Lab 4 • Spectrophotometric Determination of an Equilibrium Constant

PURPOSE: To determine the value of the equilibrium constant for a reaction.

CONCEPTS: The concentration of the species present at equilibrium can be determined by spectrophotometric methods. Equilibrium calculations, Equilibrium constants, reaction quotients, and the state of equilibrium and disturbing equilibrium- Le Chatelier's principle

In this experiment we will study the equilibrium properties of the reaction between iron (III) ion and thiocyanate ion:

$$Fe^{3+} \; + \; SCN^- \; \leftrightarrows \; [Fe(SCN)]^{2+} \qquad\qquad \text{Equation 1}$$

Metal ion + ligand   metal-ligand complex ion

When solutions containing Fe^{3+} ion and thiocyanate ion (SCN^-) are mixed, Reaction 1 occurs to some extent, forming the $FeSCN^{2+}$ complex ion, which has a deep red color. As a result of the reaction, the equilibrium amounts of Fe^{3+} and SCN^- will be less than they would have been if no reaction occurred; for every mole of $FeSCN^{2+}$ that is formed, one mole of Fe^{3+} and one mole of SCN^- will react.

According to the Law of Chemical Equilibrium, the equilibrium constant expression K_c for Reaction 1 is formulated as follows:

$$\frac{[FeSCN^{2+}]}{[Fe^{3+}][\,SCN^-]} \; = \; K_c \qquad\qquad \text{Equation 2}$$

Overview of this experiment.

In this experiment you will use 0.050 M HNO_3, 0.0020 M KSCN and 0.200 M $Fe(NO_3)_3$ solutions to prepare a series of solutions that contain known concentrations of $[Fe(SCN)]^{2+}$ ions. From equilibrium concentrations of the absorbing $[Fe(SCN)]^{2+}$ ions, the stoichiometry of the reaction (Eq. 2), and the initial concentrations of $Fe(NO_3)_3$ and KSCN, the equilibrium concentrations of all species can be calculated.

$$Fe^{3+} + SCN^- \leftrightarrows [Fe(SCN)]^{2+}$$

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

PROCEDURES:

Part A. Preparation of Standard Solutions and Determination of Absorbances of the Standard Solutions

Preparation of Standard Solutions – known concentration of FeSCN^{2+}

Beaker	0.00200 M KSCN	0.200 M Fe(N0$_3$)$_3$	0.050 M HNO$_3$
1	5.0 mL	5.0 mL	15.0 mL
2	4.5 mL	5.0 mL	15.5 mL
3	4.0 mL	5.0 mL	16.0 mL
4	3.0 mL	5.0 mL	17.0 mL
5	2.0 mL	5.0 mL	18.0 mL
6	1.5 mL	5.0 mL	18.5 mL
7	1.0 mL	5.0 mL	19.0 mL
8	0.5 mL	5.0 mL	19.5 mL

Note:

The volume in each beaker is 25.0 mL

In this set of beakers the concentration of Fe^{3+} ions is overwhelming greater than the concentration of SCN- ions. This shifts the equilibrium to the right so far that ALL the SCN$^-$ ions will react to become FeSCN^{2+} ions.

So in this set of beakers the concentration of the FeSCN^{2+} ions will be equal to the initial concentration of the SCN- ions. This initial concentration can be calculated using MV=MV to find the new concentration of ions in the new volume of 25.0mL.

With known concentration of **FeSCN^{2+}** we can calculate the absorbance of the solution using the measured percent absorbance. Graphing the Absorbance as a function of concentration will yield a line that will allow us to find the concentration of other solutions that we do not already know the concentration.

RESULTS and CALCULATIONS:

Data Table #1. Percent Transmittance of Standard Solutions

| Solution	Volume of .00200M KSCN	Step 5 Initial [SCN⁻]	Step 5 Final [Fe(SCN)²⁺]	Step 10 Percent Transmittance Blue	Step 10 Percent Transmittance Green
1	5.0 mL	0.0004	0.0004 4×10^{-4}	3	
2	4.5 mL		3.6×10^{-4}	5.1	
3	4.0 mL		3.2×10^{-4}	5.2	
4	3.0 mL		2.4×10^{-4}	10.4	
5	2.0 mL	0.00016	0.00016 1.6×10^{-4}	18.9	
6	1.5 mL			26	
7	1.0 mL			45	
8	0.5 mL		0.00004 4×10^{-5} 0.4×10^{-4}	59.1	
		Calculate using MV = MV	Calculate using MV = MV	Measure	Measure

Solution 1 MV= MV   0.002 (5) = x (25) x = 0.0004 M

Table #2. Calculated Absorbance of Standard Solutions

Solution	[Fe(SCN)²⁺]	Step 12 Absorbance Blue	Step 12 Absorbance Green
1	0.0004 4×10^{-4}	$\log (100/3) =$ 1.52	
2			
3			
4			
5	0.00016 1.6×10^{-4}	$\log (100/18) =$ 0.724	

6			
7			
8			
	Transfer value from, table above	Calculate using $A = \log 100/\%T$	Calculate using $A = \log 100/\%T$

Step 12. Complete your graph. Include clearly labeled axes, line of best fit and a title.
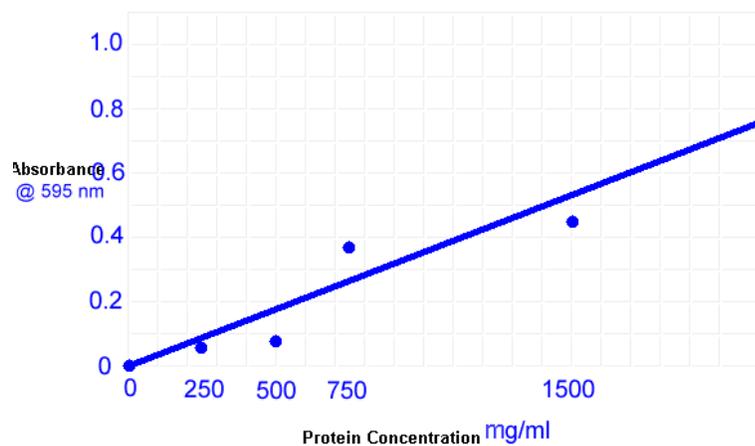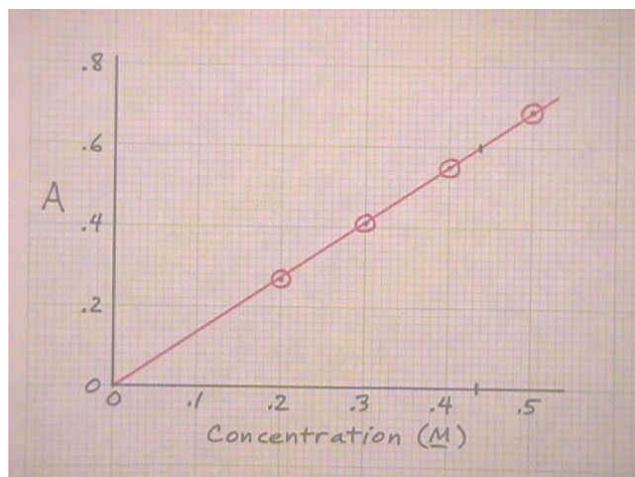
Part B. Preparation of Equilibrium Solutions and Measurements of Absorbances

Beaker	0.00200 M Fe(NO₃)₃	0.00200 M KSCN	0.050 M HNO₃
1	5.0 mL	2.0 mL	3.0 mL
2	5.0 mL	2.5 mL	2.5 mL
3	5.0 mL	3.0 mL	2.0 mL
4	5.0 mL	3.5 mL	1.5 mL
5	5.0 mL	4.5 mL	0.5 mL

Beaker	**0.00200 M Fe(NO₃)₃**	0.00200 M KSCN	0.050 M HNO₃
1	5.0 mL	2.0 mL	3.0 mL
2	5.0 mL	2.5 mL	2.5 mL
3	5.0 mL	3.0 mL	2.0 mL
4	5.0 mL	3.5 mL	1.5 mL
5	5.0 mL	4.5 mL	0.5 mL

MV=MV 0.002(5) = x (10)

Table #3. Absorbance of Equilibrium Solutions

Solution	Initial $[SCN^-]$	Initial $[Fe^{3+}]$	Percent Transmittance	Absorbance	Equilibrium $[FeSCN^{2+}]$
1	0.0004	0.001	15.9	0.799	1.52×10^{-4}
2			12.7		
3			12		
4			26.6		
5			15.7 Sample data		
	Calculate using MV = MV	Calculate using MV = MV	Measure	Calculate using A = log 100/%T	Use calibration graph

Calculation of Equilibrium Concentration using ICE Tables
Show five complete ICE tables and calculations of Kc for each solution.
Show one complete for each sample. These samples should be clearly labeled.

ANALYSIS:

Procedural Questions:

1. Describe the function of the "blank".
   The blank allows us to set the 100% transmittance to take into account the cuvette and the solution so that any differences in transmittance can be attributed to the solution under study.

2. a. Why was 0.050 M HNO_3 used in the "blank"?
   The nitric acid was present in all the solutions.
   b. Why was it necessary to include HNO_3 in the solution?
   Iron (III) ions form colored complex ions with hydroxide ions. By adding acid, we reduce the concentration of hydroxide ions and thus the formation of these colored complex ions that would interfere with our absorbance.

3. How did you calculate the absorbance of the solution from the measured value of the percent transmittance? Show the algebra used to rearrange the two equations.

$$\%T = I_t/T_0 \text{ x } 100 \quad \rightarrow \quad A = \log I_0/T_t$$

$$\%T = I_t/T_0 \text{ x } 100$$

4. How was the concentration of $FESCN^{2+}$ a known in Part A, but an unknown in Part B?

   In this set of beakers (part A) the concentration of Fe^{3+} ions is overwhelmingly greater than the concentration of SCN- ions. This shifts the equilibrium to the right so far that ALL the SCN^- ions will react to become $FeSCN^{2+}$ ions. In part B, the concentration of Fe^{3+} ions and SCN- ions is similar and relatively small, thus the reaction reaches equilibrium in these beakers and the final concentrations are a function of the equilibrium constant.

5. Explain why the percent transmittance changed as the solution concentration changed in Part A. Compare the visible appearance of the eight solutions.

   The decreasing concentration of the deep red $FeSCN^{2+}$ ions in the beakers resulted progressively lighter solution. The lighter solutions absorb less light and so the percent transmittance increased. A progressively greater fraction of light passes through the solution.

6. Explain how your standard graph allowed you to determine the concentrations of the solutions at equilibrium.

The standard graph or calibration curve showed the linear relationship between absorbance and concentration. By measuring the percent transmittance of a solution of unknown concentration, we could calculate its absorbance. By finding this absorbance on the y-axis we could find the corresponding concentration of the solution on the x-axis.

In questions 7 – 10, explain how the following actions would cause the quantity in question to be too large, too small, or no change.

7. An error was made in preparing the $Fe(NO_3)_3$ solution in Part A. Its concentration was 0.250 molar but was labeled as 0.200 molar. How would the slope of the calibration curve (absorbance on the y-axis versus concentration of $Fe(SCN)^{2+}$ on the x-axis) be affected?

Since the Fe^{3+} concentration is great excess in part A, this error would have no impact on the outcome. The SCN^- concentration determines the concentration of $FeSCN^{2+}$.

8. An error was made in preparing the KSCN solution in Part A. Its concentration was 0.003 molar but was labeled as 0.002 molar. How would the slope of the calibration curve (absorbance on the y-axis versus concentration of $Fe(SCN)^{2+}$ on the x-axis) be affected? How would this impact your Kc in Part C?

Since the SCN^- concentration determines the concentration of $FeSCN^{2+}$, this error will impact the outcome. The concentration of the $FeSCN^{2+}$, will be higher than we intended it to be. This will decrease the measured percent transmittance and thus decrease the absorbance. So the slope of the line will be less than it should have been.

9. How would your calculated value of K_c compare to the actual value if the determination of absorbance were done on a solution that had been placed in a cell that was:
a. wet on the inside with rinse water? Explain.

Wet on the inside, would decrease the concentration of the solution, so the percent transmittance will increase and absorbance will decrease. When we find absorbance on the y-axis it will be a lower value than it would have been without this error. So, the concentration of the $FeSCN^{2+}$ will lower. Since the $FeSCN^{2+}$ is on top of the fraction, the calculated Kc will also be lower.

b. had fingerprints on the outside? Explain

Finger prints on the outside will have the opposite effect. The fingerprints will absorb light and decrease the percent transmittance and absorbance will higher than it would have been without the fingerprints. When we find absorbance on the y-axis it will be a higher value than it would have been without this error. So, the concentration of the $FeSCN^{2+}$ we find using the graph will be higher. Since the $FeSCN^{2+}$ is on top of the fraction, the calculated Kc will also be higher.

10. When adding the solution of HNO_3 from the buret in Step 14 to beaker 4, you added about 2 mL instead of 1.0 mL for a total volume of 11.0 mL. How would the absorbance differ? How would the calculated value of the equilibrium constant be affected for this sample?

With the increased volume of the solution, the concentration would be decreased. So the measured absorbance would be less and the measured concentration from the graph would also be less. This would lead to a smaller calculated K.

Concept Questions:
11. a. State Beer's Law.

Beer's Law – the absorbance of the solution depends upon the concentration of the solution. Increasing concentration of a colored ion in solution will absorb more light.

> Excerpt from the lab tech
> The Beer-Lambert Law relates the concentration of a solution to its absorbance. It is reasonable to assume that the intensity of light passing through a solution would be influenced by the distance the light must travel through the solution and by the concentration of the absorbing solution. The mathematical relationship for these influences is known as the Beer-Lambert law shown in equation 3.
> $$A = \varepsilon bc \qquad\qquad\qquad \text{Equation 3}$$
> Where A = absorbance (defined in eq. 2), ε= molar absorptivity, b = thickness of the absorbing solution (in cm), and c = concentration of the absorbing substance (in moles of solute per liter of solution).
> Molar absorptivity is a proportionality constant. It has a specific value for each absorbing substance at each wavelength. In most experimental work, cuvettes with a uniform diameter are used for the entire determination, so that b is constant. When doing an experiment with a fixed wavelength and cuvettes of uniform size, the absorbance, A, is directly proportional to the concentration, c. A graph of A versus c should be a straight line.

b. Explain the significance of each term in the equation.
$$A = \varepsilon bc$$
ε = molar absorptivity constant is a constant that depends upon the solution
b = distance the light travels – increasing distance would increase the absorption
c = concentration of the solution

c. Which of these terms will vary and which will remain constant in this experiment? Relate this to $y = mx + b$ to explain the linear graph.
$$A = \varepsilon b\ c$$
$$y = m\ \ x$$
Absorbance is the y and graphed on the y-axis — a variable function of concentration
Concentration is the x and graphed on the x- axis — the independent variable

The slope of the line is the εb. Since we graphed the data for the solution and will use the same cuvette– it was not necessary to find the εb. We can simply use the graph.

d. Explain how Beer's Law allow you to determine the concentration of a solution.

Since the relationship between absorbance and concentration is linear. We first used solutions of known concentrations, measured their percent transmittance, calculated their absorbance, and graphed absorbance as a function of concentration. We then use this straight line graph to find the concentration of the other solutions. We measure percent transmittance and then calculate absorbance. Using the graph we find the concentration of solution associated with that absorbance.

12. The equilibrium reaction that we have represented as, $Fe^{3+} + SCN^- \leftrightarrows [Fe(SCN)]^{2+}$, is actually a displacement reaction. Which species is replaced by which other species? Write the alternative version of this reaction to show the species displaced.

$$[Fe(OH_2)_6]^{3+} + SCN^- \rightarrow [Fe(OH_2)_5SCN]^{2+} + H_2O$$

The iron ion is covalently bonded to six water molecules as a complex ion. One of the water molecules is displaced and replaced by the thiocyanate ion.

13. Ions in solution from complexes. Coordination complexes.

Excerpt from background

There is a universal tendency of metal ions to form complexes with negatively charged ions (e.g. SCN^-) and with neutral molecules (e.g., water, H_2O, and ammonia, NH_3) that have lone pairs of electrons (nonbonding pairs). This tendency can be understood as the result of the attractive force between positively charged ions and negatively charged ions or negatively charged lone pair of electrons. Complex ions are examples of Lewis acid/base pairs. The Lewis base is the electron pair donor, while the Lewis acid is the electron pair acceptor. Therefore when you dissolve a metal salt in water, the metal ions will form complexes with either the water, with the anions of the salt, or with any other anions, or neutral molecules that have lone pairs of electrons that may be added. The ions or neutral molecules bound to the metal ion are called ligands.
 When it has a net charge, the complex will remain in solution as a complex ion. The $[Fe(SCN)]^{2+}$ complex ion behaves this way. The equilibrium is called a homogenous equilibrium because all of the reactants and products are present together in one phase, the solution.
 Some neutral complexes are very insoluble and precipitate out of solution. An example of this kind of behavior is the precipitation of solid $BaSO_4$ when a solution Na_2SO_4 is added to a solution of $BaCl_2$. The equilibrium between a solid insoluble salt and its constituent ions in solution is called a heterogenous equilibrium because the system involves two phases: a solid phase consisting of the pure insoluble salt and a liquid phase containing constituent ions of the salt in solution. $BaSO_4(s), \leftrightarrows Ba^{2+} (aq) + SO_4^{2-}(aq)$

a. Describe the formation of a complex that is insoluble. What is the charge on the insoluble complex?
Write the reversible reaction for a sample. Why is this a heterogenous equilibrium.
Write the equilibrium constant expression for this equilibrium condition. Describe the state of equilibrium. Include rates and conditions.

When the complex ion has no net charge the ions precipitate out of solution. The neutral complex are not then attracted to the polar water molecules.
Example--
$$BaSO_4(s), \leftrightarrows Ba^{2+} (aq) + SO_4^{2-}(aq) \qquad Ksp = [Ba^{2+}][SO_4^{2-}]$$
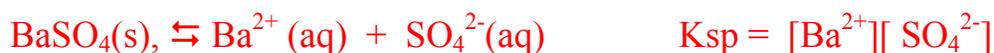
Equilibrium results when the two reactions occur at equal rates. The ions are dissociating into solution at the same rate that the ions crystallize into the solid. The concentration of the ions in the solution remains constant.

We may model this as the breaking and forming of the ionic bond between these ions or we can also use the model of the complex ions. The sulfate ligand is displaced by water molecules as the ions move into the solution. The Barium with sulfate ion coordination complex is neutral and thus not attracted to the water. But when the sulfate ion is displaced the ions are attracted to water.

This is a heterogenous equilibrium because there is an equilibrium between two states: solution and solid.

b. Describe the formation of a complex ion that remains in solution. Why do complex ions remain in solution? Write the reversible reaction for a sample. Why is this a homogenous equilibrium. Write the equilibrium constant expression for this equilibrium condition.

We previously observed several colored complex ions involving copper (II) ion. The copper (II) has empty orbitals and can thus form covalent bonds with a species with lone pairs of electrons – a ligand or Lewis base (electron pair donor). Lone pairs of electrons are attracted the positive charge of the copper(II). This attraction leads to the formation of a covalent bond (bond formation is energetically favorable). When the coordination complex has a net charge the coordination complex will likely remain in solution (until saturated). The ion is attracted to the polar water molecule- again the formation of attractions is energetically favorable.

$$[Cu(OH_2)_6]^{2+} \; + \; Cl^- \rightleftharpoons [CuCl_4]^{2-} \; + \; H_2O$$
light blue   green
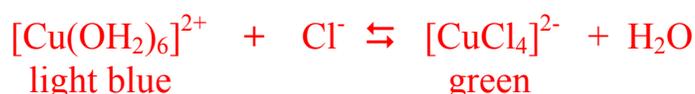
c. Draw the Lewis structure for water. Describe how the water molecule forms a bond with the iron (III) ion. What part of the water molecule is involved and what part of the iron (III) ion is involved? Identify the Lewis Acid and Lewis Base.

Fe^{3+} ion has an empty orbital; with that empty orbital the iron can overlap its orbital to form a covalent bond. The water molecule has two lone pairs of electrons. The water molecule donates its electron pair to form this covalent bond acting as a Lewis base. (This is just like a Bronsted-Lowry base that accepts a proton by forming a covalent bond with the H+. The H+ (proton) does not have any electrons but will form covalent bonds with another that has alone pair of electrons. The Fe3+ ion accepts the lone pair of electrons acting as a Lewis acid.
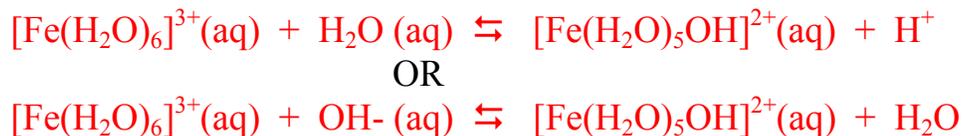
d. Draw the Lewis Structure for the SCN⁻ ion. Explain why the Fe(SCN)²⁺ ion has a positive two charge. Relate this to the charge on each ion that combined to form this complex ion. Identify the Lewis Acid and Lewis Base.
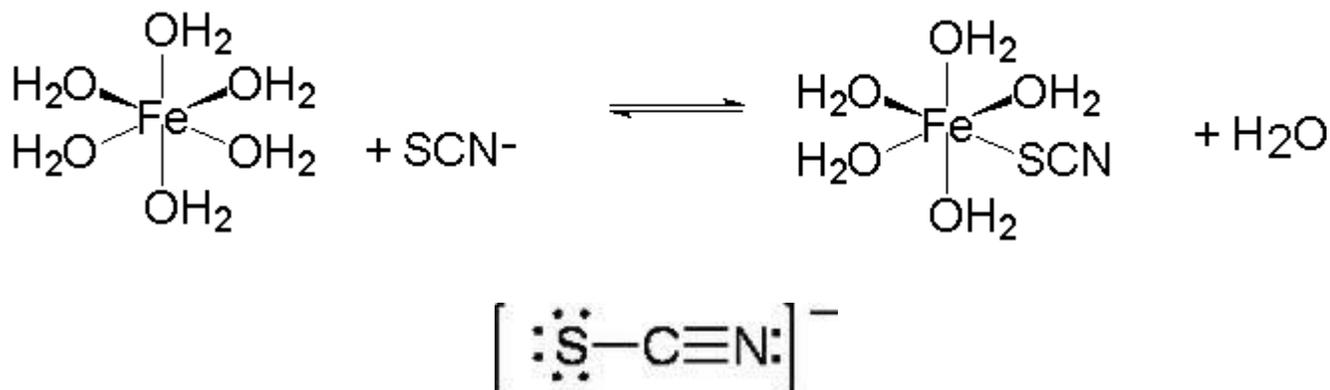
The thiocyante ion has a lone pair of electrons and thus can be an electron pair donor (Lewis base) or a proton accepter (Bronsted-Lowry base) by forming a covalent bond with the H+ ion. In this case it acts as a Lewis base by donating a pair of electrons to the Fe^{3+} ion and forming covalent bond and a coordination complex (complex ion).

The Fe^{3+} ion complex with six water molecules has a net +3 charge since the water molecules are all netural. The Fe^{3+} ion complex with five water molecules and the thiocyante ion (-1) has a net charge of +2.

14. Write the equation for the hydrolysis of $[Fe(H_2O)_6]^{3+}$ ions. Nitric acid is present in the solutions to prevent hydrolysis of this ion. Why is nitric acid effective for this purpose?

$$[Fe(H_2O)_6]^{3+}(aq) + H_2O (aq) \leftrightarrows [Fe(H_2O)_5OH]^{2+}(aq) + H^+$$

OR

$$[Fe(H_2O)_6]^{3+}(aq) + OH\text{-} (aq) \leftrightarrows [Fe(H_2O)_5OH]^{2+}(aq) + H_2O$$

The coordination complex with hydroxide ion is an orange colored ion that interferes with our absorbance.

Adding the acid, the H+ ions react with hydroxide ions in solution. This shifts the second equilibrium to the left by removing reactant. Or if you consider the first equilibrium, adding excess H+ ions shifts that equilibrium to the left by adding product.

Iron(III) ion introduces a complication because of its reaction with water to form iron hydroxide, which is insoluble in water:

$$Fe^{3+} (aq) + 3 H_2O (l) \Longleftrightarrow Fe(OH)_3 (s) + 3 H^+ (aq)$$
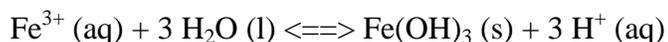
To avoid precipitation of iron (III) hydroxide, you will include excess nitric acid (HNO_3) in all solutions, to shift this equilibrium far to the left. Because neither hydrogen ions nor nitrate ions are components of the iron (III) thiocyanate equilibrium, nitric acid does not affect the equilibrium position of the reaction that produces $FeSCN^{2+}$.

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15. Electromagnetic Radiation.
   a. Describe the relationship between wavelength and frequency.
   Frequency and wavelength are inversely related. The longer the wave (higher wavelength) is associated with less waves per second (lower frequency)
   b. Describe the relationship between frequency and energy of the photon.
   Frequency and energy are directly related. Higher frequency is associated with higher energy.
   c. Describe the interaction of a photon and atom or ion. What happens to electrons?
The photon of light may interact with the atom to move an electron to higher energy level if the energy of that photon corresponds to the difference in energy between the two states. The electron moves to a higher energy (with more potential energy the electron in this state is less stable). The electron may then fallback to the lower energy and release this absorbed energy. The resulting wavelength may be within the visible light range and we would observe this a colored light.
16. Explain why transition metal ion are often colored. List the colors of some transition ions.

The transition metals have valence electrons in d-orbitals. The difference in energy between these orbitals is small enough to fall within the range of visible colored light.

Additional Calculations:
17. a. Calculate the initial concentrations of SCN^- ions and Fe^{3+} ions when a solution was prepared by mixing 5.00 mL of 0 .00200 M KSCN, 6.00 mL of 0.220 M $Fe(NO_3)_3$, and 14.00 mL of 0.050 M HNO_3. (NOTE: The total final volume of these solutions is 25.0 mL.)

   $MV = MV$

   5.00 mL of 0 .00200 M KSCN
   $0.002(5) = x(25)$ $x = 0.0004M$

   6.00 mL of 0.220 M $Fe(NO_3)_3$
   $0.220(6) = x(25)$ $x = M$

   b. If you assume this reaction is driven to completion because of the large excess of one ion, what is the concentration of $Fe(SCN)^{2+}$ that would be formed?

   Since the Fe3+ concentration is in large excess the concentration $Fe(SCN)^{2+}$ of the is a function of the SCN- ion concentration. All of the SCN-ions reacted to form $Fe(SCN)^{2+}$. So the concentration of $Fe(SCN)^{2+}$ is 0.0004M.

18. A student prepared an equilibrium solution by mixing the following solutions: 2.00 mL of 0.00250M $Fe(NO_3)_3$, 5.00 mL of 0.00250 M KSCN, and 3.00 mL of 0.050 M HNO_3. From a plot of absorbance vs. concentration, the equilibrium concentration of $Fe(SCN)^{2+}$ was determined to be 3.6×10^{-5} M.

    a. Calculate the initial concentrations of all ions before reaction
       MV=MV
       0.0025(2) = x (10) x = 0.0005 M Fe3+
       MV=MV
       0.0025(5) = x (10) x = 0.00125 M SCN-

    b. Complete the table to show the concentrations at equilibrium.

	Fe^{3+} (aq) +	SCN-(aq) ⇆	$Fe(SCN)^{2+}$(aq)
initial concentration	0.0005	0.00125	0
change in concentration	-x - 3.6×10^{-5} M	-x - 3.6×10^{-5} M	+x 3.6×10^{-5} M
equilibrium concentration			3.6×10^{-5} M

    c. Calculate the value of the equilibrium constant for the reaction:

19. A volume of 3.0 mL of 0.010 M D is added to 4.0 mL of 0.018 M E and 3.0 mL of water. At equilibrium the solution is 0.0014 M in F. Calculate Kc for the following reaction. Show the table.
        D + 2E ⇆ F

  Calculate the initial concentrations of all ions before reaction
     MV=MV
     0.01(3) = x (10) x = 0.003M D
     MV=MV
     0.018 (4) = x (10) x = 0.009M E

Complete the table to show the concentrations at equilibrium.

	D +	2E ⇆	F
initial concentration	0.003	0.009	0
change in concentration	-x - 0.0014	-2x - 0.0028	+x 0.0014
equilibrium concentration	0.0016	0.0062	0.0014

      K= [F] / [D][E]^2
        $(0.0014) / (0.0016)(0.0062)^2$

The Reaction Quotient

20. $K = 5.6 \times 10^{-12}$ at 500 K for the dissociation of iodine molecules to iodine atoms. I_2 (g) $\leftrightarrows$ 2 I (g). A mixture has $[I_2] = 0.020$ mol L and $[I] = 2.0 \times 10^{-8}$ mol/L. Is the reaction at equilibrium (at 500 K)? If not, which way will the reaction proceed to reach equilibrium? (16.10)

$Q = [I]^2/[I_2] = (2.0 \times 10^{-8})^2 / 0.020 = 2.0 \times 10^{-14}$ since the Q<K, the reaction is not at equilibrium. The Q needs to get bigger and the Q = P/R so the products (on top of fraction) need to increase so the system will shift to the right.

21. The reaction $2NO_2$ (g) $\leftrightarrows$ N_2O_4 (g) has the equilibrium constant, K, of 171 at 25°C. If 2.0×10^{-3} moles of NO_2 is present in a 10.0 L flask along with 1.5×10^{-3} moles of N_2O_4, is the system at equilibrium? If it is not at equilibrium, does the concentration of NO_2 increase or decrease as the system reaches equilibrium? (16.11)

$Q = [N_2O_4]/[NO_2]^2$
$= [1.5 \times 10^{-3}$ moles of $N_2O_4/ 10.0$ L] / [2.0×10^{-3} moles of $NO_2 / 10.0$ L]^2
$= 275$

Q is bigger than K so the Q (P/R) needs to get smaller shift to reactants

22. The equilibrium constant, K, for the reaction 2 NOCl (g) $\leftrightarrows$ 2 NO (g) + Cl_2 (g) is 3.9×10^{-3} at 300K. A mixture contains the gases at the following concentrations: $[NOCl] = 5.0 \times 10^{-3}$ M, $[NO] = 2.5 \times 10^{-3}$ M, and $[Cl_2] = 2.0 \times 10^{-3}$ M. Is the reaction at equilibrium (at 300 K)? If not, which way will the reaction proceed to reach equilibrium? (16.13)

$Q = [NO]^2[Cl_2]/[NOCl]^2$
$= [2.5 \times 10^{-3} M]^2[2.0 \times 10^{-3} M]/[5.0 \times 10^{-3} M]^2$
$= 5 \times 10^{-4}$

$Q = 5 \times 10^{-4}$ and $K = 3.9 \times 10^{-3}$
Q too small need to get bigger so shift to right towards product

Calculating Equilibrium Constants

23. An equilibrium mixture of SO_2, O_2, and SO_3 at 1000K contains the gases at the following concentrations: $[SO_2] = 3.77 \times 10^{-3}$ M, $[O_2] = 4.30 \times 10^{-3}$ M, $[SO_3] = 4.13 \times 10^{-3}$ M. Calculate the equilibrium constant, K, for the reaction $2\ SO_2(g) + O_2(g) \leftrightarrows 2\ SO_3(g)$ (16.15)

$$K = [SO_3]^2/[SO_2]^2[O_2]$$
$$= [4.13 \times 10^{-3}]^2/[3.77 \times 10^{-3}]^2[4.30 \times 10^{-3}]$$
$$= 279$$

24. Hydrogen and carbon dioxide react at a high temperature to give water and carbon monoxide. (16.17)
$$H_2(g) + CO_2(g) \leftrightarrows H_2O(g) + CO(g)$$
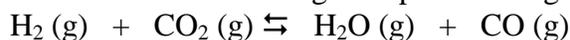
a. Laboratory measurements at 986°C show that there is 0.11 mole each of CO and H_2O vapor and 0.087 mole each of H_2 and CO_2 at equilibrium in a 1.0 L container. Calculate the equilibrium constant for the reaction at 986°C.

$$K = [H_2O][CO]/[CO_2][H_2]$$
$$\frac{(0.11\text{mol }H_2O /L)\ (0.11\text{mol }CO /L)}{(0.087 \text{ mol } H_2/L)\ (0.087 \text{ mol } CO_2/L)}$$
$$K = 1.6$$

b. Suppose 0.050 mol each of H_2 and CO_2 are placed in 2.0 L container. When equilibrium is achieved at 986°C, what amounts of CO and H_2O, in moles will be present? (Use K from part a)

	H_2 (g) +	CO_2 (g) $\leftrightarrows$	H_2O (g)	+ CO (g)
Initial	0.05 mol/ 2L	0.05 mol/ 2L	0	0
Change	-x	-x	+x	+x
Equilibrium	0.025-x	0.025-x	x	X
	0.011	0.011	0.014	0.014

$$K = [H_2O][CO]/[CO_2][H_2] = 1.6$$
$$K = [x][x]/[0.025\text{-}x][0.025\text{-}x] = 1.6$$
$$x = .014$$

25. You place 3.00 mol of pure SO_3 in an 8.00 L flask at 1150 K. The system reaches equilibrium according to the following reaction: $2 SO_3(g) \rightleftarrows 2 SO_2(g) + O_2(g)$ At equilibrium, 0.58 mol of O_2 has been formed. Calculate K for the reaction at 1150 K. (16.19)

	2 SO₃(g)	⇄ 2 SO₂(g)	+ O₂(g)
Initial	3 mol SO₃/8L **0.375 M**	0	0
Change	-2x - 0.145	+2x + 0.145	X = 0.0725
Equilibrium	0.23	0.145	**0.58 mol/8L Given 0.0725 M**

$K = [O_2][SO_2]^2 / [SO_3]^2$

$K = [0.0725][0.145]^2 / [0.23]^2$

$K = 0.029$

26. Carbon tetrachloride can be produced by the reaction: $CS_2 (g) + 3 Cl_2 (g) \rightleftarrows S_2Cl_2 (g) + CCl_4 (g)$ Suppose 1.2 mol of CS_2 and 3.6 mol of Cl_2 are placed in a 1.00 L flask. After equilibrium has been achieved, the mixture contains 0.90 mol CCl_4. Calculate K.

	CS₂ (g) +	3 Cl₂ (g) ⇄	S₂Cl₂ (g)	+ CCl₄ (g)
Initial	1.2 M	3.6 M	0	0
Change	-x	- 3x	+x	+x x = 0.9
Equilibrium	0.3	0.9	0.9	0.90M

$K = [S_2Cl_2][CCl_4]/[Cl_2]^3[CS_2] = [0.9][0.9]/[0.9]^3[0.3] = 3.7$

Using Equilibrium Constants

27. The equilibrium constant for the reaction N_2O_4 (g) $\leftrightarrows$ 2 NO_2 (g) at 25°C is 5.88 x 10^{-3}. Suppose 15.6 g of N_2O_4 is placed in 5.00 L flask at 25°C. Calculate (16.23)
    a. The number of moles of NO_2 present at equilibrium
    b. The percentage of the original N_2O_4 that is dissociated

	N_2O_4 (g)	$\leftrightarrows$ 2 NO_2 (g)
Initial	15.6 g 1 mol 5L 92.016g **0.0339M**	0
Change	-x	+2x
Equilibrium	0.0339 - x	2x

$$K = [NO_2]^2/[N_2O_4] = 5.88 \text{ x } 10^{-3} = (2x)^2 / 0.0339 - x$$

$$5.88 \text{ x } 10^{-3} (0.0339 - x) = 4x^2$$

$$x = 0.00636$$

28. Carbonyl bromide decomposes to carbon monoxide and bromine. $COBr_2$ (g) $\leftrightarrows$ CO (g) + Br_2 (g) K = 0.190 at 73°C. If you place 0.500 mol $COBr_2$ of in a 2.00 L flask and heat it to 73°C, what are the equilibrium concentrations of $COBr_2$, CO, and Br_2? What percentage of the original $COBr_2$ decomposed at this temperature? (16.24)

	$COBr_2$ (g)	$\leftrightarrows$ CO (g)	+ Br_2 (g)
Initial	0.0500 mol $COBr_2$/8L **0.250 M**	0	0
Change	-x	+x	+x
Equilibrium	0.25 - x	x	x

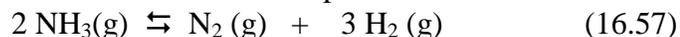$$K = [CO][Br_2]/[COBr_2] = (x)(x)/(0.25 - x) = 0.190$$
$$0 = x^2 - 0.190(0.25-x)$$
solve using quadratic equation
x = 0.143 and - 0.333 eliminate - 0.333 as not reasonable so x = 0.143
$$[COBr_2] = 0.25-x = 0.107 M \quad [CO] = [Br_2] = x = 0.143$$

% $COBr_2$ decomposed = 0.143M/0.250 x 100 = 57.1%

29. At 450ºC 3.60 mol of ammonia are placed in a 2.00 L vessel and allowed to decompose to its elements.

$$2 NH_3(g) \leftrightarrows N_2 (g) + 3 H_2 (g) \qquad (16.57)$$

If the experimental value of K is 6.3 for the reaction at this temperature, calculate the equilibrium concentration of each reagent. (show the ICE table). What is the total pressure in the flask?

	$2 NH_3 (g)$	$\leftrightarrows N_2 (g)$	$+ 3 H_2$
Initial	1.80	0	0
Change	-2x	+x	+3x
Equilibrium	1.8 - 2x	x	3x

$$K = 6.3 = [N_2][H_2]^3 \Big/ [NH_3]^2 = (x)(3x)^3 \Big/ (1.8 - 2x)^2 = 27x^4 \Big/ (1.8\text{-}x)^2$$

Square root both sides to simply and then use quadratic formula

Disturbing a Chemical Equilibrium

30. Dinitrogen trioxide decomposes to NO and NO_2 in an endothermic process ($\Delta H = 40.5$ kJ/mol) (16.32)

$$N_2O_3\ (g) \leftrightarrows\ NO\ (g)\ +\ NO_2\ (g)$$

Predict and explain which way equilibrium will shift when each of the following changes is made:

    a. Adding more N_2O_3 (g)

The change - Adding more reactant
The system responds to counteract – remove reactant so shift to the RIGHT

    b. Adding more NO_2 (g)

The change - Adding more product
The system responds to counteract – remove product so shift to the LEFT

    c. Increasing the volume of the flask

The change – Increase in volume decreased the pressure
The system responds to counteract – increase pressure (caused by collisions)
    so shift to the side with more molecules (more collisions) shift to RIGHT

    d. Lowering the temperature

Energy + $N_2O_3\ (g) \leftrightarrows\ NO\ (g)\ +\ NO_2\ (g)$ Since the ΔH is positive energy
is added – an endothermic reaction that increases the enthalpy
    The change – decreasing temperature removes energy – a reactant
    System responds to replace energy – a reactant shift LEFT

31. A reaction in the formation of smog is $O_3\ (g)\ +\ NO\ (g) \leftrightarrows O_2\ (g)\ +\ NO_2\ (g)$ K= 6.0×10^{34} (16.62)

    a. If the initial concentrations are $[O_3] = 1.0 \times 10^{-6}$ M, $[NO] = 1.0 \times 10^{-5}$M, $[NO_2] = 2.5 \times 10^{-4}$M, and $[O_2] = 8.2 \times 10^{-3}$M, is the system at equilibrium? If not in what direction will it proceed?

$Q = [O_2][\ NO_2]/[\ NO][\ O_3]$
    $= [8.2 \times 10^{-3}$M,$][\ 2.5 \times 10^{-4}$M$]/[\ 1.0 \times 10^{-5}$M$][\ 1.0 \times 10^{-6}$ M$]$
    $=$

    b. If the temperature is increased, as on a very warm day, will the concentration of products increase or decrease? (Hint: You will need to calculate ΔH to determine whether the reaction is endothermic or exothermic.)

Manipulating K expressions

32. K_p for the formation of phosgene, $COCl_2$ is 6.5×10^{11} at 25°C. CO (g) + Cl_2 (g) $\leftrightarrows COCl_2$ (g)

    What is the value of Kp for the dissociation of phosgene $COCl_2$ (g) $\leftrightarrows$ CO (g) + Cl_2 (g)? (16. 38)

Kp = $[COCl_2]/[\ CO][Cl_2]\ =\ 6.5 \times 10^{11}$

so Kp for reverser reaction is simply flipped over or the inverse

Lab 4. Spectrophotometric Determination of Equilibrium Constant

$Kp = [CO][Cl_2] / [COCl_2] = 1 / 6.5 \times 10^{11}$ or $1/ Kp = 1/ ([COCl_2]/[CO][Cl_2])$

33. For the reaction N_2 (g) + O_2 (g) $\rightleftarrows$ 2 NO (g) K = 1.7×10^{-3} at 2300 K. (16. 37)
    a. What is K for the reaction when written as 1/2 N_2 (g) + 1/2 O_2 (g) $\rightleftarrows$ NO (g)

since the reaction is multiplied by ½ the K is raised to ½ power K =0.041

    b. What is K for the reaction when written as   2 NO (g) $\rightleftarrows$ N_2 (g) + O_2 (g)
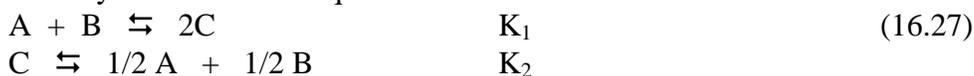
since the reaction is reversed the K is flipped take inverse 1/K   K = 588

34. Which of the following correctly relates the two equilibrium constants for the two reactions shown?
                              A + B $\rightleftarrows$ 2C K_1 (16.26)
                             2A + 2B $\rightleftarrows$ 4C K_2
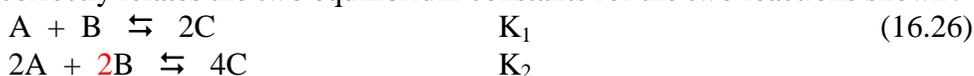
  a. $K_2 = 2 K_1$ b. $K_2 = 1/K_1$ c. $K_2 = K_1^2$ d. $K_2 = 1/K_1^2$

35. Which of the following correctly relates the two equilibrium constants for the two reactions shown?
                              A + B $\rightleftarrows$ 2C K_1 (16.27)
                              C $\rightleftarrows$ 1/2 A + 1/2 B K_2

  a. $K_2 = 1/ (K_1)^{1/2}$ b. $K_2 = K_1^2$ c. $K_2 = 1/K_1$ d. $K_2 = -K_1^{1/2}$

36. The equilibrium constant for the reaction CO_2 (g) $\rightleftarrows$ 1/2 O_2 (g) + CO (g) is 6.66×10^{-12} at 1000K.
    Calculate K for the reaction O_2 (g) + 2 CO (g) $\rightleftarrows$ 2 CO_2 (g)   (16.29)

Reverse reaction and multiply by two so the K is inversed and squared.
  $1/K^2 = 2.25 \times 10^{22}$

Calculating and Using Kp

37. 3.00 moles of pure $SO_3(g)$ are introduced into an 8.00 L container at 1105 K. At equilibrium, 0.58 mol of $O_2(g)$ has been formed. For the reaction at 1105 K :

$$2SO_3(g) \leftrightarrows 2SO_2(g) + O_2(g)$$

a. Calculate Kc

	2SO₃(g) ⇆	2SO₂(g) +	O₂(g)
Initial	3 mol/8 L = 0.375 given info	0 given info	0 given info
Change	-2x -2 (0.725)	+2x + 2(0.0725)	+x + 0.0725
Equilibrium	0.375 – 0.145 = 0.23	0.145	0.58 mol/8L = 0.0725 given info

Now use those concentrations at equilibrium to calculate the Kc

$$Kc = [SO_2]^2[O_2]/[SO_3]^2 = [0.145]^2[0.0725]/[0.23]^2 = 0.0288$$

b. Calculate Kp for this equilibrium.

To turn Kc into Kp need to turn concentrations into pressure (P = n/v RT)

$Kc = [SO_2](RT)^2[O_2](RT)/[SO_3](RT)^2$ **notice the (RT)2 cancel leaving just multiply by RT so the Kc (RT) = Kp 0.0288 (0.0821)(1105) Kp = 26.1**

Or if you memorize the equation $Kp = Kc (RT)^{\Delta n}$

from the AP formula sheet

Δn = change in the number of moles of gas = n_f - n_i

3 moles – 2 moles so change in moles = 1

38. $SO_2(g)$ and $O_2(g)$ in the ratio **2 moles : 1 mole** were mixed at constant temperature and a constant pressure of 9 atmospheres in the presence of a catalyst. At equilibrium, one third of the $SO_2(g)$ had been converted to $SO_3(g)$. Calculate the equilibrium partial pressures and the Kp.

	$2SO_2(g)$ +	$O_2(g)$ ⇆	$2SO_3(g)$
Initial P_{total} = **9 atm** P_{total} = P_{SO2} + P_{O2} 9 = 2x + x so x = 3	**2x** **given info** 6	**X** **given info** 3	**0** **given info**
Change	-2	-1	+2
Equilibrium	4	2	**2** **(1/3 of original SO2)**

$$Kp = = 2^2/2(4)^2 = 0.125$$

39. Ammonium hydrogen sulfide decomposes on heating. (16.52)

$$NH_4HS \ (s) \ ⇆ \ NH_3 \ (g) \ + \ H_2S \ (g) \qquad Kp = 0.11 \ (at \ 25°C)$$

a. When the partial pressures are measured in atmospheres , what is the total pressure in the flask at equilibrium?

b. Calculate the value of Kc at 25°C.

40. Nitrosyl bromide, NOBr, dissociates readily at room temperature. NOBr (g) ⇆ NO (g) + ½ Br$_2$(g) Some NOBr I is placed in a flask at 25°C and allowed to dissociate. The total pressure at equilibrium is 190 mmHg and the compound is found to be 34% dissociated. What is the value of Kp. (16.70)

Ptotal = 190 mmHg compound 34% dissociated = P_{NOBR}

41. Hemoglobin(Hb) can form a complex with both O_2 and CO. For the reaction,

$$HbO_2 \ (aq) \ + \ CO \ (g) \ ⇆ \ HbCO \ (aq) \ + \ O_2 \ (g)$$

At body temperature, K_c is about 2.0×10^2.

If the ratio of [HbCO]/[HbO$_2$] comes close to 1, death is probable. (16.68)

a. Explain why the K_c and the K_p are equal in this case.

b. What partial pressure of CO in the air is likely to be fatal? Assume P_{O2} is 0.20 atm.

42. The total pressure for a mixture of N_2O_4 and NO_2 is 1.5 atm. (16.58)

$$2 \ NO_2 \ (g) \ ⇆ \ N_2O_4 \ (g) \qquad Kp = 6.75 \ (at \ 25°C)$$

a. Calculate the partial pressure of each gas in the mixture.

b. Calculate the value of Kc at 25°C.