EXPERIMENT B4: CHEMICAL EQUILIBRIUM

Learning Outcomes

Upon completion of this lab, the student will be able to:

1) Analyze the absorbance spectrum of a sample.
2) Calculate the equilibrium constant for a chemical reaction using data obtained by spectrophotometric methods.

Introduction

Electromagnetic Spectrum

A wave is often defined as a "vibrating disturbance by which energy is transmitted". An electromagnetic wave is a type of wave that has associated with it an electrical field and a magnetic field that are perpendicular to one another. Light that can be seen by the naked eye, also known as visible light, is an example of an electromagnetic radiation. Waves such as radio waves, microwaves, or x-rays are also examples of electromagnetic radiation.

Mathematically, waves such as electromagnetic waves are known as propagating waves, and can be represented by a repeating or periodic function uch as sine wave. There are three characteristic properties associated with these kinds of waves:

1. Wavelength (λ)- the distance between identical points on successive waves
2. Frequency (ν)- the number of waves that pass through a particular point in a second
3. Amplitude- the height of the peak or trough of a wave.

What makes one electromagnetic wave different from another wave is the wavelength and frequency associated with it. These two are inversely related to each according to the formula:

$$c = \nu\lambda, \text{ where c is the speed of light} = 3.00 \times 10^8 \text{ m/s}$$

The electromagnetic spectrum (Figure 1) is an arrangement of the different kinds of waves in the order of increasing wavelengths (or decreasing frequencies).

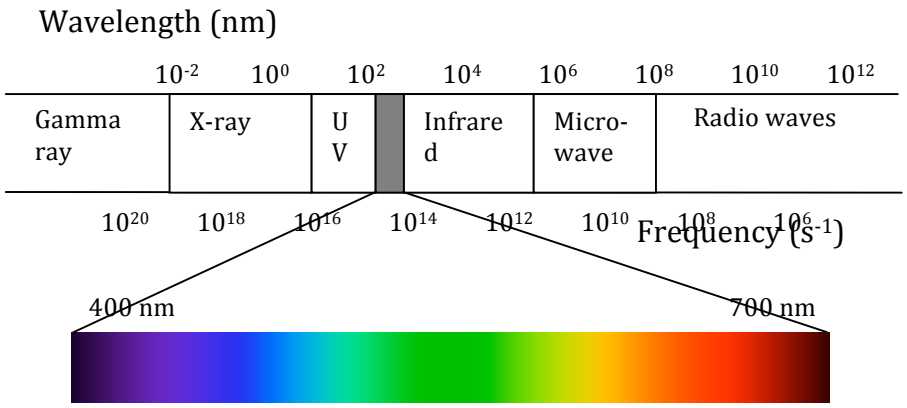


FIGURE 1

As mentioned above, electromagnetic radiation at certain wavelengths, is visible to the human eye, ranging from red light with longer wavelengths (~ 700 nm) to violet light with shorter wavelengths (~400 nm).

A solution containing a substance that absorbs light in the visible region of the electromagnetic spectrum will appear colored to the eye. The color that is observed depends on the wavelength of the radiation that substance absorbs. For instance, if you look at a solution of vitamin B_2 (also known as riboflavin) under a white light, it appears yellow in color. A solution of vitamin B_2 absorbs the maximum light at a wavelength of 450 nm. From Figure 1, light with a wavelength of 450 nm corresponds to violet-blue light. The molecules of riboflavin therefore are absorbing the violet-blue parts of the visible light, and all the rest of the visible light will not be absorbed but instead transmitted through the solution. The riboflavin is essentially removing the blue-violet light from the white light and as a result the color you observe for riboflavin is a mixture of the rest of the "un-absorbed" colors. In general the color of a solution that can be observed by the human eye is the "complement" of the color of the light it absorbs. The following "color-wheel" is a representation of complementary colors (Figure 2).

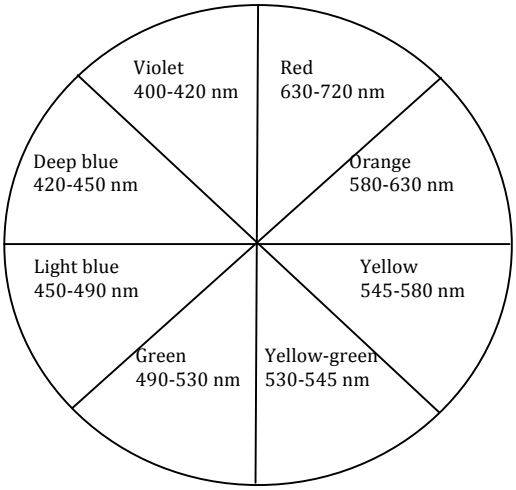


FIGURE 2

In the case of riboflavin since the solution absorbed light with a wavelength of 450 nm corresponding to blue light, it should appear to be yellow to yellow-green, which are the complementary colors. And indeed, a solution of riboflavin does appear to be yellow in color.

Spectrophotometry

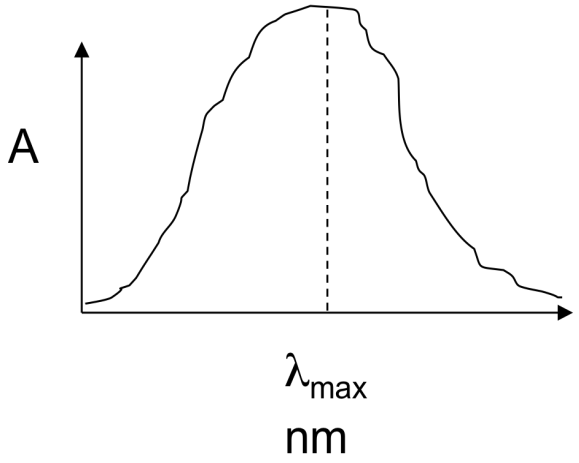
A *spectrophotometer* is an instrument used to measure the amount of light that a sample absorbs. This method is known as *spectrophotometry*. The instrument operates by passing a beam of light through a sample and measuring the intensity of the transmitted light reaching a detector. The most basic arrangement of a spectrophotometer is shown in Figure 3.

FIGURE 3

However, as discussed before different samples absorb light of different wavelengths. The amount of light absorbed by the sample will depend on the wavelength of the light. In order to select light of a particular wavelength to shine on the sample, the light must pass through a *monochromator*, which is essentially a filter that allows a selected wavelength of light to pass through the sample.

When analyzing a sample for the first time, it is unlikely that one will know the wavelength at which the sample absorbs maximum light. Therefore the complete *absorbance spectrum* of the sample must first be determined. The absorbance spectrum shows how the absorbance of light depends upon the wavelength of the light. The spectrum is a plot of absorbance (y-axis) versus wavelength (x-axis). The

wavelength at which the absorbance is the highest is often denoted as λ_{max}. The λ_{max} is characteristic of each compound and provides information on the electronic structure of the analyte.



The absorbance of a particular solution depends on another important parameter: the amount of the analyte present in the solution.

Beer's law states that the absorbance is directly proportional to the number of molecules per unit volume of light-absorbing compound through which the light passes. The mathematical form corresponding to Beer's law is given by:

$$\mathbf{A = \varepsilon \times c \times l}$$

The variables in the above equation are:

- A = absorbance of the sample (this is a unit-less quantity)
- c = concentration of the analyte (typically in units of Molarity or moles/liter)
- ε = molar extinction coefficient (units of $Molarity^{-1}cm^{-1}$)
- l = path length through which light travels

The path length depends on the spectrophotometer and the sample holder or cuvette being used and is typically 1.00 cm for most instruments. The extinction coefficient ε that is used in the above equation is a constant for a particular sample at a particular wavelength. The extinction coefficient for several substances has been experimentally determined.

Chemical Equilibrium

In this experiment, the analytical method of spectrophotometry described in the preceding section will be used to examine the chemical equilibrium of a particular reaction. As should be evident from the earlier discussion, in order to use this

analytical method, the chemical substances studied must absorb light in the visible region of the electromagnetic spectrum.

The reaction that will be studied is between aqueous solutions of the iron(III) ion (Fe^{3+}) and thiocyanate ion (SCN^-). The ionic equation for the reaction and the expression for the equilibrium constant are given below.

$$Fe^{3+}_{aq} + SCN^-_{aq} \Leftrightarrow Fe(SCN)^{2+}_{aq}$$

$$K_C = \frac{[Fe(SCN)^{2+}]_{eq}}{[Fe^{3+}]_{eq}[SCN^-]_{eq}}$$

At the wavelength of maximum absorbance, λ_{max}, the molar extinction coefficient, ε, for the product, $Fe(SCN)^{2+}$, is 6120 $M^{-1}cm^{-1}$. Since the initial concentrations of the reactants are known and the product concentration is related to its absorbance, the method of spectophotometry can be used to determine the equilibrium constant for this reaction.

Assume that the initial concentration of Fe^{3+} is A and that of CNS^- is B. The following table describes how the concentrations of all ions at equilibrium can be determined. Since the ions are all in a 1:1 stoichiometric relationship with each other, the amount of one of the ions consumed in terms of concentration (-x) will be the sameamount as the other ion consumed and will result in an equal amount of product being formed (+x).

	Fe^{3+} +	SCN^- ⇔	$Fe(SCN)^{2+}$
Initial concentrations	A	B	0
Amount reacted to reach equilibrium	-x	-x	+x
Equilibrium concentrations	A-x	B-x	x

$$K_C = \frac{x}{(A-x)(B-x)}$$

Since “A” and “B” are known quantities, in order to determine the equilibrium constant K_C, it is necessary to determine the change in concentration“x”. Fortuntely, the change in concentration is equal to the equilibrium concentration of the complex, $Fe(SCN)^{2+}$.

The equilibrium concentration of the complex, $Fe(SCN)^{2+}$, can be determined by measuring its absorbance at λ_{max} and employing Beer’s law:

$$C = x = \frac{A}{\varepsilon \times l}$$
$$\varepsilon = 6120 M^{-1} cm^{-1}$$
$$l = 1 cm$$

The value of "l" (the path length) is specific to the spectrophotometer. The spectrophotometers used in this laboratory have a path length of 1.00 cm.

Experimental Design

0.00200 M aqueous solutions of Fe^{3+} and SCN^- are provided. These solutions are prepared in 0.50 M HNO_3. Different initial concentrations of these two solutions will be combined to form the $Fe(SCN)^{2+}$ complex. The absorbance of the equilibrium mixture will be measured at λ_{max} using a spectrophotometer.

The λ_{max} for the complex, $Fe(SCN)^{2+}$, must first be determined. In order to do this, the complete absorbance spectrum of the complex (from 370 nm to 700 nm) must be obtained.

Reagents and Supplies

0.00200 M Fe^{3+}, 0.00200 M SCN^-, 0.50 M HNO_3

Spectrophotometer, cuvettes

(See posted Material Safety Data Sheets)

Procedure

PART 1: DETERMINATION OF λ_{MAX} FOR $Fe(SCN)^{2+}$

1. Obtain two cuvettes and a spectrophotometer. Power up the spectrophotometer and allow the instrument to warm up for 10 minutes. The instructor will demonstrate the proper use of the spectrophotometer.

2. In a large test tube combine 4.00 ml of Fe^{3+} and 3.00 ml of SCN^-. Thoroughly mix the contents and allow the mixture to equilibrate (~ 5 minutes).

3. Fill one cuvette with 0.50 M HNO_3 (this will be the "blank") and the second cuvette with the $Fe(SCN)^{2+}$ complex prepared in step 2 (this will be the "sample").

4. Wipe the sides of the cuvettes with kimwipes and make sure there are no smudges or fingerprints.

5. Set the wavelength of the spectrophotometer to 370 nm.

6. Ensure that there is no sample in the sample compartment and that the lid to the compartment is closed. Set the spectrophotometer to transmittance mode. Using the appropriate controls, adjust the transmittance to zero.

7. Place the cuvette containing the "blank" inside the sample compartment, align the guide mark on the cuvette with the guide mark at the front of the sample compartment, and close the lid. Set the spectrophotometer to absorbance mode. Using the appropriate controls adjust the absorbance reading to zero.

8. Now place the cuvette containing the "sample" inside the sample compartment, align the guide mark on the cuvette with the guide mark at the front of the sample compartment, close the lid and record the absorbance.

9. Change the wavelength to 380 nm and then repeat Steps 6 through 8. Continue this process in 10 nm increments of the wavelength, until absorbance values have been recorded at 700 nm.

10. Empty the contents of the cuvettes into a large beaker labeled as "Waste". Rinse and clean the cuvettes. Dispose all the reagents in an appropriate labeled waste container provided by the instructor

11. Plot a graph of absorbance (y-axis) vs. wavelength (x-axis). From the plot determine the wavelength at which the absorbance maximum is found. This wavelength will be used for all subsequent measurements.

PART 2: DETERMINATION OF K_C FOR THE REACTION BETWEEN Fe^{3+} AND SCN^-

1. Obtain a spectrophotometer and turn the power on and allow the instrument to warm up for at least 10 minutes.

2. Obtain nine large test tubes and number them from 1 to 9.

3. Combine Fe^{3+} and SCN^- in each of the test tubes according to the following table. These will be the "sample" test tubes. Thoroughly mix the contents after combining the two solutions and allow the resulting mixture to equilibrate for at least five minutes.

Solution Number	**Fe^{3+} (mL), Solution A**	**SCN^- (mL), Solution B**
1	0.50	3.00
2	1.00	2.50
3	1.25	2.25
4	1.50	2.00
5	1.75	1.75
6	2.00	1.50
7	2.25	1.25
8	2.50	1.00
9	3.00	0.50

4. Measure the temperature of the equilibrium mixture. The temperature is not used in any of the calculations. But equilibrium constant values are always reported at a particular temperature as the value changes with temperature.

5. In another cuvette obtain about 3.50 mL of nitric acid. This will serve as the "blank".

6. Set the wavelength of the spectrophotometer to the value determined from Part 1 of the experiment. Calibrate the spectrophotometer using the method described in Part 1: Steps 6 & 7.

7. Record the absorbance values of each of the nine samples (use the method described in Part 1 (Step 8).

8. Dispose all the reagents in an appropriate labeled waste container provided by the instructor.

Data Table

PART 1: DETERMINATION OF λ_{MAX} FOR $Fe(SCN)^{2+}$

Wavelength (nm)	Absorbance
370	
380	
390	
400	
410	
420	
430	
440	
450	
460	
470	
480	
490	
500	
510	
520	
530	
540	
550	
560	
570	
580	
590	
600	
610	
620	
630	
640	
650	
660	
670	
680	
690	
700	

PART 2: DETERMINATION OF K_C FOR THE REACTION BETWEEN Fe^{3+} AND SCN^-

Solution	Absorbance
1	
2	
3	
4	
5	
6	
7	
8	
9	

Temperature of the equilibrium mixture =

Data Analysis

PART 1: DETERMINATION OF λ_{MAX} FOR $Fe(SCN)^{2+}$

1. Draw a graph of absorbance (*y*-axis) vs. wavelength (nm).

2. From the plot, identify the wavelength at which the maximum absorbance occurs. There will be two absorbance maxima in this spectrum. Use the larger of the two wavelengths for all subsequent measurements.

GRAPH

The λ_{max} for $Fe(SCN)^{2+}$ was found to be =

PART 2: DETERMINATION OF K_C FOR THE REACTION BETWEEN Fe^{3+} AND SCN^-

The net ionic equation and the expression for the equilibrium constant for the reaction between Fe^{3+} and SCN^- is given by:

$$Fe^{3+}_{aq} + SCN^-_{aq} \Leftrightarrow Fe(CNS)^{2+}_{aq}$$

$$K_C = \frac{[Fe(CNS)^{2+}]_{eq}}{[Fe^{3+}]_{eq}[CNS^-]_{eq}}$$

As mentioned before, if the initial concentration of Fe^{3+} is A and that of CNS^- is B, then the following table describes the equilibrium process.

	Fe^{3+} +	SCN^- ⇔	$Fe(SCN)^{2+}$
Initial concentrations	A	B	0
Amount reacted to reach equilibrium	-x	-x	+x
Equilibrium concentrations	A-x	B-x	x

$$K_C = \frac{x}{(A-x)(B-x)}$$

The equilibrium concentration of the complex, $Fe(SCN)^{2+}$, can be determined from its absorbance at λ_{max} and employing Beer's law.

$$C = x = \frac{A}{\varepsilon \times l}$$

$$\varepsilon = 6120 M^{-1} cm^{-1}$$

$$l = 1 cm$$

1. First the initial concentrations of Fe^{3+} and SCN^- must be determined for each of the six reaction conditions.

   For instance, in sample 1 (0.50 mL of Fe^{3+} + 3.00 mL of SCN^-):

   Concentration of Fe^{3+} in the mixture = $\frac{0.50 mL \times 0.00200 M}{3.50 mL} = 0.000286 M$

   Concentration of SCN^- in the mixture = $\frac{3.00 mL \times 0.00200 M}{3.50 mL} = 0.00171 M$

Determine the concentrations of Fe^{3+} and SCN^- in all the samples in the same manner.

Solution Number	Fe^{3+} (mL)	$[Fe^{3+}]$, M = A	SCN^- (mL)	$[SCN^-]$, M = B
1	0.50	**0.000286**	3.00	**0.00171**
2	1.00		2.50	
3	1.25		2.25	
4	1.50		2.00	
5	1.75		1.75	
6	2.00		1.50	
7	2.25		1.25	
8	2.50		1.00	
9	3.00		0.50	

2. Determine the concentration of the complex, $Fe(SCN)^{2+}$, for each of the six solutions from the absorbance value.

Solution	Absorbance	$[Fe(SCN)^{2+}]$, M = $\frac{A}{6120} = x =$
1		
2		
3		
4		
5		
6		
7		
8		
9		

3. Calculate the equilibrium constant K_C for each reaction using the formula:

$$K_C = \frac{x}{(A - x)(B - x)}$$

Solution	K_C
1	
2	
3	
4	
5	
6	
7	
8	
9	
AVERAGE	
STANDARD DEVIATION	

NOTE: Equilibrium constant values are temperature dependent. Be sure to measure the temperature of the solution and report the average value of the equilibrium constant at the specific temperature at which the experiment was conducted.

Result

The equilibrium constant, K_C, for the reaction between aqueous solutions of Fe^{3+} and SCN^-, which resulted in the complex $Fe(SCN)^{2+}$, was found to be (specify the temperature):