prepare the test solutions in Part A. Use the dilution equation to ***calculate the concentrations of Fe3+ and SCN–***ions in each Test solution before any reaction occurs. Enter the results of these calculations in scientific notation in the Test Solutions Data Table. *Hint:* The final volume (*V*2) of each test solution is 5.0 mL.

|  |  |  |  |
| --- | --- | --- | --- |
| **Sample** | **Volume of 0.0020M**  **Fe(NO3)3 Solution** | **Volume of 0.0020M** | **Volume of Distilled** |
| **KSCN Solution** | **Water Added** |
| Test solution #6 | 2.5 mL | 0.5 mL | 2.0 mL |
| Test solution #7 | 2.5 mL | 1.0 mL | 1.5 mL |
| Test solution #8 | 2.5 mL | 1.5 mL | 1.0 mL |
| Test solution #9 | 2.5 mL | 2.0 mL | 0.5 mL |
| Test solution #10 | 2.5 mL | 2.5 mL | 0 mL |

# Materials: iron(III) nitrate , Fe(NO3)3, 0.200M*,*† 10 clean large test tubes, Iron(III) nitrate, Fe(NO3)3, 0.0020 M†, cuvettes, potassium thiocyanate, KSCN 0.0020 M*,* potassium thiocyanate, KSCN, 0.0002 M, deionized water, Labquest colorimeter and spectrophotometer, stirring rod, kimwipes, burets/stands. *† CAUTION!! contains 1 M nitric acid as the solvent.*

# Safety Precautions: *iron(III) nitrate solutions contains 1 M nitric acid and it is a corrosive liquid; it will stain skin and clothing . Notify the teacher and clean up all spills immediately. Potassium thiocyanate is toxic by ingestion; it can generate poisonous hydrogen cyanide gas if heated strongly. Avoid contact of all chemicals with eyes and skin. Wear chemical splash goggles and chemical - and apron. Wash hands thoroughly with soap and water before leaving the laboratory.*

# Procedure

***Part A. Preparing the Solutions***

1. Obtain ten large test tubes.

2. Prepare the five reference solution test tubes listed in the table below. Use the correct buret to obtain appropriate volumes of each reagent. Mix each solution by gently shaking or tapping the test tube. Label the test tubes with the corresponding reference solution number (or just keep them in order).

|  |  |  |
| --- | --- | --- |
| **Standard** | **Volume of 0.200 M**  **Fe(NO3)3 Solution** | **Volume of 0.00020 M**  **KSCN Solution** |
| Reference solution #1 | 4.0 mL | 1.0 mL |
| Reference solution #2 | 3.5 mL | 1.5 mL |
| Reference solution #3 | 3.0 mL | 2.0 mL |
| Reference solution #4 | 2.5 mL | 2.5 mL |
| Reference solution #5 | 2.0 mL | 3.0 mL |

3. Using the correct buret for each reagent to be added, combine the following volumes of reagents to prepare the test solutions. *Note:* Label the tubes with the corresponding solution numbers 6 through 10.

|  |  |  |  |
| --- | --- | --- | --- |
| **Sample** |  | **Reagents** |  |
| **0.0020 M Fe(NO3)3** | **0.0020 M KSCN** | **Distilled Water** |
| Test solution #6 | 2.5 mL | 0.5 mL | 2.0 mL |
| Test solution #7 | 2.5 mL | 1.0 mL | 1.5 mL |
| Test solution #8 | 2.5 mL | 1.5 mL | 1.0 mL |
| Test solution #9 | 2.5 mL | 2.0 mL | 0.5 mL |
| Test solution #10 | 2.5 mL | 2.5 mL | 0 mL |

Measure the temperature of one of the solutions and record it in the Test Solutions Data Table.

***Transfer the reference and test solutions to the glass cuvets (2/3 full - about 7mL) for the spectrophotometer and the*** ***plastic cuvets (3/4 - full about 3mL) for the colorimeter. Make sure to keep the cuvets in order!***

***Part B. Colorimetry Measurements***

1. The spectrophotometer is used as follows: Turn the instrument on and allow it to warm up for 15 minutes. Set the wavelength at **470** nm *(to match the colorimeter)*. With no light passing through the instrument to the phototube *(no cuvet in the chamber)*, set the *percent transmittance* *to zero* with the “zero” control knob. Handle cuvets at the top so no fingerprints are in the light path. Polish cuvets with a kimwipe. Place a cuvet which is about 2/3 full of distilled water *(blank)* into the sample holder close the lid and set the *percent transmittance to 100%* with the appropriate control (not the zero control). Remove the blank cuvet and place the cuvet with ***Reference*** Solution #1 in the spectrophotometer and close the lid and read the absorbance (not transmittance). Record the absorbance in the Reference Solutions Data Table.
2. Measure the absorbance of each of the other ***Reference*** Solutions #2-5 at **470** nm. Record the absorbance value for each reference solution used in the Reference Solutions Data Table. Also record the color (and intensity of the color) of each solution compared to the others.  *If absorbance is difficult to measure precisely on the meter because it is in the high range where the numbers are close together, measure percent transmittance and calculate the absorbance for each solution. Absorbance = –log T, where T is transmittance expressed as a decimal. Inform the instructor if your readings do not make sense.*
3. Repeat step 2 for each of the ***Test*** Solutions. Record the absorbances in the Test Solution Data Table.

Also record the color (and intensity of the color) of each solution compared to the others.

*Dispose of the contents of the cuvets and of the remaining solutions in the sink with plenty of water. Soak the glass cuvettes in a beaker filled with warm water and a small amount of alconox. Do NOT use brushes –they will scratch the glass. Repeatedly rinse the cuvettes with tap (warm if needed) water and then rinse with deionized water. Shake out the cuvets and allow to dry inverted in a test tube rack.*

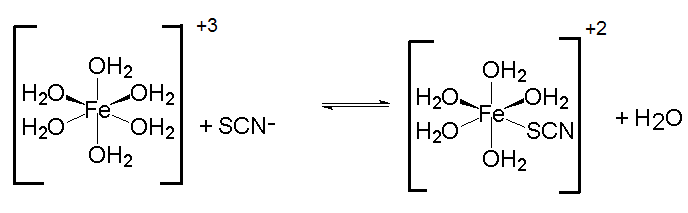
***Actual complex ion reaction***

pale yellow blood red

Fe[(H2O)6]3+ (aq) + SCN1- (aq) ⇌ Fe[(H2O)5(SCN)] 2+ (aq) + H2O (*1*)

hexaaquairon(III) ion iron(III) pentaaquathiocyanato complex ion

or pentaaquathiocyanatoiron(III) ion



Water molecules are attached to the central iron(III) ion via a co-ordinate bond using one of the lone pairs on the oxygen. These are called ligands.

Fe3+(*aq*) + SCN–(*aq*) FeSCN2+(*aq*)

<http://www.chemguide.co.uk/inorganic/complexions/whatis.html#top>

<http://www.chemguide.co.uk/inorganic/complexions/acidity.html>

<http://www.s-cool.co.uk/a-level/chemistry/transition-metals/revise-it/complex-ions>

**INSTRUCTIONS FOR USING THE COLORIMETER**

**1.** ***The Colorimeter needs to be powered for about 5 minutes before calibration.*** Plug in the power cord for the Labquest. Connect the Colorimeter to Channel 1 of the Labquest.

**2.** You should see an absorbance reading displayed on the meter screen. Press the right or left arrow button and set the wavelength to the 470nm LED.

**3. Calibrating the Colorimeter**

* Make sure the calorimeter is set to 470nm. Open the Colorimeter lid.
* Fill a clean cuvette ¾ full with distilled water. Dislodge any bubbles by gently tapping the cuvette on the lab table. Place a *lid on the cuvette* so no liquid will spill into the colorimeter. Be sure to hold the cuvettes by ridged sides. Wipe the *clear* sides with a kimwipe. Put the cuvette into the colorimeter. **Important:** Line up one of the *clear* sides of the cuvette with the ***arrow*** at the *top* of the cuvette slot. Close the Colorimeter lid.
* Next, press the CAL button on the Colorimeter to begin the calibration process. Release the CAL button when the red LED light begins to flash. The absorbance should now be 0.000 or 0.001. (This “blank” cuvette will be 100% transmittance or 0 absorbance.) When the LED stops flashing, the calibration is complete and your unit is ready to collect data.

**4. Collecting Data for the Calibration Curve**

* Tap “Mode” on the meter screen and select “Events with Entry.” Columns should be set to one. Enter “Concentration” for the column name and enter “M” for units”. Click “OK” when you have entered this information.
* While the cuvette filled with distilled water is still in the colorimeter. Press start (green arrow) the absorbance value should still be 0.000 – Press KEEP. You will be prompted to enter the concentration – enter 0. This will make zero absorbance for zero concentration a valid point in your calibration curve.
* Remove the cuvette filled with distilled water, and replace it with the cuvette containing Reference Solution #1 (with lid). An absorbance value will be displayed. Once the reading stabilizes. Press KEEP. You will be prompted to enter the concentration of the solution that produces that absorbance value. Remove the cuvette and replace it with #2. Repeat this procedure for all five Reference solutions. Be sure to also record the absorbance values in your data table.
* Click “Stop” to finish data collection after you have tested **all** five reference solutions.

**Note**: If you click “Stop” but would like to go back to collect more data, click “Start” again.

Select “Append to latest”.

* Click “File” and save your data.

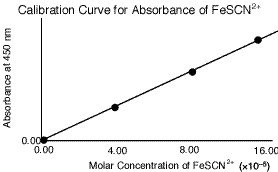
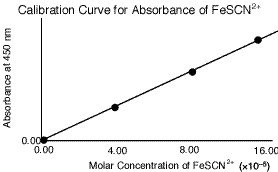
**6. Collecting Data for the Test (unknown) Solutions**

* Place the Test Solution cuvettes one at a time into the colorimeter and record absorbance values in your data table. This data will not be kept or saved. Just record the values for later calculations.

**NOTE:** *The best data would be obtained by using the SAME cuvet for the blank and each solution. After getting the blank reading, the cuvet would be rinsed 2-3times with 1mL of the next solution and then filled to obtain the reading. The cuvet would then be rinsed with distilled water and then 2-3 times with the next solution and so on until all readings are taken. This would minimize any differences between cuvets.*

*Dispose of the contents of the cuvets and of the remaining solutions in the sink with plenty of water. Soak the cuvets in a beaker filled with warm water and a small amount of alconox. Do NOT use brushes –they will scratch the plastic. Repeatedly rinse the cuvettes with tap (warm if needed) water and then rinse with deionized water. Shake out cuvets and allow to dry inverted in the cuvet rack.*

# Post-Lab Calculations and Analysis



1. Plot absorbance versus molar concentration of FeSCN 2+ by using the Analyze tab on the Labquest. Click “Analyze”, select curve fit, check absorbance, and Choose Fit “Linear”. Obtain the equation of your line for the calibration curve.

Use your calculator to produce the plot for the spectrophotometer data. (Include the origin (zero absorbance for zero concentration) as a valid point.

2. Determine the unknown concentration of FeSCN2+ ions in each test solution by using the Labquest graph or equation of the line from linear regression. (“x” = [FeSCN2+] and “y” = abs)

Record the FeSCN2+ concentration for each test solution in the Results Table.

3. Calculate the equilibrium concentration of Fe3+ ions in each Test solution #6–10: subtract the equilibrium concentration of FeSCN2+ ions from the initial concentration of Fe3+ ions (see the Test Solutions Data Table). (Note: *ICE table below*). Enter the results in the Results Table. [Fe3+]eq = [Fe3+]initial – [FeSCN2+]eq

4. Calculate the equilibrium concentration of SCN– ions in each Test solution #6–10: subtract the equilibrium concentration of FeSCN2+ ions from the initial concentration of SCN– ions (see the Test Solutions Data Table). Enter the results in the Results Table. [SCN–]eq = [SCN–]initial – [FeSCN2+]eq

5. Use the Keq expression (Equation 4 in the Background section) to calculate the value of the equilibrium constant *Keq* for each Test solution #6–10. Enter the results in the Results Table.

6. Calculate the *mean* (average value) of the equilibrium constant for the five Test solutions. Record in the Results Table.

7. Calculate the *average deviation* for *K*eq: Find the absolute value of the difference between each individual value of the equilibrium constant and the mean. The average of these differences for solutions #6–10 is equal to the average deviation. Record in the Results Table.

Fe3+(*aq*) + SCN–(*aq*) FeSCN2+(*aq*)

|  |  |  |  |
| --- | --- | --- | --- |
| **Initial** | [Fe3+]o | [SCN–]o | 0 |
| **Change** | -X | -X | +X |
| **Equilibrium** | [Fe3+]eq | [SCN–]eq | X |

←determined from calibration curve

Name\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_ Date \_\_\_\_\_\_\_\_ Period \_\_\_\_

# Data Tables Labquest #:\_\_\_\_\_\_

***Reference Solutions***

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Sample** | **[FeSCN2+]** | **Absorbance (Spect 20)** | **Absorbance (colorimeter)** | **Solution Color/Intensity** |
| **Reference solution #1** |  |  |  |  |
| **Reference solution #2** |  |  |  |  |
| **Reference solution #3** |  |  |  |  |
| **Reference solution #4** |  |  |  |  |
| **Reference solution #5** |  |  |  |  |

***Test Solutions***

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Sample** | **[Fe3+]\*** | **[SCN–]\*** | **Absorbance (spect 20)** | **Absorbance (colorimeter)** | **Solution Color/Intensity** |
| **Test solution #6** |  |  |  |  |  |
| **Test solution #7** |  |  |  |  |  |
| **Test solution #8** |  |  |  |  |  |
| **Test solution #9** |  |  |  |  |  |
| **Test solution #10** |  |  |  |  |  |

\*These are the concentrations of ions in solution immediately after mixing and before any reaction has occurred. See the *Pre-Lab Questions* for calculations.

# Results Table

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Sample** | **[FeSCN2+]eq** | **[Fe3+]eq** | **[SCN–]eq** | ***K*eq** | ***Deviation*** |
| **Test Solution #6** |  |  |  |  |  |
| **Test Solution #7** |  |  |  |  |  |
| **Test Solution #8** |  |  |  |  |  |
| **Test Solution #9** |  |  |  |  |  |
| **Test Solution #10** |  |  |  |  |  |
|  |  |  | **Average** |  |  |

**Pre-lab Questions**

1) During this lab you will mix iron (III) nitrate and potassium thiocyanate to produce the complex iron (III) thiocyanate ion. Why is the nitrate ion and potassium ion not included in equation 3 of the pre-lab?

2) In what 2 ways could you shift the equilibrium to the right for this reaction? What will you observe to know that the shift has occurred? *(assume constant temperature)*

3) Compare the concentrations of the two solutions which will be used to produce the Reference solutions. How many times more concentrated is the iron (III) solution compared to the thiocyanate solution?

“The ***equilibrium concentration*** of FeSCN2+ ions in each reference solution is essentially equal to the concentration of SCN– ions in solution before any reaction occurs”. Use LeChâtelier’s Principle to explain why this statement is true. *(Use these terms in your answer: shift; stress; consume or react.)*

4) Why does the concentration of Fe3+ essentially not change during the reaction used to produce the Reference Solutions?

**Pre-lab Calculations**

1) Show the calculation for the concentration of ***SCN–*** ions in the *Reference solution #1* before any reaction occurs. Remember this will equal the concentration of ***FeSCN2+*** ions at equilibrium. Repeat for the other reference solutions. Record the values in the table.

2) Show the calculations for the concentration of ***Fe3+*** and ***SCN–*** ions in *Test solution #6* before any reaction occurs. Repeat for the other test solutions and record the values in the table.

**Post-Lab Calculations**

1) Equation of the line from Labquest or Calculator \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

2) Show the calculation for the concentration of **FeSCN2+** ions in Test Solution #6 using the equation.

3) Show the calculation for the equilibrium concentration of **Fe3+** ions in Test Solution #6.

4) Show the calculation for the equilibrium concentration of **SCN−** ions in Test Solution #6.

5) Show the calculation for Keq for Test Solution #6.

6 & 7) Show the calculation for the mean Keq and the for the absolute deviation of Test Solution #6.

**Analysis**

1) How do the colors/intensities of the Reference solutions relate to their absorbance values and concentrations?

2) Why was a value of 470nm (remember 470nm was used since this was the closest wavelength to 450nm on the colorimeter) selected as the wavelength for the solutions? (What color is this?)

3) The average deviation is a measure of the precision of your results. Does the precision indicate that the equilibrium constant is indeed a “constant” for this reaction? Explain. If the value is not constant explain any large deviations.

4) In Part A if the Fe(NO3)3 solution was 0.250M instead of 0.200M would the absorbance values be affected? Explain.

In Part A if the KSCN solution was 0.0020M instead of 0.00020M would the absorbance values be affected?

Explain.

5) In Part B how would the calculated value of Keq be affected if the Test Solutions were placed into cuvets that were still wet inside after being rinsed with distilled water?