GENERAL CHEMISTRY LABORATORY II MANUAL

Spring Semester

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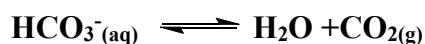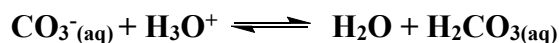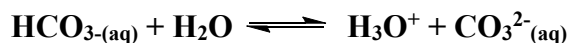# 1. Determination of Water Hardness

INTRODUCTION

Water quality is evaluated by using a number of parameters, including total ionic content, pH, total dissolved solids, organic compounds, and water hardness. Water hardness is a measure of the concentration of all the polyvalent cations dissolved in the water. Water that contains certain dissolved minerals in relatively large amounts is said to be hard. Although hard water is not necessarily unhealthy, there are two common problems associated with it. First, hard water contains certain cations, such as Ca^{2+}, which form water insoluble compounds with soaps. The formation of these precipitates reduces the cleaning ability of the soap and, at the same time, results in the formation of unsightly "scum" on clothing and in tubs and sinks. If Fe^{3+} is present, a red-brown deposit might form on the surfaces of sinks and tubs. Second, hard water encourages the buildup of boiler scale in water heaters, pipes, etc., which can cause considerable damage to expensive equipment and require time and expense for periodic cleaning.

The major ions responsible for natural water hardness are Ca^{2+}, Mg^{2+}, Fe^{3+} and HCO_3^- . The presence of bicarbonate ion is classified as temporary hardness because the water may be "softened" by boiling. Heating removes HCO_3^- and $CO_2(g)$, but also produces boiler scale when CO_3^{2-} ion is formed and precipitates with Ca^{2+}, Mg^{2+}, and Fe^{3+} ions. The equilibrium in an aqueous solution of carbonate ion is summarized in the following chemical equations, and the net equation represents the heating reaction that can serve to reduce temporary hardness.

$$HCO_{3-(aq)} + H_2O \rightleftharpoons H_3O^+ + CO_3^{2-}{}_{(aq)}$$

$$CO_3^-{}_{(aq)} + H_3O^+ \rightleftharpoons H_2O + H_2CO_{3(aq)}$$

$$HCO_3^-{}_{(aq)} \rightleftharpoons H_2O + CO_{2(g)}$$

$$\text{Net equation: } 2HCO_3^-{}_{(aq)} \rightleftharpoons H_2O + CO_3^{2-}{}_{(aq)} + CO_{2(g)} \tag{1}$$

Water that contains ions that cannot be removed by heating, such as Ca^{2+}, Mg^{2+}, Fe^{3+}, and SO_4^{2-}, is said to be permanently hard.

Hardness is defined as calcium and magnesium ion content. Since most analyses do not distinguish between Ca^{2+} and Mg^{2+}, and since most hardness is caused by carbonate mineral deposits, hardness is usually reported as parts per million (ppm) of calcium carbonate (by weight).

Water Hardness	
calcium carbonate (ppm)	designation
0-43	Soft
43-150	Slightly Hard
150-300	Moderately Hard
300-450	Hard
450	Very Hard

Figure 1. Water Hardness Scale

The purpose of this experiment is to determine the concentration of permanent hardness in water by titration with a standard solution of ethylenediaminetetraacetic acid, EDTA. This reagent is a weak acid that can lose four H on complete neutralization; the structural formula of the tetraprotic EDTA molecule follows:
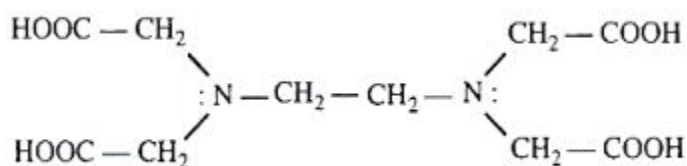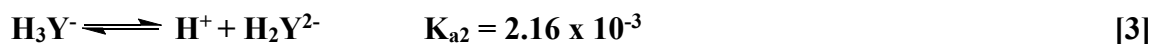

Figure 2. Structural Formula of EDTA

This acid acts as a polydentate ligand for most metal cations in aqueous solutions. The four acid oxygen sites and the two nitrogen atoms have unshared electron pairs, which can form bonds to a metal ion forming a complex ion or coordination compound. Most of the complexes formed are quite stable and, therefore, the use of EDTA as a titrant in chemical analysis has found widespread application.

Often the term H_4Y is used to indicate the above substance. Because H_4Y is a polyprotic acid, several ionization equilibriums are involved. The most important are:

$$H_4Y \rightleftharpoons H^+ + H_3Y^- \qquad K_{a1} = 1.00 \times 10^{-2} \qquad [2]$$

$$H_3Y^- \rightleftharpoons H^+ + H_2Y^{2-} \qquad K_{a2} = 2.16 \times 10^{-3} \qquad [3]$$

$$H_2Y^{2-} \rightleftharpoons H^+ + HY^{3-} \qquad K_{a3} = 6.92 \times 10^{-7} \qquad [4]$$

$$HY^{3-} \rightleftharpoons H^+ + Y^{4-} \qquad K_{a4} = 5.50 \times 10^{-11} \qquad [5]$$

Because the parent acid H_4Y is only sparingly soluble in water, the relatively soluble and readily available disodium salt ($Na_2H_2Y.2H_2O$) serves as the starting material for the preparation of standard EDTA solutions used in titrimetry. Since the predominant species in a solution of this salt is the H_2Y^{2-} ion, the pH of the resulting solution of this salt is approximately $\frac{1}{2}(pK_2+pK_3)$, or 4.4. The distribution of EDTA among its undissociated and dissociated forms varies considerably with pH. At any particular pH the distribution of EDTA species may be calculated from the four acid dissociation constants. These calculations can be plotted graphically as a distribution diagram. For example, by using the EDTA distribution diagram in Figure 1, which plots the fractional amount of each species as a function of pH, it can be seen in the 9-12 pH range only Y^{4-} and HY^{3-} are present in significant concentrations, and in the 6-9 pH range, H_2Y^{2-} and HY^{3-} predominate.
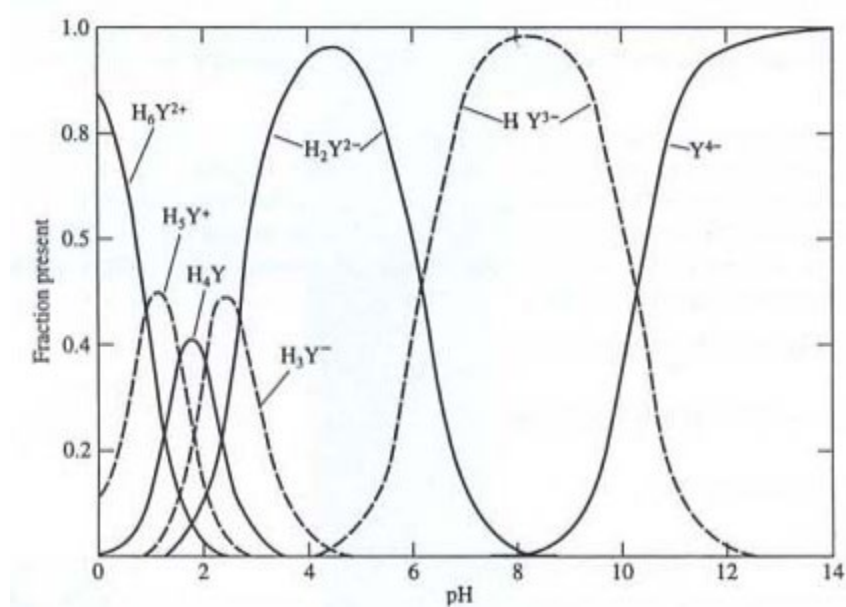
Figure 3. Distribution of EDTA Species as a Function of pH

The Y^{4-} ion forms very stable, one-to-one complexes with practically every metal ion, depending on pH and other conditions. Above pH=12, the Y^{4-} species predominates, and it is available to coordinate metal cations.

$$M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4} \tag{6}$$

An example of a six-coordinated species of an octahedral central metal ion and an EDTA molecule is the cobalt (III)-EDTA complex, CoY^-, whose structure is shown in Figure 4.

Most metal ion-EDTA titrations are performed in neutral or alkaline solutions because, although metal-EDTA complexes formed in titrations are quite stable, they can undergo dissociation in the presence of acid, which causes the equilibrium to shift away from the formation of the complex. This equilibrium (eqn 7) will lie to the left if the pH is maintained at a neutral or alkaline level.
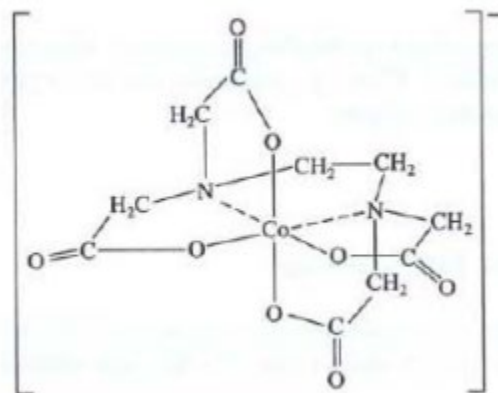

Figure 4. Cobalt (III)-EDTA Complex Ion

$$MY^{n-4} + 2H^+ \rightleftharpoons M^{n+} + H_2Y^{2-} \tag{7}$$

As can be seen from Figure 3, the predominant species in neutral and slightly alkaline solutions are H_2Y^{2-} and HY^{3-} , and the net titration reactions can be written as in the following two equations:

$$M^{n+} + H_2Y^{2-} \rightleftharpoons MY^{n-4} + 2H^+ \tag{8}$$

$$M^{n+} + HY^{3-} \rightleftharpoons MY^{n-4} + H^+ \tag{9}$$

The precise titration reaction, of course, depends upon the exact pH of the solution. The liberation of H^+ ions during titration would cause the pH to decrease and adversely affect the formation of the metal-EDTA complex. Therefore, in practice, a large excess of an inert buffer system, such as NH_3/NH_4Cl, is used to keep pH near the desired value for the particular application. In addition to maintaining the desired pH, the NH_3 system forms stable complexes with some metal ions, such as Cd^{2+}, Cu^{2+}, Ni^{2+}, and Zn^{2+}, and thus serves to prevent the undesired precipitation of these ions as metal hydroxides.

A very large number of indicators has been studied and employed for complexometric titrations. The term metallochromic indicator is frequently used to describe these substances because they form stable, highly colored complexes with most of the metal ions of interest. They are acid-base indicators as well, and the combination of their metal ion and acid-base indicating properties is used to obtain the indicator behavior desired in complexometric titrations. For example, Eriochrome Black T (EBT) forms a wine-red complex with most metal ions, such as Ca^{2+}.

$$Ca^{2+} + EBT \rightleftharpoons Ca(EBT)^{2+} \qquad\qquad [10]$$

If EDTA is added to this solution, the Ca^{2+} is gradually removed from the Ca-EBT complex and forms more stable CaY^{2-} complex ion.

$$Ca(EBT)^{2+} + Y^{4-} \rightleftharpoons CaY^{2-} + EBT \qquad\qquad [11]$$

wine-red   *blue*

Thus, the uncomplexed free form of the EBT increases in concentration as it is displaced by the EDTA titrant. When almost no Ca-EBT complex remains, the pure blue color of the free EBT predominates and denotes the end point (The end point color change is sharpened by the presence of Mg^{2+} ion).

SAFETY PRECAUTIONS

None of the reagents in this procedure is particularly dangerous. However, the normal safety precautions should be followed. Wear eye protection and never pipette by mouth. Always use a suction device when drawing solution into a pipette.

PROCEDURE

Required Laboratory Materials

<u>Chemicals</u>	<u>Glassware</u>
0.01 M Ca^{2+} Solution	Erlenmayer Flask (100 mL, 250 mL)
0.01 M EDTA Solution	Graduated Cylinder (10 mL, 50 mL)
NH_3-NH_4Cl Buffer Sol.	Pipette
Eriochrome Black T	Suction Device
Top Water	Stand
	Burette-Burette Clamp
	Spatula
	Funnel

A. Standardization of 0.01 M EDTA Titrant

1. Rinse a 10.00-mL pipette with small portions of standard 0.0100 M Ca^{2+} solution, and then pipette a 10.00-mL aliquot of the solution into a clean 250-mL Erlenmeyer flask.

2. Add 2.00 mL of NH_3-NH_4Cl buffer solution from a graduated cylinder and dilute the mixture to approximately 50 mL with distilled water.

3. Add small portion of Eriochrome Black T indicator.

4. Rinse a 50-mL burette with small (5-10 mL) portions of the EDTA solution. Then fill it with EDTA solution, and record the initial position of the meniscus. Read the volume to the nearest 0.01 mL.

5. Titrate the Ca^{2+} solution with EDTA until the wine-red color of the Ca indicator complex changes from purple-red to the pure blue color of the free form of the indicator. If you are not certain of the color change, go to the window and use natural sunlight to see it or compare it to the color of titrated blank sample (see Note). Add titrant in drops and fractions of a drop until the color change from wine-red to pure blue is permanent. Record the final position of the meniscus after waiting 30 sec for the burette to drain.

Note: Sometimes it is difficult to tell if the exact end point color has been reached. The actual color at the end point can be seen if you make a blank sample containing 90.00 mL of distilled water, 10.00 mL of buffer, and indicator. Then add several drops of titrant, and if the water is not contaminated with minerals, the color formed will be the blue of the free, uncomplexed indicator.

Titrate at least three samples of the standard Ca^{2+} solution with EDTA. Calculate the concentrations of EDTA as follows. In all titrations using EDTA, only one EDTA molecule is used for each metal ion. Thus,

$$\text{Molarity of EDTA} = \frac{\left(\text{molarity of Ca}^{2+}\right)(10.00mL)}{\text{ml EDTA used}}$$

B. Determination of Permanent Hardness (as ppm CaCO₃)

1. Thoroughly rinse the pipette with the water sample and then pipette exactly 10.00 mL of the water sample into a clean 250-mL Erlenmeyer flask.

2. Add 2.00 mL of buffer solution (which brings the pH to about 10) and enough indicator (EBT) to get a distinct color.

3. Refill the 50-mL burette with more of the EDTA titrant used in the standardization titrations and record the initial volume.

4. Titrate the sample solution with EDTA solution until the color changes from purple-red to the first color of pure blue. Be sure to swirl the solution after each addition of titrant. Also, near the end point, rinse down the walls of the flask with distilled water and add the EDTA dropwise.

5. Repeat the titration procedure two times.

Disposal: All solutions are non-hazardous and may be flushed down the sink with running water.

Hardness Calculation

It is not convenient to determine the concentration of each cation separately, so assume that all the hardness is due to the presence of only Ca^{2+} ions in the form of calcium carbonate, $CaCO_3$. The concentration can be expressed in terms of molarity of $CaCO_3$, but it is expressed more commonly as mg $CaCO_3$ per liter of water.

(parts per million CaCO₃ = ppm CaCO₃ = mg CaCO₃/L)

$$\text{Molarity of Ca}^{2+} = \frac{\left(\text{mmol of Ca}^{2+} ion\right)}{mL} = \frac{\left(\text{molarity of EDTA}\right) \times \left(\text{mL EDTA added}\right)}{10.00\,\text{mL of water sample}}$$

$$\text{ppm CaCO}_3 = \left(\text{molarity of Ca}^{2+}\right) \times \frac{1\,\text{mol CaCO}_3}{1\,\text{mol Ca}^{2+}} \times \frac{100.1\,\text{g CaCO}_3}{1\,\text{mol CaCO}_3} \times \frac{10^3\,mg}{1\,g}$$

Name_____Department_____Group____

DATA

A. Standardization of EDTA solution

Molarity of Ca^{2+} solution = _____ M

	Trial 1	Trial 2	Trial 3
Initial burette reading (±0.1mL)	_____	_____	_____
Final burette reading (±0.1mL)	_____	_____	_____
mL of EDTA used	_____	_____	_____

B. Hardness titration

	Trial 1	Trial 2	Trial 3
mL of water sample	_____	_____	_____
Initial burette reading (±0.1mL) Final	_____	_____	_____
burette reading (±0.1mL)	_____	_____	_____
mL of EDTA used	_____	_____	_____

Name_____Department_____Group____

CALCULATIONS

A. Standardization of EDTA Solution

	CALCULATIONS	RESULT
Trial 1 Molarity of EDTA solution		
Trial 2 Molarity of EDTA solution		
Trial 3 Molarity of EDTA solution		
Average Molarity of EDTA		
Relative Average Deviation (R.A.D.)		

Name_____Department_____Group_____

B. Hardness Titration

	CALCULATIONS	RESULT
Trial 1 ppm $CaCO_3$ in solution (mg/L)		
Trial 2 ppm $CaCO_3$ in solution (mg/L)		
Trial 3 ppm $CaCO_3$ in solution (mg/L)		
Average ppm $CaCO_3$		
Relative Average Deviation (R.A.D.)		

Name_____**Department**_____**Group**____

QUESTIONS

1. If the pH became too low during the titration of unknown by EDTA, how would the titration reaction's equilibrium is affected?

2. Water sample A and water sample B are identical except that B contains less iron (III) ion. How would the value of ppm $CaCO_3$ of A compare to that of B (larger, smaller, the same)? Explain.

3. In step 4 of the procedure to standardize the EDTA solution a student forgets to rinse the burette with a small portion of EDTA solution (The burette contains water droplets from washing). If this incorrect concentration of EDTA is used to calculate the ppm $CaCO_3$ of a hard water sample, will the resulting value be too high, too low, or correct? Explain briefly.

4. Why does the Eriochrome Black T indicator change from red to blue when EDTA is added to a solution of cations? Describe what is responsible for the color change.

Name_____Department_____Group____

PRELAB QUESTIONS

1. Boiler scale may be composed of what three compounds?

2. At pH=8, which acid form of EDTA is predominant in the solution?

3. When temporarily hard water is boiled,

    a) What gas is evolved?

    b) What solid product is formed?

4. 25.00 mL of 0.01 M Ca^{2+} is titrated to an Eriochrome Black T (EBT) end point with EDTA solution. If the pure blue end point color occurs at 27.50 mL, what is the molarity of the EDTA?

5. A 100.0 mL water sample requires 22.25 mL of 0.01 M EDTA to reach an Eriochrome Black T end point. Calculate the hardness of this sample in units of ppm $CaCO_3$.

2. Synthesis of Soap (Saponification)

INTRODUCTION

Soap is made by mixing lye and water with fats or oil. Through a complex chemical reaction lye which is also called sodium hydroxide (a base) converts Fats or Oil (an acid) to soap. This process is called saponification. When oil or fats (acid) come into contact with the lye or sodium hydroxide (base) the saponification process begins with the lye turning the oil/fat into a thicker and more uniform solution. The point at which the solution begins to thicken is called a trace. Any oils/fats or other ingredients added at this point will not be substantially converted and will basically remain in the soap in their original form. At the trace stage (in this stage, any essential oil and dye can be added 1-2 drop) the soap can be poured into molds where it will continue to harden.

The process that the home soap maker will use is referred to as "cold process soap making". Even though it is called a cold process, heat is required for the chain reaction to take place. This heat is provided by the chain reaction of the water and the lye and their incorporation into the oil or fat. (You will notice that when the lye is poured into the water it heats up immediately) Stirring the oil/fat/lye mixture helps this process to continue and to be uniform.

Soap is prepared by carrying out a hydrolysis reaction in which an ester is treated with water using a base catalyst to give a carboxylic acid and alcohol. When a base is used as the catalyst this process is often called saponification-literally soap making. Fats and oils are esters of glycerol, (CH2OHCHOHCH2OH), a tri-alcohol, and three long chain fatty acid. There are therefore three ester groups per molecule, and thus fats or oils are often called triglyceride. The following reaction is called as saponification
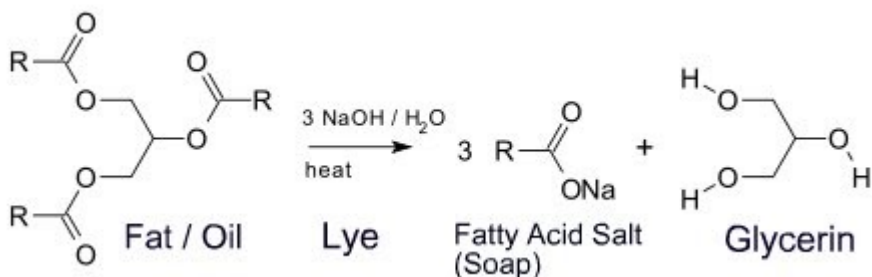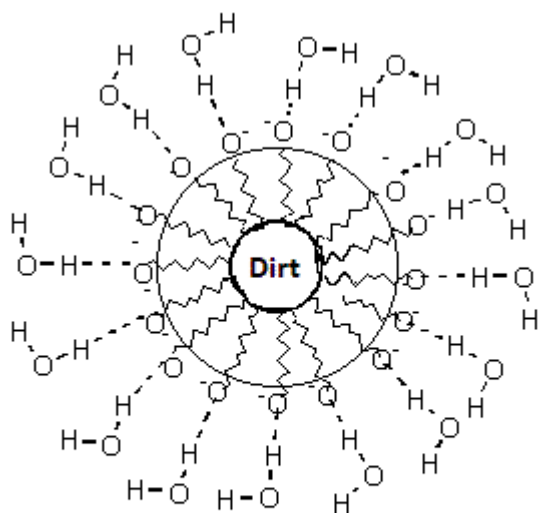
The soap molecule has two different ends, one that is hydrophilic (polar head) that binds with water and the other that is hydrophobic (non-polar hydrocarbon tail) that binds with grease and oil. When greasy dirt or oil is mixed with soapy water, the soap molecules arrange themselves into tiny clusters called micelles. Since the micelle is soluble in water, it can easily be washed away.

A Soap Micelle

hydrophobic group   *hydrophillic group*
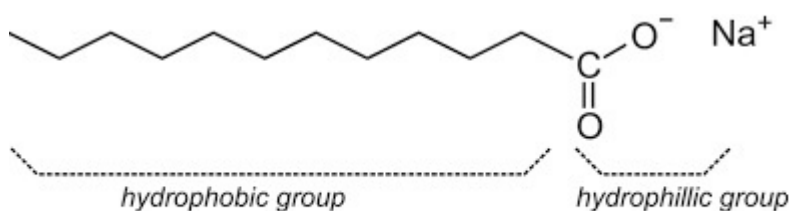
Soaps do not work well in hard water containing calcium and magnesium ions, because the calcium and magnesium salts of soap are insoluble; they tend to bind to the calcium and magnesium ions, eventually precipitating.

SAFETY PRECAUTIONS

In this experiment, the normal safety precautions should be followed. Wear eye protection and never pipette by mouth. Always use a suction device when drawing solution into a pipette.

NaOH: Ulceration of the nasal passages and irritation of the skin, eyes can occur when into direct contact with sodium hydroxide.

Required Laboratory Materials

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Chemicals	**Glassware**
20 grams of olive oil	Erlenmeyer Flask (250 mL)
20 mL Ethyl alcohol	Graduated Cylinder (50 mL)
5M NaOH solution	Heater
Saturated NaCl solution	Buchner Flask and Funnel
	Filter Paper
	Vacuum Pump.

PROCEDURE

1. Place 20 grams of olive oil in a 200 mL Erlenmeyer flask.

2. Add 20 mL of ethyl alcohol.

3. SLOWLY AND CAREFULLY (this staff is dangerous) add 25 mL of 5M sodium hydroxide.

4. Gently heat this mixture under low heat, (maintain a constantly boiling mixture), stirring with a glass stirring rod until the base has completely reacted with the oil (about 20 to 30 minutes).

5. After all of the base has reacted, cool the mixture and add 100 mL of saturated sodium chloride solution.

6. Let this new mixture cool completely. The solid cake is the soap. (What is left, if you do it out chemically, is glycerol)

7. Filter the cooled mixture.

Name_____**Department**_____**Group**_____

PRELAB QUESTIONS

1. Draw out the structure of a general soap molecule.

2. Describe how soap cleans.

3. Describe the words below:

    a) Saponification:

    b) Esterification

3. Molecular Models and Covalent Bonding

INTRODUCTION

Much of the chemical behavior of matter can be related to the detailed structures and shapes of molecules. Structural theory is useful when one wishes to relate experimental evidence to the more theoretical concepts of chemical bonding. The arrangement of atoms and ions in molecules and crystals is related to the distribution of bonding electrons within the structure. Molecules often are represented by pictures or molecular models in which balls or some other geometrical centers represent atoms and sticks, or tubes represent the bonds between the atoms.

The purpose of this experiment is to use molecular models to help understand fuller the theoretical concepts of covalent bonding and molecular structure. Lewis structure of molecules, covalent bonding, hybridization, polarity and Valence Shell Electron Repulsion Theory (VSPER) will be discussed using molecular models.

Molecular models are designed to reproduce molecular structures in three-dimensional space. If models are correctly assembled, many subtle features concerning shapes of molecules (such as, dipole moment, polarity, and bond angle) become clearer to us. One aspect of molecular structure is called isomerism. The most obvious type of structural isomerism is that in which there exists more than one way to assemble the atoms of a compound correctly. Sometimes only one of the possible structures is the stable form of a compound, but many times two or more structures are stable enough to exist in more than relatively small amounts. An example of a structural isomer is that of ethyl alcohol and dimethyl ether, shown in Figure 1. Note that both have the same molecular formula, C_2H_6O.

Figure 1. Two structural isomers of C_2H_6O.

Determining Lewis Structure of Molecules

Lewis structures are a simple way to find out bonding electrons, non-bonding electrons, and formal charges in molecules. Lewis structure of a molecule is important factor in determining its structure, stoichiometry, and properties. To make a Lewis structure follow these steps:

1. Find total number of valence shell electrons of molecule. Add 1 additional electron per negative charge if the structure is an anion. Subtract 1 electron per positive charge if the structure is a cation.

2. Use the formula of the molecule or ion to help you determine the arrangement of the atoms in molecule.

3. Predict the central and terminal atoms. In general, central atom has lower electronegativity and terminal atom has higher. But hydrogen is always terminal atom and carbon is always central atom.

4. Beginning with the terminal atoms, add enough electrons to each atom to give each atom an octet (two for hydrogen). If any electrons are left over, place them on the central atom.

5. Use valence electrons to make 2-electron bonds to connect the atoms in the structure. If the central atom has fewer electrons than an octet, use lone pairs from terminal atoms to form multiple (double or triple) bonds to the central atom to achieve an octet. You can make single bonds (2 electrons), 2 bonds or a double bond (4 electrons), 3 bonds or a triple bond (6 electrons) in some cases. Be sure that you don't exceed the maximum.

6. Use the remaining electrons to make lone pairs of electrons on atoms. When there is an odd number of electrons, there will be a single electron on some atom (radical).

7. There may be more than one possible Lewis structure. If so, the one with the fewest formal charges is usually the best. A correct Lewis structure always includes the formal charges.

Formal Charge

Formal charge can show us the electron rich and electron poor regions of a compound. It is an important part of the Lewis structure. For each atom in the structure:

1. Sum 1/2 of all electrons in bonds to that atom and add any other non-bonding electrons.

2. Formula of calculating formal charge is:

Formal charge on an atom [F.C] = [total number of electrons in the free atom] – [total number of non-bonding (lone pair) electrons] -½[total number of bonding(shared pair) electrons]

3. Compare that number to the number of formal charges of atoms and determine the best Lewis structure.

$$H\cdot + \cdot\ddot{O}\cdot + \cdot H \longrightarrow H\!:\!\ddot{O}\!:\!H \quad H-\ddot{O}-H$$

Figure 2. Lewis Structure of H_2O molecule.

Look at the example below for formal charges. There are three possible Lewis structure of N_3 molecule. The second structure has resonance, so it is not shown here.
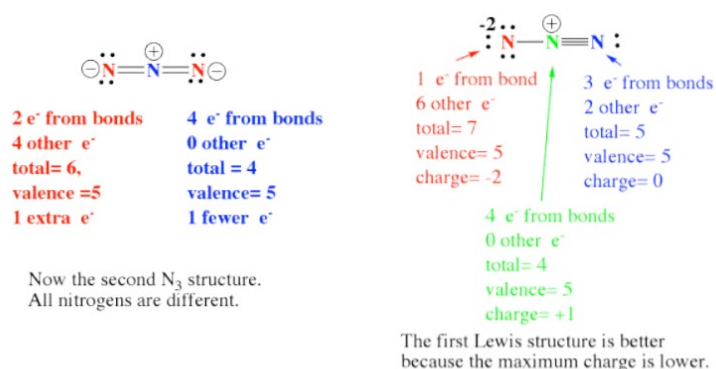
Figure 3. Formal charges on N_3 molecule.

Exceptions to the Octet Rule

Some atoms do not possess octet rule because of the number of valence electrons and formal charges. Here some examples of molecules with odd electron atoms, incomplete octet and expanded octet.
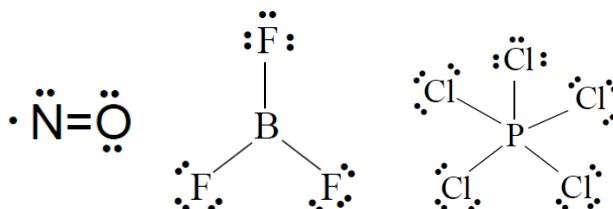

Figure 4. Exceptions to octet rule. Odd electron species (left), incomplete octet (middle) and expanded octet (right).

Resonance

Some compounds cannot be represented by a single definite structure rather more than one structure. Thus, the various structure written for a compound to explain the known properties of the compound are called as resonating or contributing or canonical structure. The phenomenon is resonance.
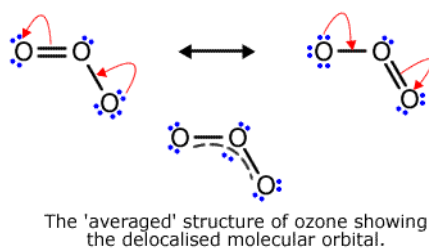

The 'averaged' structure of ozone showing the delocalised molecular orbital.

Figure 5. Resonance structures of Ozone molecule (O_3).

Valence Shell Repulsion theory (VSPER)

Valence shell electron-pair repulsion theory (VSEPR theory) enables us to predict the molecular structure, including approximate bond angles around a central atom, of a molecule from an examination of the number of bonds and lone electron pairs in its Lewis structure. The VSEPR model assumes that electron pairs in the valence shell of a central atom will adopt an arrangement that minimizes repulsions between these electron pairs by maximizing the distance between them. The electrons in the valence shell of a central atom form either bonding pairs of electrons, located primarily between bonded atoms, or lone pairs. The electrostatic repulsion of these electrons is reduced when the various regions of high electron density assume positions as far from each other as possible.

General Rules for Predicting Molecular Geometries by Valence Shell Electron Pair Repulsion Theory [VSEPR]

1. Count the valence electrons in the entire molecule or ion.
2. Adjust this count for charge, if any, by adding (for anions) or subtracting (for cations) electrons.
3. Arrange atoms in the most symmetrical fashion.
4. Bond each terminal atom to the central atom.
5. Complete the octet on each terminal atom (except H).
6. Any unused electrons go on the central atom as unshared or lone pairs.
7. If the central atom is in periods 2 and 3, complete its octet, using multiple bonds if necessary.
8. Determine the molecular geometry based on mutual repulsion of electron pairs. Remember that nonbonding pairs are more repulsive than bonding pairs.

Polarity

Polarity is the phenomenon about the electronegativies of the atoms in molecule. Polar covalent bonds connect two atoms with different electronegativities. Since the electrons are pulled toward the more electronegative atom, one atom has a partial positive charge ($\delta+$) and the other atom has a partial negative charge ($\delta-$).This separation of charge gives rise to a bond dipole moment. Dipole moment vectors are shown as arrows pointing along the bond from the less electronegative atom toward the more electronegative atom. If net dipole moment is zero, the molecule is nonpolar. If dipole moment is greater than zero, than the molecule is said to be polar. The dipole moment measures the extent of net charge separation in the molecule as a whole.
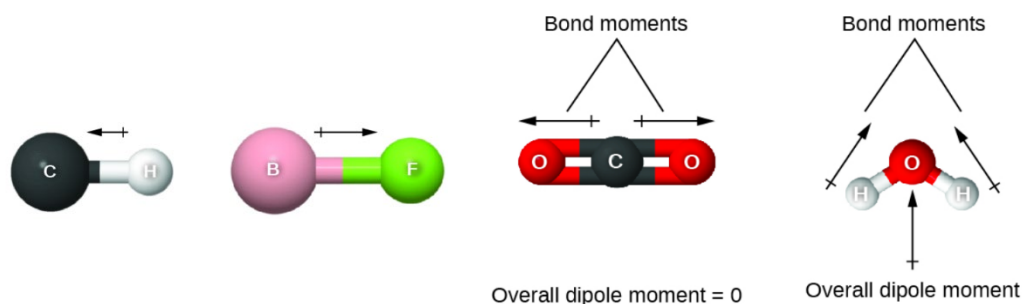

Figure 6. Dipole moment on different molecules.

Hybridization

Hybridization is used to explain the nature of bonds, and shape of the polyatomic molecules. According to the hybridization, certain atomic orbitals of nearly the same energy undergo mixing to produce equal number of new orbitals. The new orbitals are called as hybrid orbitals. The process of mixing of the atomic orbitals to form new hybrid orbitals is called hybridization. All hybrid orbitals of a particular kind have equal energy, identical shapes and are symmetrically oriented in space.
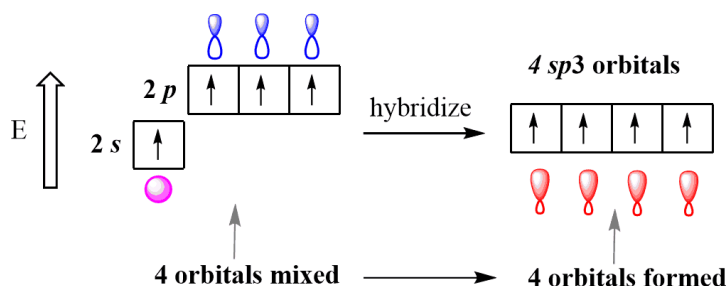
Figure 7. sp^3 hybridization.

Hybridization rule for central atom in molecules with different electron grup geometries:

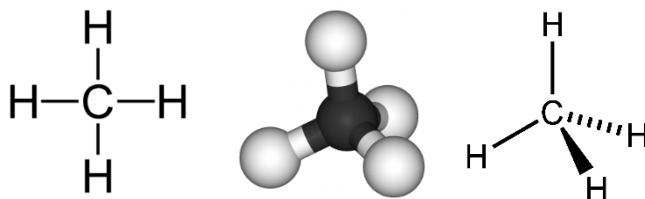| Electron group geometry	Hybridization
Linear	sp
Trigponal Planar	sp^2
Tetrahedral	sp^3
Trigonal bipyramidal	sp^3d
Octahedral	sp^3d^2

PROCEDURE
Perform the following operations, when applicable, on each compound in the list provided by your instructor.
1. Draw the correct Lewis structure and any resonance forms.
2. Determine if any structural isomers exist.
3. Assemble a molecular model for the compound. Construct a model for each isomer from step 2 (Resonance structures require only one model).
4. Sketch only one model, using a solid line for a bond in the plane of the paper, a wedge bond for a bond coming out of or in front of the plane of paper, and a dashed line for a bond in back of the plane of paper.
5. Indicate the following for each Lewis structure
a. Hybridization on central atom(s) (there may be more than one).
b. Overall molecular geometry and electron pair geometry.
c. Whether the molecule is polar or nonpolar. (Polar in this sense means that the species has a net dipole. Nonpolar means that there are no dipoles present, or that, if present, they cancel, resulting in no net dipole moment.)

Example:

Here is the Lewis structure, sketch of the molecule and molecular shape of CH_4 molecule respectively.

Figure 8. Lewis structure (left), sketch (middle) and molecular shape of CH_4 molecule.

Electron group geometry and molecular geometry of methane is both tetrahedral because there is no lone pair in central atom. Hybridization of carbon atom is sp^3 and molecule is not polar.

Name_____**Department**_____**Group**____

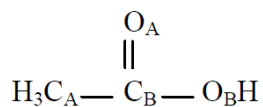| No	Lewis Structure(s)	Sketch	Central Atom Hybridization	Electron Pair Geometry	Molecular Geometry	Polarity
1.						
2.						
3.						
4.						

Name _____ **Department** _____ **Group** _____

No	Lewis Structure(s)	Sketch	Central Atom Hybridization	Electron Pair Geometry	Molecular Geometry	Polarity
5.						
6.						
7.						
8.						

Name_____Department_____Group_____

REPORT QUESTIONS
Consider the molecule

$$\begin{array}{c} O_A \\ \| \\ H_3C_A\!\!-\!\! C_B\!\!-\!\! O_BH \end{array}$$

1. Indicate the hybridization employed by each central atom.

a. C_A : _____   b. C_B : _____
c. O_A : _____   d. O_B : _____

2. Indicate the electron pair geometry about each central atom.

a. C_A : _____   b. C_B : _____
c. O_A : _____   d. O_B : _____

3. Indicate the predicted bond angles around each central atom having more than one bond.

   a. C_A : _____   b. C_B : _____   c. O_B : _____

4. Describe all the σ and π bonds in this molecule in the form of a hybridization and bonding scheme. For example, a *hypothetical* O-H bond = O (2 sp2) – H (1 s).
          <u>sigma bond(s)</u>   <u>pi bond(s)</u>

5. Which bond is the:

a. shortest? _____
b. strongest? _____

Name_____**Department**_____**Group**____

PRELAB QUESTIONS

1. What are isomers?

2. Sketch the Lewis structures for the isomers of $C_2H_4Cl_2$.

3. Under what circumstances in writing Lewis structures for a molecule may one conclude that the molecule exhibits resonance?

4. A triple bond consists of _____sigma bond(s) and _____pi bond(s).

5. Under what circumstances is the molecular geometry the same as the electron pair geometry? Which of the molecules fits this description?

PCl_3 or PCl_5
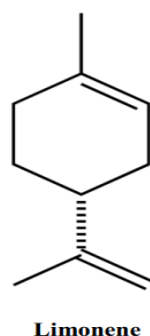
4. Steam Distillation

Introduction

Distillation is a process in which the components of a substance or liquid mixture are separated by heating it to a certain temperature and condensing the resulting vapors. The process is mainly based upon the boiling point of liquid substances. Some substances (such as crude oil) have components that vaporize at different temperatures and thus can be separated by condensing their vapors in turn. Distillation is also used as a purification process in which non-volatile components are separated from volatile ones and as separation of liquids in industrial and lab. scales. Distillation is used for many commercial processes, such as production of gasoline, distilled water, xylene, alcohol, paraffin, kerosene, and many other liquids. This process can be performed in different ways (at atmospheric pressure, under vacuum). The liquid formed at the end of distillation is named as distillate and the remaining in the flask is named as residue. Generally, distillate has lower boiling point compared with residue. The vapor pressure of a system, composed of immiscible liquid components, is equal to the sum of vapor pressures of each component. The boiling point of this system is lower than those of its components.

Many compounds, that have high boiling point and immiscible with water can be distilled at relatively lower temperatures by passing through water vapor. During boiling, mole fractions of components in the vapor phase are directly proportional with their vapor pressures. In other words, the volatile component exists in the vapor phase in a greater amount. The mole fractions of components can be calculated by separation of components after condensation of the vapor phase and determining their amounts. If the molecular weight of a component is not known, it can be estimated from mole fraction.

In this laboratory exercise we will employ steam distillation to isolate an essential oil from lemon peel. This will involve distilling a mix of lemon peels and water to obtain the oil,

extracting the oil from the water, and then isolating the oil from the extraction solvent. Essential oils are a mix of fragrant compounds common to a number of plants such as mint, lavender, pine, etc. which are isolated via steam distillation. Because these oils were once considered to be the essence of the plant, they were initially sought as possible pharmaceuticals and are a part of early medicine's contribution to modern chemistry. Today they are used as flavorings, perfumes and deodorants.

Limonene takes its name from the peel of the lemon. Limonene is a chiral molecule, and biological sources produce one enantiomer: the principal industrial source, citrus fruit, contains D-limonene ((+)-limonene), which is the (R)-enantiomer. D-Limonene is obtained commercially from citrus fruits through two primary methods: centrifugal separation or steam distillation.


Limonene

PROCEDURE

In this experiment, the molecular weight of limonene will be determined by steam distillation of limonene-water mixture. Steam distillation is used when organic compound codistills with water. It is a great way to isolate the organic compounds with high boiling points.

1.   First, prepare the distillation set up given in Figure 1. Take three medium lemons and grate the peels of lemons and measure the mass of the peel. Add the peels to the distilling pot, a 250 mL flat bottom flask (Flask 2), using a wide-mouth funnel and a stirring rod. Add enough water so that the distilling pot is about 2/3 full. Add boiling chips to the round-bottom flask (Flask 1) that is full with water prior to passing steam. Then connect the two flasks with a rubber

tube, heat Flask 1- 2. Turn on the condenser water and seal the distilling pot. Start passing steam through.

2. As the mixture boils and distills, you will be losing water from the distillation mixture. It is important to watch the water level because of the high concentration of sugar in lemons. If the water level gets too low, the sugar will carmelize and burn. Keep the heat at a low, steady level.

3. Collect the condensed liquid a tared erlenmayer flask. In the process, all the hot vapors produced are immediately channelled into a condenser which cools and condenses the vapors. Therefore the distillate will not be pure. Since water and lemonene are immiscible. (Figure 1.)
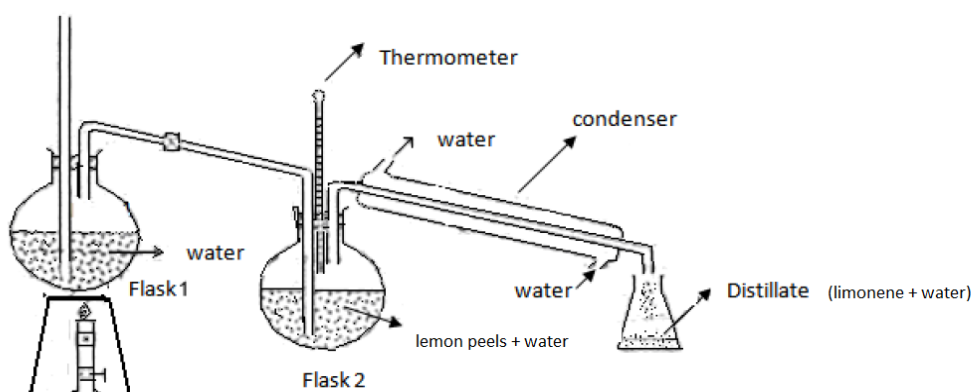

Figure 1. Distillation set-up

4. Transfer your distillate to a 100 mL separatory funnel. Add 10 mL dichloromethane (DCM) and extract the oil. Drain the DCM layer of into a 100 mL erlenmayer flask (Figure 2.).
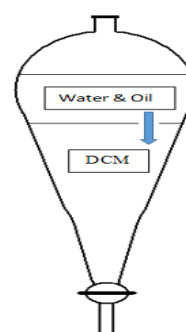
5. Dry the DCM with a little anydrous magnesium sulfate. This is required because trace amounts of water will dissolve in the DCM. The anhyrous magnesium sulfate will absorb the water and produce solid magnesium sulfate decahydrate:

$$MgSO_4 \text{ (s)} + 10H_2O \longrightarrow MgSO_4.10H2O_{(s)}$$
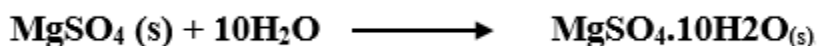
6.   Allow the system to dry for 10-15 minutes. Decant the liquid into a small beaker (don't forget to weigh the empty beaker!) . Keep the beaker in a fume hood at least one day in order to vaporize the DCM. One day later, weigh the beaker and limonene. Determine the molecular weight of limonene by using equation 4.1.

$$\frac{P_{limonene}}{P_{water}} = \frac{X_{limonene}}{X_{water}} = \frac{n_{limonene}}{n_{water}} = \frac{m_{limonene}/M_{limonene}}{m_{water}/M_{water}} \qquad \text{Eqn. 4.1}$$

$P_{limonene} + P_{water} = P_{total}$

$P_{limonene}$ and P_{water} : the partial pressure of limonene and water, respectively.

$X_{limonene}$ and X_{water} : the mole fractions of limonene and water, respectively.

P_{water} at distillation temperatures can be found from vapor pressure table of water. Since

M_{water} , $m_{limonene}$ and m_{water} are known $M_{limonene}$ can be calculated.

Name_____**Department**_____**Group**_____

DATA

Temperature of distillation (° C)   _____

Pressure during distillation (atm)   _____

Weight of beaker (g)   _____

Weight of beaker and distillate (g)   _____

Weight of beaker and$_{limonene}$(g)   _____

Water vapor pressure at distillation temp (atm)   _____

Molecular weight of water (g/mol)   _____

RESULTS

Pressure of^{limonene}at distillation Temp.(atm)   _____

Amount of^{limonene}in distillate (g)   _____

Amount of water in distillate (g)   _____

Molecular weight of$_{limonene}$(g/mol)   _____

Name_____**Department**_____**Group**_____

CALCULATION

$M_{limonene}$ can be calculated by using eqn 4.1. Show all your work on the sheet, use proper unit and fill the result in your data sheet.

Name_____**Department**_____**Group**_____

REPORT QUESTIONS

1. What is the purpose of application of steam distillation method?

2. A and B liquids form ideal solutions. At the boiling point of solution consists of 0.2 mole B and 0.6 mole A, pure B has a vapor pressure of 0.650 atm.

a.　　　What is the vapor pressure of A at this temperature?

b.　　　Find the mole ratio of A in vapor phase which is in equilibrium with the solution when the boiling started.

5. Molecular Weight Determination from Freezing Point Depression

INTRODUCTION

In this experiment the student will learn how to determine the freezing point of a substance and the molecular weight of a solute by freezing point depression of solvent. The molecular weight of sulfur will be determined by freezing point depression of its solution in naphthalene.

Freezing of a liquid

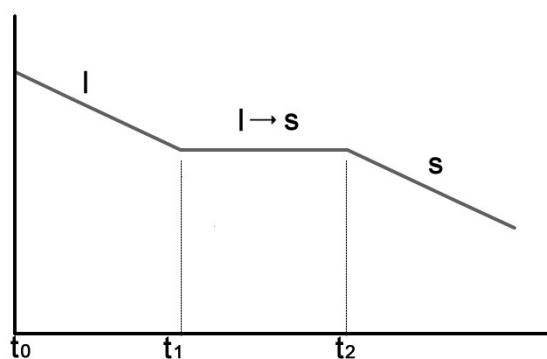The temperature at which the liquid and solid coexist is defined as freezing point of a substance.

Figure 1. Cooling curve of a liquid

As you can follow from Figure 1, at temperature T_1 liquid begins to convert to solid and during this conversion, from T_1 to T_2, the temperature remains constant.

During freezing, the particles line up in a definite geometric pattern as they go from liquid state to solid state, and the potential energy of the substance begins to drop. Therefore, during freezing, formation of solid particles produces heat, and this energy compensates for the heat removed by cooling. As a result, until freezing is complete the temperature stays constant. This phenomenon will help us to determine the freezing point of naphthalene in this experiment.

Freezing point depression

The addition of a solute will generally raise the boiling point and depress the freezing point of a solvent. When a substance starts to freeze, the molecules slow down by decreasing temperature, and the intermolecular forces become stronger. The molecules will then arrange themselves in a pattern, and form a solid. For example, as water is cooled to the freezing

point, its molecules slow down and hydrogen bonds become stronger, eventually ice is formed. If a compound is added to the water, the ions or molecules of this compound attract to the water molecules and interfere with the formation of ice. In order to solidify, the solution must be cooled to an even lower temperature.

Freezing point depression is a colligative property; that is, it does not depend on the identity of the substance itself but depends on the ratio of solute to solvent particles. For dilute solutions, the freezing point depression of a solvent is directly proportional to total molality of the solution.

Molality, m, is defined as the number of moles of a solute in 1000 g of solvent.

$$Molality = \frac{number\ of\ moles\ of\ solute\ (n)}{1000g\ of\ solvent}$$

Freezing point depression is defined by the following formula;

$$\Delta T = K_f \cdot m$$

ΔT : change in freezing point depression
K_f : molal freezing point depression constant
m : total molality in this solution

Example 1:

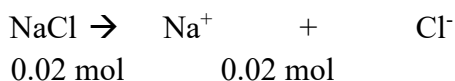1.17 g of NaCl is dissolved in 2000 g of water. Calculate ΔT.
K_f for water is 1.86°C/m
$FW_{NaCl} = 58.5$ g/mol

Solution:

(1.17 g) / (58.5 g/mol) = 0.02 moles

$NaCl \rightarrow \quad Na^+ \quad + \quad Cl^-$
0.02 mol   0.02 mol

Total molality = ((0.02+0.02)moles / 2000g H_2O) x 1000 = 0.02
$\Delta T = (1.86)*(0.02) = 0.04$ °C

In order to calculate molecular weight, we can express molality in a more convenient form.

$$m = \frac{n_1}{W_2} \times 1000$$

n_1 = number of moles of solute

$$m = \frac{W_1/MW_1}{W_2} \times 1000$$

W_1 = weight of solute
W_2 = weight of solvent

$$MW = \frac{(1000)(W_1)}{(m)(W_2)}$$

Therefore;

$$MW_1 = \frac{1000.K_f.(W_1)}{\Delta T.(W_2)}$$

Example 2:

When 1.15 g of naphthalene is dissolved in 100 g of benzene, the resulting solution has a freezing point of 4.95°C. What is the molecular weight of naphthalene?

For pure benzene T_f =5.40°C, and K_f =5.12

Solution:

$m = \Delta T / K_f = (5.40\text{-}4.95) / 5.12 = 0.088$

$W_1 = 1.15$ g
$W_2 = 100$ g

$MW = (1000)*(1.15) / (0.088)*(100) = 128$ g/ mol

In Example 1, two distinct solute species are present. When a salt such as NaCl is dissolved in water, a 1 m solution of NaCl contains 1 mole of Na^+ and 1 mole of Cl^- ions in 1000 g of solvent. Therefore total molality is 2 m. But in Example 2, only one distinct solute species which is naphthalene is present; therefore a solution of 1 mole of solute will give a total molality of 1 m.

In this exercise the solvent is naphthalene. The freezing point is lowered 6.8°C for every mole of solute dissolved in 1000 g of naphthalene. By dissolving a known weight of sulfur in a known weight of naphthalene and measuring the freezing point depression we can determine the molecular weight of sulfur.

PROCEDURE

Required Chemicals	**Required Lab. Materials**
Naphthalene	Thermometer
Sulfur	Stirring wire
Acetone (test tube cleaning)	Beaker
	Large test tube
	Bunsen burner
	Two-holed cork
	Spatula
	Clamp
	Ring stand

1. Assemble the apparatus as shown in Figure 2. When placing your thermometer in a two-holed cork or a one-holed cork (with a slit in the side), wrap the cork and thermometer with a towel and twist the thermometer slowly and gently into the hole. Otherwise you may break the thermometer.
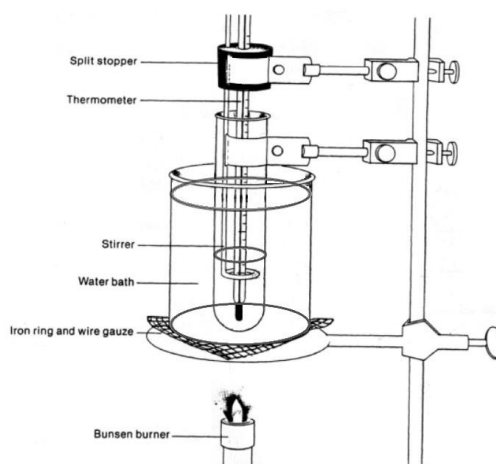

Figure 2

2. On a previously weighed piece of paper, weigh out about 5 g of naphthalene to the nearest 0.03 g. Pour the naphthalene on the paper before you put the paper on the balance. Record your weighing as W_2, weight of the solvent.
3. Make sure that the tube is <u>not wet</u> before you fill it. Pour the naphthalene into a large test tube; make sure it gets on the bottom of the tube.
4. Insert the thermometer and wire stirrer, place the test tube in a beaker of water, and heat gently until all the naphthalene has melted. Melting point should be observed around 85°C.
5. Remove the Bunsen burner and, while stirring, record the temperature for every 30 seconds from 85°C to 65°C. With these data you will plot the cooling curve for naphthalene.
6. On a clean piece of previously weighed paper, weigh about 1.0 g of sulfur to the nearest

0.01 g. record your weighing as W_1, weight of the solute.

7. Add the sulfur to naphthalene; make sure it gets as far down into the test tube as possible.

8. Heat the mixture in a water bath until the sulfur and naphthalene have formed a clear solution.

9. Remove the Bunsen burner and record the temperature at 30 seconds intervals from 85°C to 65°C.

10. To clean the test tube, reheat in water bath until the contents melt, remove the thermometer, and pour the molten naphthalene into a baker labeled "Waste Naphthalene" DO NOT POUR LIQUID NAPHTHALENE INTO THE SINK!

11. Plot cooling curves for pure naphthalene and sulfur-naphthalene solution.

12. Determine the freezing points from cooling curves.

13. K_f value for naphthalene is 6.8°C/m, calculate the molarity of the solution, m

14. Calculate the molecular weight of sulfur by using m, W_1 and W_2.

15. The atomic weight of sulfur is 32 g/mol. By using the result from (14), write the molecular formula of sulfur as S_n. What is n?

16. The actual molecular formula of sulfur is S_8. Calculate the theoretical molecular weight of sulfur and the percent error in your experiment.

Name_____**Department**_____**Group**____

DATA

Weight of **naphthalene** (solvent) in gram = W_2 = _____

Cooling curve data for pure naphthalene;

t	T°C	t	T°C	t	T°C

Name_____**Department**_____**Group**_____

Weight of **sulfur** (solute) in gram = W_1 = _____

Cooling curve data for the solution of sulfur in naphthalene;

t	T°C	t	T°C	t	T°C

Name_____Department_____Group____

CALCULATIONS

<u>From graph, determine the following temperatures:</u>

Freezing point of pure naphthalene $\quad\quad\quad\quad T_1 = …..°C$

Freezing point of solution $\quad\quad\quad\quad\quad\quad T_2 = …..°C$

Freezing point of depression from graph $\quad\quad \Delta T = ...°C$

- Molality of solution $\quad\quad\quad\quad\quad$ m =_____

- Molecular weight of sulfur $\quad\quad\quad\quad$ FW =_____ g/mol

- S_n $\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad\quad$ n =_____

- Molecular formula of sulfur $\quad\quad\quad\quad$ =_____

- Percent error in molecular weight $\quad\quad$ =_____

Name_____Department_____Group_____

PRELAB QUESTIONS

1. What is the unit of concentration in freezing point depression equation?

2. Give at least one example of everyday application of freezing point depression that makes the life easier for us.

3. Which is the better solvent for molar mass determinations by freezing point depression, benzene or cyclohexane? Explain.

4. Which is the better method for molar mass determination, freezing point depression or boiling point elevation? Explain.
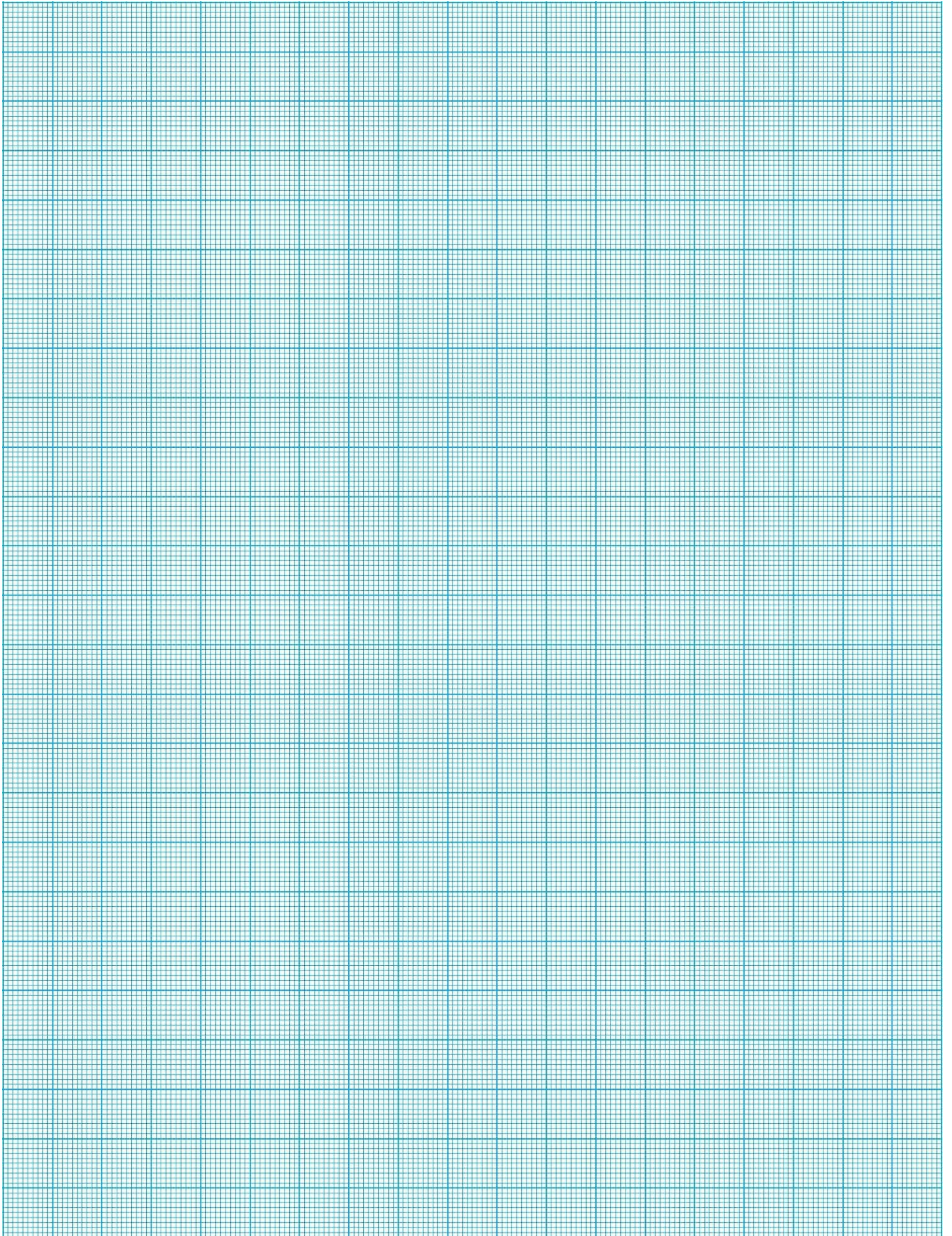
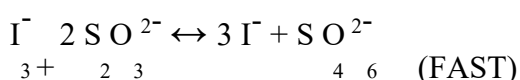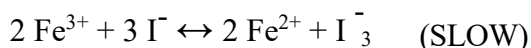# 6. Kinetic Study of the Reaction Between Ferric and Iodide Ions

INTRODUCTION

The purpose of this experiment is to study kinetics of the reaction between ferric (Fe^{3+}) and iodide (I^-) ions i.e. to determine order of the reaction with respect to both ions. Reactions to be studied in this experiment is the oxidation of I^- by Fe^{3+} ions or reduction of Fe^{3+} ions by I^- ions according to equation:

$$2\,Fe^{3+} + 3\,I^- \leftrightarrow 2\,Fe^{2+} + I_3^-$$
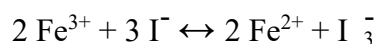
Rate expression for this reaction $= -1/2\ d[Fe^{3+}]/dt = k[Fe^{3+}]^a\,[I^-]^b$

Parts A and B of this experiment are concerned with the evaluation of exponents **a** and **b** respectively in the rate expression. The initial rate is determined by measuring the time in seconds required for 4×10^{-5} mole of Fe^{3+} to be reduced to Fe^{2+}. This is indicated by adding starch solution and a small, constant amount of $S_2O_3^{2-}$ to each mixture. The following reactions then occur:

$$2\,Fe^{3+} + 3\,I^- \leftrightarrow 2\,Fe^{2+} + I_3^- \quad \text{(SLOW)}$$
$$I_3^- + 2\,S_2O_3^{2-} \leftrightarrow 3\,I^- + S_4O_6^{2-} \quad \text{(FAST)}$$

As soon as the $S_2O_3^{2-}$ has been consumed, any additional I_3^- formed by the reaction between ferric and iodide ions will react with the starch to form a characteristic blue color. Note that when the blue color first appears, the decrease in the concentration of Fe^{3+} from its initial value is just equal to the initial concentration of $S_2O_3^{2-}$ in the mixture. Thus the initial rate, $-1/2 d[Fe^{3+}]/dt$, is equal to $1/2[S_2O_3^{2-}]i/\Delta t$, where $[S_2O_3^{2-}]i$ is the initial concentration of $S_2O_3^{2-}$ and Δt is the time in seconds between mixing and the appearance of the blue color. In order to obtain reasonable reaction times, it is necessary to use initial rate intervals which allow the Fe^{3+} concentration to decrease slightly (about 4 to 10 percent) from its initial value. To compensate for this change, it is suggested that the average Fe^{3+} concentration during this time interval be used in place of the initial concentration.

Experiment 6: Kinetic Study of the Reaction Between Ferric and Iodide Ions

CAUTIONS:

1. Be careful about performing in all the experiments at the same temperature since temperature changes affect the rate constant; use water bath to keep temperature constant.

2. HNO_3 does not participate in the reaction between ferric and iodide ions but it is used to prevent hydrolysis of the Fe^{3+} in the water environment.

3. Use 50 mL burettes to dispense H_2O, $Fe(NO_3)_3$, and HNO_3 solutions; 10 mL pipettes to dispense the KI and $Na_2S_2O_3$ solutions, and a 10 mL graduated cylinder to dispense the starch solution.

PROCEDURE

Required Chemicals
0.04 M $Fe(NO_3)_3$
0.15 M HNO_3
0.04 M KI
0.004 M $Na_2S_2O_3$
Starch
Distilled Water

Required Lab. Materials
Beaker (250 & 100 mL)
Graduated Cylinder
Water Bath

PART A. **Reaction order with respect to Fe^{3+}**

1. Prepare the mixtures for experiment 1 by adding the solution specified in Table 1 to 250 and 100 mL beakers, respectively.

2. Swirl the contents of each beaker briefly and place the beakers in a constant temperature water bath set at room temperature to reach temperature equilibrium. (Allow 10 to 15 minutes for this.)

3. Meanwhile, prepare the solution for experiment 2 in a second set of beakers, and place these also in the water bath. By this time the solutions for experiment 1 should be at bath temperature.

4. Measure and record the initial temperature of the solutions then simultaneously start the timer and add (rapidly) the contents of the 100 mL beaker to the 250 mL beaker. You may remove the solution temporarily from the water bath for this.

5. Swirl the solutions until mixed, and then return the 250 mL beaker to the bath.

6. Stop the timer at the first appearance of the blue color. Again measure the temperature, and calculate the average temperature of the solution during the reaction. Record the time interval, Δt, and the average temperature in the table in the data part.

7. Clean and dry the beakers, add the solutions for experiment 3, and place the beakers in the water bath.

8. Then measure the temperature of the solutions for experiment 2, mix the solutions and follow the reaction as you did for experiment 1.

9. Continue in this manner through experiment 5.

PART B. **Reaction order with respect to I^-**

1. This part is performed exactly as in Part A, except that the concentration of ferric ion is kept constant while the concentration of iodide ion is varied. The composition of the various reaction mixtures to be used is given in Table 1, experiments 6, 7 and 8.

Experiment 6: Kinetic Study of the Reaction Between Ferric and Iodide Ions

Table 1

| EXP | 250 mL beaker | | | 100 mL beaker | | | |
	0.04 M Fe^{3+}, mL	0.15 M HNO$_3$, mL	H$_2$O, mL	0.04 M KI, mL	0.004 M S$_2$O$_3^{2-}$, mL	Starch, mL	H$_2$O, mL
1	10	20	20	10	10	5	25
2	15	15	20	10	10	5	25
3	20	10	20	10	10	5	25
4	25	5	20	10	10	5	25
5	30	0	20	10	10	5	25
6	10	20	20	5	10	5	30
7	10	20	20	15	10	5	20
8	10	20	20	20	10	5	15

DATA

Temperature (°C): ……….

Table 2

EXP	Δt (s)
1	
2	
3	
4	
5	
6	
7	
8	

Experiment 6: Kinetic Study of the Reaction Between Ferric and Iodide Ions

Name_____**Department**_____**Group**____

CALCULATIONS

By performing the calculations, fill up Table 3.

1. Calculate $[S_2O_3^{2-}]_i$ which is constant in all experiments.

$$[S_2O_3^{2-}]_i = 0.004 \text{ M x } 10 \text{ mL } / 100 \text{ mL}$$

2. Calculate the initial reaction rate by using time data.

$$\text{Rate} = 1/2 \ [S_2O_3^{2-}]_i \ / \ \Delta t$$

3. Take logarithm of the rate.

4. Calculate initial Fe^{3+} concentration. Take the volume of Fe^{3+} according to the corresponding assignment number.

$$[Fe^{+3}]_i = ... \text{mL } Fe^{3+} \text{ x } 0.04 \text{ M } /100 \text{ mL}$$

5. Calculate average Fe^{+3} concentration by using the equation below:

$$[Fe^{+3}]_{av} = [Fe^{+3}]_i - 4x10^{-4}/2 = [Fe^{+3}]_i - 2x10^{-4}$$

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6. Take logarithm of average Fe^{+3} concentrations.

7. Calculate initial I^- concentration. This will be equal to average I^- concentration.

$$[I^-]_i = \text{................} mL\ I^- \times 0.04\ M\ /100\ mL$$

8. Take logarithm of average I^- concentrations.

9. Plot log rate vs. log $[Fe^{+3}]_{avg}$ for experiments 1 to 5 to your graph paper.

10. Find the slope of the line; this will be equal to **a**, reaction order with respect to ferric ion.

11. Plot log rate vs. log $[I^-]$ for experiments 1, 6, 7, 8. to your graph paper.

12. Find the slope of the line; this will be equal to **b**, reaction order with respect to iodide ion.

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Table 3

EXP	$[S_2O_3^{2-}]_i$	Rate= $1/2[S_2O_3^{2-}]_i/\Delta t$	log rate	$[Fe^{+3}]_i$
1				
2				
3				
4				
5				
6				
7				
8				
EXP	$[Fe^{+3}]_{avg}$	log $[Fe^{+3}]_{avg}$	$[I^-]_{avg}$	log $[I^-]_{avg}$
1				
2				
3				
4				
5				
6				
7				
8				

QUESTIONS

1. What is the overall rate of this reaction?

2. How would you evaluate reaction rate constant, k, of this reaction?

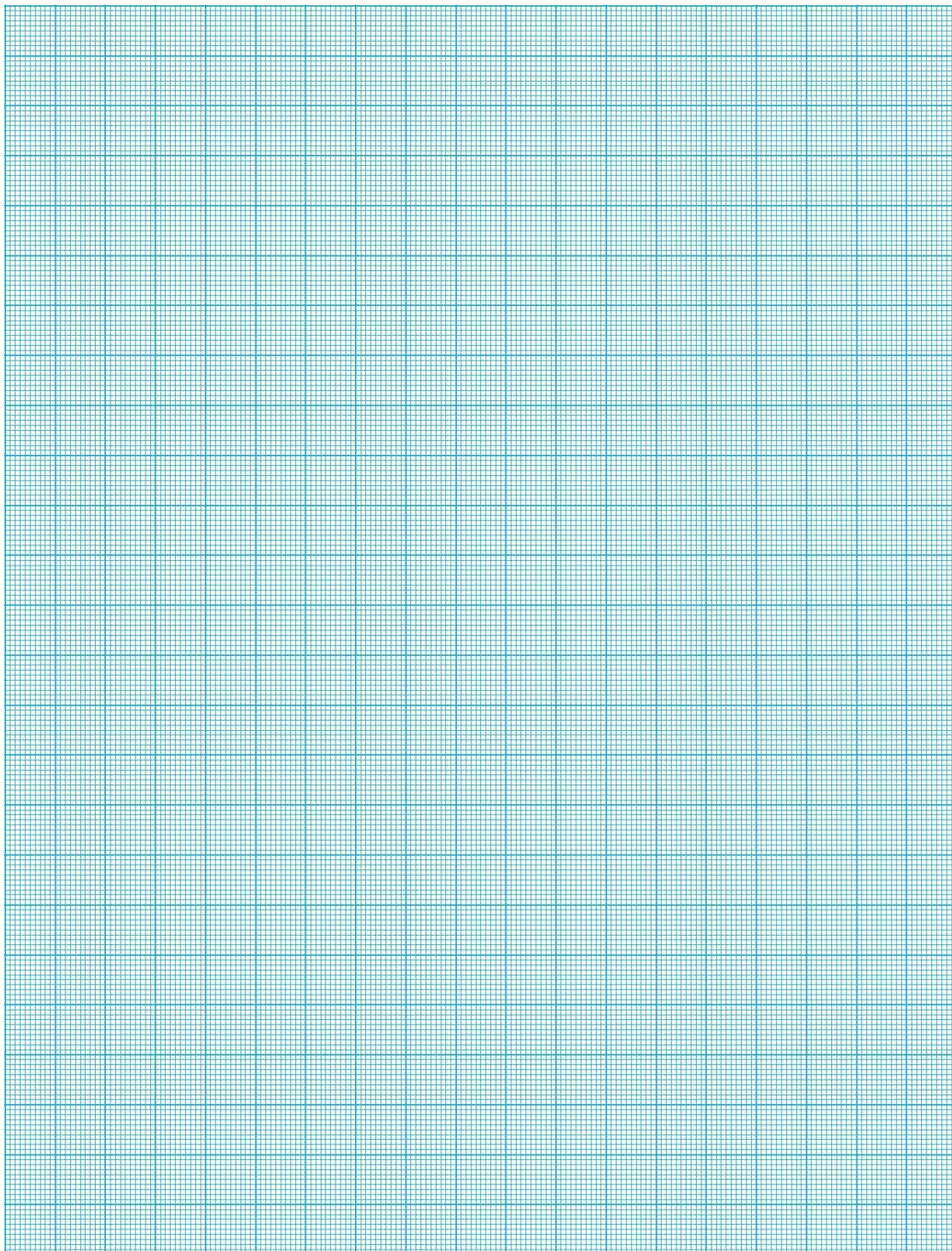**Name**_____**Department**_____**Group**_____

PRELAB QUESTIONS

1. Define the Rate Law.

2. What is the unit that is used to describe reaction rate?

3. What are the factors that affect the reaction rate? List four of them.

4. What is the order of reaction if the rate of reaction is independent of concentration of the reactants?

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7. Chemical Equilibrium

INTRODUCTION

Until now, we have stressed reactions that go to completion and concepts of stoichiometry that allow us to calculate the outcomes of such reactions. This time you will investigate chemical equilibrium where two opposing reactions take place at equal rate.

In this experiment you will take a quantitative look at the reaction between ferric and thiocyanate ions (Eqn 1). You will determine the concentration of each of the ions at equilibrium, and then seek an expression that relates these quantities mathematically in a simple, convenient manner.

$$Fe^{3+} (aq) + SCN^- (aq) \leftrightarrow FeSCN^{2+} (aq) \qquad \text{(Eqn 1)}$$
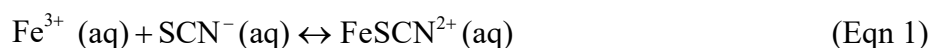
The determination of the concentration of red colored iron-thiocyanate complex will be done colorimetrically. A colorimeter is a light-sensitive instrument used in colorimetry for measuring the color intensity of an object or color sample. In your laboratory simple colorimeter will be build using diffuse light source and reference colored solution (known concentration of $FeSCN^{2+}$) for comparison of the solution with varied concentration of same compound. If you have ever looked critically at a glass full of colored liquid, such iced tea, you know that the color intensity as viewed through the sides of the glass is much less than the color intensity as viewed from the top down. This is because the color intensity depends upon the concentration of the colored substance and on the depth of the solution (Figure 1). Thus, 1 cm depth of a 1 M colored solution will appear to have the same color intensity as a 2 cm depth of a 0.5 M solution of the same material. The concentration of two such solutions may be compared by altering their relative depths until the color intensity appears the same. the ratio of the concentrations is found to be the inverse of the ratio of the depths. Note that this procedure gives only relative values for the concentrations. To get absolute values, a standard solution of known concentration must be used.
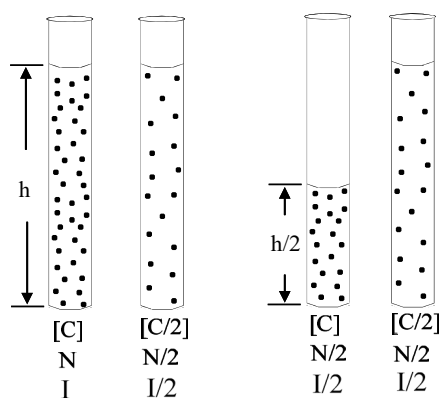

Figure 1. Effect of concentration and depth of solution on color intensity of solutions ([C]: concentration of colored compound, N: number of molecules in tube of colored compound and I: color intensity observed)

PROCEDURE

In preparing the standard solution in step *a* of this experiment, you will use a low, known concentration of thiocyanate ion, $SCN^-(aq)$, and add a large excess of ferric ion, $Fe^{3+}(aq)$. You can assume that essentially all of the thiocyanate ion will be used in forming complex thiocyanoiron(III) ion, $FeSCN^{2+}(aq)$, and the equilibrium concentration of the $FeSCN^{2+}(aq)$ ion will be essentially the same as the concentration of the $SCN^-(aq)$ ion with which you started.

Arrange your data sheet so that you can record the depth of the solution in each test tube and the depth of the standard solution compared with each of the other test tubes.

a. Line up five clean test tubes, all of the same diameter, and label them 1, 2, 3, 4, 5. Add 5.0 ml of 0.001 M potassium thiocyanate, KSCN, to each of these five test tubes. To test tube 1 add 5.0 mL of 0.1 M ferric nitrate, Fe $(NO_3)_3$. This tube will be used as the standard.

b. Measure 10.0 ml of 0.2 M Fe $(NO_3)_3$ in your graduated cylinder and dilute it to the 25.0 ml with distilled water. Pour the solution into a clean dry beaker to use it as a stock solution. Pipette 5.0 ml of this solution and pour it into test tube 2. (Save the remainder of the Fe $(NO_3)_3$ solution for Part *c*.) Calculate the concentration of this solution.

c. Measure 10.0 mL of the stock solution from the beaker into your graduated cylinder and dilute it to 25.0 mL with distilled water. Pour the solution into a clean dry beaker and pipette 5.0 mL of this solution into test tube 3. Continue dilution in this manner until you have 5.0 mL of successively more dilute solution in each test tube. Calculate the concentration of each of the solutions.

After preparation of the solutions, compare the color intensities of solutions in each of the test tubes with the standard tube (number 1) in order to determine the concentration of the thiocyanoiron(III) ion, $FeSCN^{2+}(aq)$.

Wrap a strip of a paper around test tubes 1 and 2 to exclude light from the side. Look vertically down through the solutions toward a diffused light source, as shown in Figure 2.

- If the color intensities appear the same, measure the depth of each solution to the nearest millimeter and record this.
- If the color intensities do not appear the same, remove some of the solution from the standard tube with a medicine dropper until the color intensities are the same. (Put the portion you removed into a clean dry beaker, since you may have to use some of this solution later.) In fact, the matching may be accomplished by removing more standard than seems necessary and then replacing part of it drop by drop. When the color intensities are the same in each test tube, measure the depth of both solutions to the nearest millimeter.

Repeat the procedure with test tubes 1 and 3, 1 and 4 and finally 1 and 5.

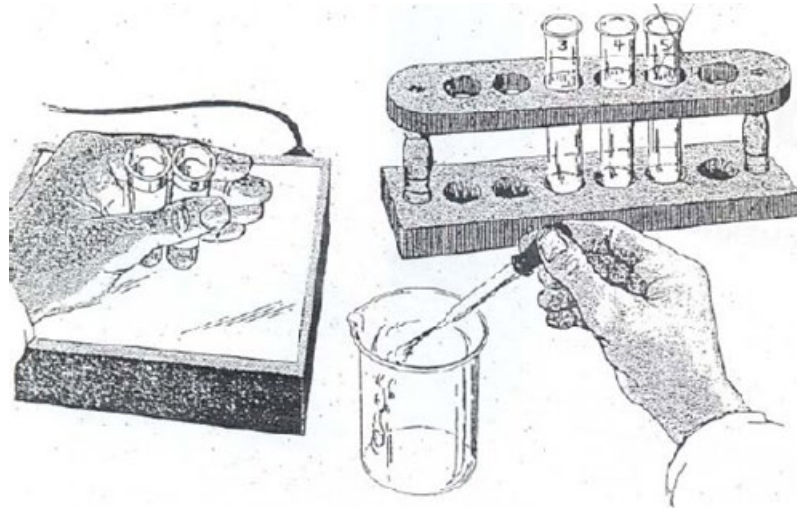Figure 2. Comparing the color of two samples over a diffuse light source

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DATA & CALCULATIONS

Depth of the Standard Solution (Tube 1)(mm)	Tube Number	Depth of the Solution (mm)	Ratio
	2		
	3		
	4		
	5		

Assume in your calculations that:

a. the ferric nitrate and the potassium thiocyanate exist in their respective solutions entirely as ions;

b. In the standard tube (number 1), essentially all the thiocyanate ions have reacted to form thiocyanate-iron (III) complex ions. Also remember that *both* solutions are diluted on mixing.

The symbol [ ] will be used to represent the equilibrium concentration in moles per liter. The formula within the brackets denotes the species. Thus the notation $[Fe^{3+}]$ stands for the equilibrium concentration of the ferric ion, Fe^{3+} (*aq*) in moles per liter.

Do all of the calculations for each test tube 2 through 5 as follows in the calculation tables:

1. a) Calculate the ratio of depths in the color comparison.

$$\text{Ratio} = \frac{\text{Depth of standard matched with tube 2}}{\text{Depth of liquid in tube 2}}$$

b) From these ratios calculate the equilibrium concentration of thiocyanate-iron (III) ion, $[FeSCN^{2+}]$:

$$[FeSCN^{2+}] = (\text{Ratio of depth}) \times (\text{Conc. of standard})$$

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2. From your dilution data calculate the *initial* concentration of $Fe^{3+}(aq)$ ion.

3. Calculate the equilibrium concentration of $Fe^{3+}(aq)$, $[Fe^{3+}]$, by subtracting the equilibrium concentration of the $FeSCN^{2+}(aq)$ ion from the initial concentration of $Fe^{3+}(aq)$ ion.

Tube Number	$[FeSCN^{2+}]_e$	$[Fe^{3+}]_i$	$[Fe^{3+}]_e$
2			
3			
4			
5			

4. Calculate the equilibrium concentration of $SCN^-(aq)$, $[SCN^-]$, in the same manner for the $Fe^{3+}(aq)$ ion. Subtract the equilibrium concentration of the $FeSCN^{2+}(aq)$ ion from the initial concentration of $SCN^-(aq)$ ion.

Tube Number	$[SCN^-]_i$	$[SCN^-]_e$
2		
3		
4		
5		

Name＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿＿**Department**＿＿＿＿＿＿＿＿＿＿＿＿**Group**＿＿＿

5. Now try to find some constant numerical relationship between the equilibrium concentrations of the ions in each test tube by multiplying and dividing the values obtained in each test tube in various concentrations.

Tube Number	$\dfrac{[SCN^-]}{[Fe^{3+}]\cdot[FeSCN^{2+}]}$	$[Fe^{3+}]\cdot[FeSCN^{2+}]\cdot[SCN^-]$	$\dfrac{[FeSCN^{2+}]}{[Fe^{3+}]\cdot[SCN^-]}$
2			
3			
4			
5			

QUESTIONS

1. Which of the combinations of concentrations, (a), (b) or (c), gives the most constant numerical value? This form is known as the equilibrium constant expression.

2. Restate this expression, in words, using the terms reactants and products.

3. Give a possible explanation as to why such a relationship might exist.

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PRELAB QUESTIONS

1. Describe the chemical equilibrium process.

2. How can you know that an equilibrium is dynamic?

3. Briefly explain why equilibrium constant expression do not contain concentration terms for pure solids or pure liquids phases?

4. What is the concentration unit used in equilibrium constant expressions for the liquids? (K_c)

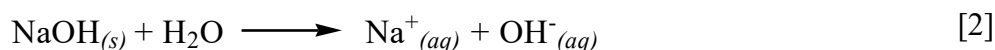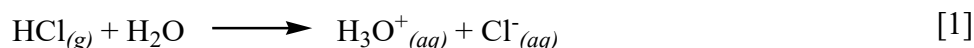# 8. Weak Acids, Weak Bases and Their Salts

INTRODUCTION

The purpose of this experiment is to determine the pH values of various concentrations of acids, bases, and salts. The pH values are determined by one of three methods.

1. Matched indicators
2. pH paper
3. pH meter

These data will be used to determine the acid-base dissociation constants of the substances being investigated. The variation of the degree of ionization of a weak acid and of a weak base using concentration also will be determined.

A. Strong Acids and Strong Bases

When a strong acid such as HCl or strong base such as NaOH is dissolved in water, it dissociates completely into ions as shown in equations [1] and [2].

$$HCl_{(g)} + H_2O \longrightarrow H_3O^+_{(aq)} + Cl^-_{(aq)} \qquad [1]$$

$$NaOH_{(s)} + H_2O \longrightarrow Na^+_{(aq)} + OH^-_{(aq)} \qquad [2]$$

As a result, the concentration of hydronium ions, $[H_3O^+]$, or the concentration of hydroxide ions, $[OH^-]$, essentially is equal to the concentration of the strong acid or the strong base, respectively.

Hydronium ion concentrations commonly range from 1.0 M to 10^{-14} M and frequently are expressed on logarithmic scale of pH.

$$pH = -\log [H_3O^+] \qquad [3]$$

Furthermore, $[OH^-]$ is related to $[H_3O^+]$ by the ion product of water, K_w, which at 25°C has the value

$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14} \qquad [4]$$

The relationship between pH and pOH (-log[OH⁻]) is obtained from equation [4].

$$-\log K_w = -\log[H_3O^+] - \log [OH^-] = +14.00$$
$$pK_w = pH + pOH = 14.00 \tag{5}$$

Consequently, if one of pH, pOH, $[H_3O^+]$, or $[OH^-]$ is known, the other three may be calculated by using equations [3], [4] and [5].

B. Weak Acids and Weak Bases

In contrast to strong acids and bases, weak acids and weak bases do not dissociate completely in solution. They ionize only partly, as shown for nitrous acid (HNO_2) and hydrazine (N_2H_4) in equations [6] and [7].

$$HNO_{2(aq)} + H_2O \rightleftharpoons H_3O^+{}_{(aq)} + NO_2^-{}_{(aq)} \tag{6}$$

$$N_2H_{4(aq)} + H_2O \rightleftharpoons OH^-{}_{(aq)} + N_2H_5^+{}_{(aq)} \tag{7}$$
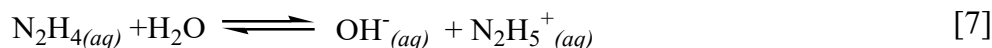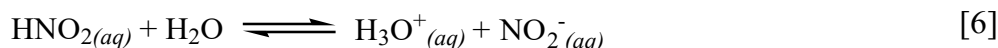
The equilibrium constants for these reactions are known as dissociation or ionization constants. For a given weak acids or weak bases, the ionization constant has a definite value at a specific temperature. The ionization constant expressions and their values at 25°C for nitrous acid and hydrazine are:

$$K_i = K_a (HNO_2) = \frac{[H_3O^+] [NO_2^-]}{[HNO_2]} = 4.5 \times 10^{-4} \tag{8}$$

$$K_i = K_b (N_2H_4) = \frac{[OH^-] [N_2H_5^+]}{[N_2H_4]} = 9.8 \times 10^{-7} \tag{9}$$

Where K_i is ionization constant, K_a is an acid ionization constant, and K_b is a base ionization constant.

Ionization constants are determined experimentally by a method very similar to that used in this experiment. The pH of a solution of weak acid or base of known concentration is determined, and these data are used to calculate the value of the ionization constant.

EXAMPLE: The pH of a 1.0 M solution of benzoic acid, C_6H_5COOH, is 2.11. Calculate the ionization constant of benzoic acid.

A pH of 2.11 is equivalent to $[H_3O^+] = 0.0078$ M. The ionization reaction follows, and the initial and equilibrium concentrations are given below each species

$$C_6H_5COOH_{(aq)} + H_2O \rightleftharpoons C_6H_5COO^-{}_{(aq)} + H_3O^+{}_{(aq)}$$
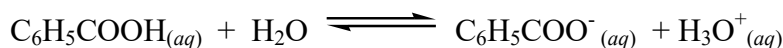
Initial: 1.00 M   -   -
Equilibrium: (1.00 – 0.0078) M   0.0078 M   0.0078 M

Since only equilibrium concentrations are used in the ionization constant, K_a becomes

$$K_a = \frac{[H_3O^+]\,[C_7H_5O_2{-}]}{[HC_7H_5O_2]} = \frac{(0.0078)(0.0078)}{(1.00 - 0.0078)} = 6.1 \times 10^{-5} \qquad [10]$$

Because weak acids and bases only partially ionize, the degree of ionization, α, of a weak acid or base often is calculated. For example, if a weak base, B, ionizes according to Eqn. 11,

$$B_{(aq)} + H_2O \rightleftharpoons BH{+}_{(aq)\,+}\,OH{-}_{(aq)} \qquad [11]$$
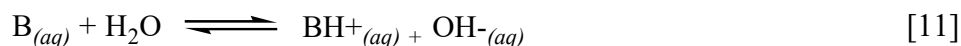
$$\alpha = \frac{[BH^+]_{eq}}{[B]_{init}} = \frac{[OH^-]_{eq}}{[B]_{init}} \qquad [12]$$

The subscript "eq" indicates equilibrium concentration and the subscript "init" indicates initial concentration. While the ionization constant of a given acid or base depends only on temperature, the degree of ionization also varies inversely with concentration.

C. Salts of Weak Acids and Weak Bases

Although soluble salts dissociate completely into their ions when they dissolve in water, the fate of these ions depends on the acid or base from which they are derived. The anions of strong acids and the cations of strong bases do not react with water except to become hydrated – surrounded by water molecules. On the other hand, the anions and cations of weak acids and bases react with water by a process sometimes known as *hydrolysis*.

Thus, the salt sodium nitrite, $NaNO_2$, first dissociates completely in water

$$NaNO_{2(aq)} + H\ O \rightleftharpoons Na^+{}_{(aq)} + NO\ ^-{}_{(aq)} \qquad [13]$$

and then the nitrite ion acts as a weak base, accepting proton from water to form its conjugate acid, HNO_2.

$$NO_2{}^-{}_{(aq)} + H_2O \rightleftharpoons HNO_{2(aq)} + OH^-{}_{(aq)} \qquad [14]$$
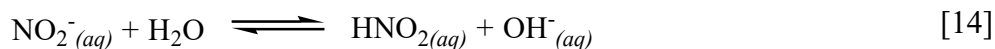
The equilibrium constant, K_b, for equation [14] is

$$K_b = \frac{[HNO_2]\,[OH^-]}{[NO_2{}^-]} \qquad [15]$$

Values of K_b for anions are rarely tabulated since they may be calculated from the ionization constants of the corresponding conjugate acids. Algebraic manipulation of equation [15] shows the relationship between K_a and K_b of a conjugate acid–base pair.

$$K_b = \frac{[HNO_2][OH^-]}{[NO_2^-]} \times \frac{[HNO_2][H_3O^+]}{[H_3O^+]} = \frac{[HNO_2]}{[H_3O^+][NO_2^-]} \times [[H_3O^+][OH^-] = \frac{1}{K_a} \times K_w = \frac{K_w}{K_a} \quad [16]$$

For the salt hydrazine iodide, N_2H_5I, the equations analogous to [13]-[16] are [17]-[20].

$$N_2H_5I + H_2O \rightleftharpoons N_2H_5^+{}_{(aq)} + I^-{}_{(aq)} \quad [17]$$

$$N_2H_5^+{}_{(aq)} + H_2O \rightleftharpoons N_2H_{4(aq)} \quad {}_3{}^+{}_{(aq)}$$

$$K_a = \frac{[N_2H_4][H_3O^+]}{[N_2H_5^+]} \quad [19]$$
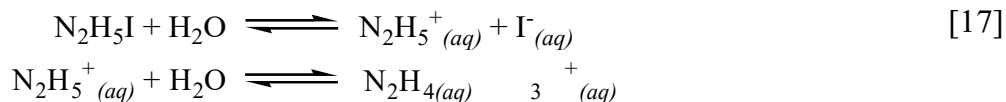
$$K_a = \frac{K_w}{K_b} = [H_3O^+][OH^-] \times \frac{[N_2H_4][H_3O^+]}{[N_2H_5^+]} \quad [20]$$

The pH and concentration of a salt dissolved in water are the data necessary to determine the values of K_a and K_b for a weak conjugate acid–base pair.

EXAMPLE: A 1.00 M solution of sodium benzoate, $NaC_7H_5O_2$, has a pH of 9.11. What is the value of K_b for the benzoate anion (the conjugate base of benzoic acid) and the acid ionization constant of benzoic acid?

A pH = 9.11 is equivalent to pOH = 4.89 or $[OH^-]$ = 1.3 x 10^{-5} M. The hydrolysis reaction as follows:

	$C_7H_5O_2^-$	+	H_2O	$\Leftrightarrow$	$HC_7H_5O_2$	+	OH^-
Initial:	1.00 M						
Equlibrium:	$(1.0 - 1.3 \times 10^{-5})$ M	~1.00 M			1.3 x 10^{-5} M		1.3 x 10^{-5} M
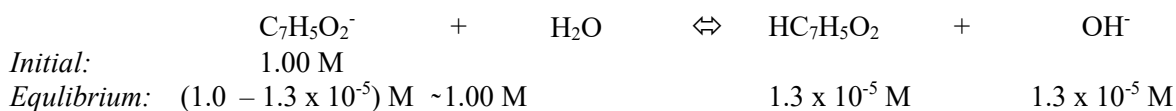
Then K_b for benzoate anion and K_a or benzoic acid can be determined. Note that for any conjugate acid-base pair, $K_aK_b = K_w$.

$$K_b = \frac{[OH^-][HC_7H_5O_2]}{[C_7H_5O_2^-]} = \frac{(1.3 \times 10^{-5}M)(1.3 \times 10^{-5}M)}{1.00\ M} = 1.7 \times 10^{-10}$$

$$K_a = \frac{K_w}{K_b} = \frac{1.00 \times 10^{-14}}{1.7 \times 10^{-10}} = 5.9 \times 10^{5}$$

PROCEDURE

You can determine the pH of the solutions investigated in this experiment using one of the three methods below.

<u>**Method I.**</u> **pH Determination Using Indicators**

Obtain about 200 mL of distilled water and boil it for 5 min to remove carbon dioxide. Carbon dioxide dissolved in water is a weak acid that will seriously affect the results of this experiment if it is not removed. For each solution to be tested, proceed as follows.

1. Rinse each of five very clean small test tubes three times with about 2 mL of boiled distilled water
2. Rinse each test tube once with about 2 mL of the solution to be tested.
3. Place about 5 mL of the solution to be tested into each of the five test tubes.
4. Add 3 or 4 drops of one of the indicators given in Figure 1 to the test tubes. Use a different indicator in each test tube.
5. Record the color in each test tube and, using the data of Figure 1, determine and record the pH of the solution to the nearest 0.3 pH unit. (You will have to estimate the last digit.)
6. Repeat steps 1-5 for each solution making sure to carefully rinse all test tubes and as directed in step 1.
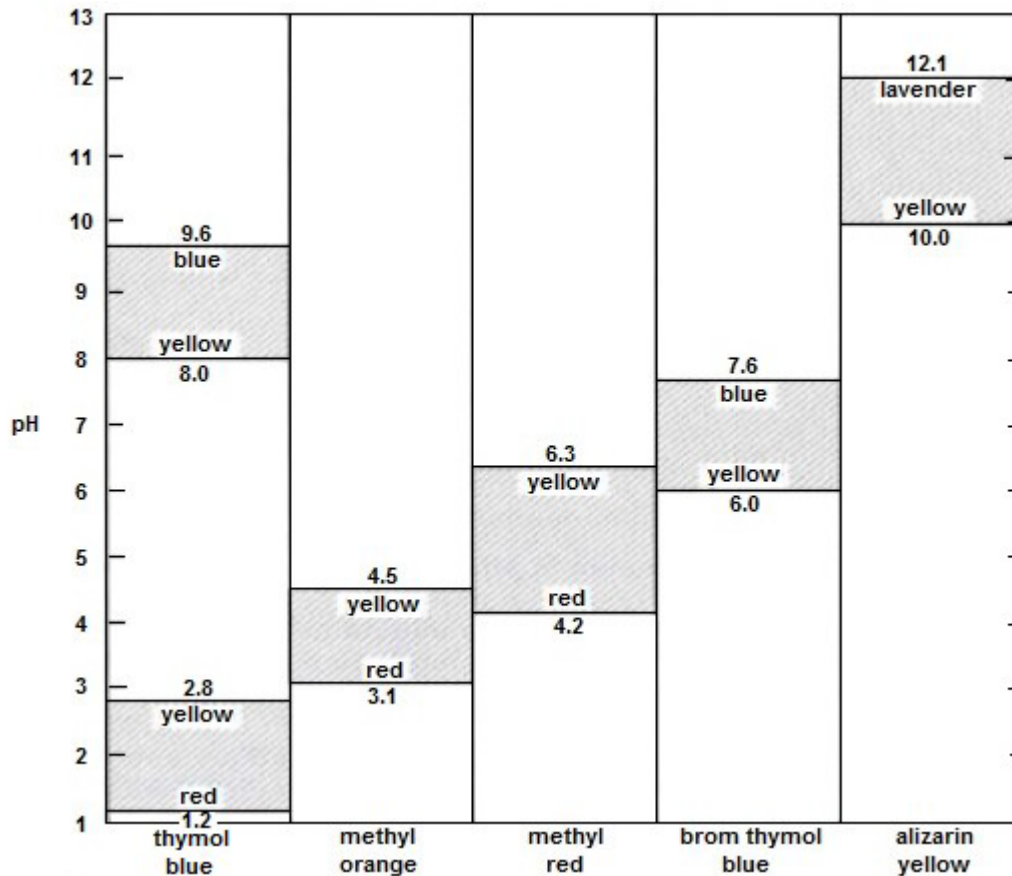

Figure 1. pH Color Change Ranges of Some Indicators

Method II. pH Determination Using pH Paper

pH paper is filter paper that has been impregnated with one or a mixture of indicators. The pH paper will display one of a number of colors depending on the pH of the solution to which it is exposed. pH paper is produced in two types: wide-range and short-range. Wide-range pH paper covers nearly the entire pH scale, whereas short-range pH paper may display all its colors within a pH range as narrow as 0.9 pH unit. The general procedure is to test the pH of a solution using wide-range pH paper to obtain an approximate pH. The short-range pH paper encompassing this approximate pH is then used to obtain a more exact pH.

Frequently, pH paper is sold in kits. A typical kit contains one wide-range pH paper with colors as follows.

Color:	Red	Orange	Yellow	Green	Blue
pH:	2	4	6	8	10

The kit also contains six short-range papers of the following ranges.

Range number:	1	2	3	4	5	6
pH range:	0.0 – 3.0	3.5 - 5.5	6.0 - 8.5	9.0 - 11.0	10.5 - 12.5	12.0 - 14.0

To usage of pH paper to determine the pH of a solution proceed as follows.

1. Obtain 200 mL of distilled water and boil it for 5 min to remove carbon dioxide gas. Place this distilled water in your wash bottle.
2. Rinse a clean stirring rod with boiled distilled water from your wash bottle and then with 10-15 drops of the solution to be tested.
3. Touch the wet stirring rod to the wide-range pH paper and record the color and approximate pH in your notebook.
4. Wet the stirring rod again with 5-10 drops of the solution to be tested. Based on the results of step 4, select the appropriate short-range pH paper and touch the wet stirring rod to it. Record the color and pH in your notebook. Try to estimate the pH to the nearest 0.1 pH unit.
5. Repeat steps 3-5 for each solution to be tested. Each piece of pH paper can be reused until it is covered completely with drops of solution. After it is totally covered, it should be discarded, and a fresh piece of pH paper then should be used.

Method III. Determination of pH with a pH Meter

pH meters differ greatly in their method of operation, but generally the following steps should be used.

1. The temperature compensation dial of the pH meter (if there is one) should be set to the temperature of the solution

2. The electrodes never should be left "high and dry". They should always be immersed in liquid except when they are being transferred from one solution to another.

3. The pH meter should be calibrated (if possible) using standard pH buffer solutions. The buffers should span the range of pH that is to be investigated. Three buffers of pH = 4.0, 7.0 and 10.0 are a particularly useful set.

4. The solution to be investigated should be placed in the smallest container possible. A combination electrode can measure the solution in a large test tube. Two electrodes can fit easily in a 50 mL beaker. Using the smallest container possible greatly reduces the amount of solution that must be used.

5. Electrodes should be rinsed with CO_2 free distilled water from a wash bottle between determinations. Electrodes should never be touched at the bottom with your hands.

6. Many pH meters have a mirror behind the needle. The needle and its mirror image should be superimposed when reading pH to avoid parallax.

7. Glass electrodes are made of very thin glass at the bottom and are very fragile. Care should be taken not to bump them on the bottom or sides of the container.

8. Record the pH in your notebook to the nearest 0.01 pH unit.

A. Determination of the pH of the Solutions

Use these three methods to determine the pH of each of the following solutions.

1. Unboiled distilled water
2. Boiled distilled water
3. 1.0 M NaCl solution
4. 1.0 M $NaHSO_4$ solution
5. 1.0 M Na_2CO_3 solution

Disposal:

Solutions: None of these solutions is particularly hazardous. Mix them all together in a large beaker and, using pH paper or phenolphthalein as an indicator, neutralize with 1 M HCl (the first disappearance of pink color) or 1 M NaOH (first appearance of permanent pink color). Flush the resulting salt solution down the sink with running water.

B. Effect of Concentration on Degree of Dissociation

Use the pH meter described previously to determine the pH of the three solutes given below at each of the following concentrations: 1.0 M, 0.10 M, and 0.010 M.

1. Acetic acid, $HC_2H_3O_2$(aq)
2. Ammonia, NH_3(aq)
3. Hydrochloric acid, HCl(aq)

If you are using a pH meter do not leave the electrodes immersed in the aqueous ammonia solutions. Place electrodes in the solution only long enough to determine the pH,

turn the meter to standby, raise the electrodes, thoroughly rinse them with distilled water, and store them in pH 7 buffer or distilled water. Basic solutions can chemically attack the glass of the electrode.

Disposal:

   Solutions: Follow the same procedure as for Part A.

Name _____**Department**_____**Group**____

DATA&CALCULATIONS

A. Determination of the pH of the Solutions

Based on your observations, fill in the following table.

	thymol blue	methyl orange	methyl red	bromothymol blue	alizarin yellow	pH range from indicators	pH paper	pH Meter
Unboiled distilled water								
Boiled distilled water								
1.0 M NaCl								
1.0 M NaHSO$_4$								
1.0 M Na$_2$CO$_3$								

Record the pH, [H$_3$O$^+$] and [OH$^-$] of each solution that you investigated.

Solution	pH	[H$_3$O$^+$]	[OH$^-$]
Unboiled distilled water			
Boiled distilled water			
1.0 M NaCl solution			
1.0 M NaHSO$_4$ solution			
1.0 M Na$_2$CO$_3$ solution			

Name _____**Department**_____**Group**_____

For each solute listed below, write the hydrolysis reaction, the expression for the base constant, K_b, if the solute is a base or the expression for the acid ionization constant, K_a, if the solution is an acid. Calculate values of K_b and K_a from your data.

Solute	Hydrolysis Reaction	Expression for K_b or K_a	Value of K_b and K_a
$NaHSO_4$			
Na_2CO_3			

A. Effect of Concentration on Degree of Ionization

Record the pH, $[H_3O^+]$ and $[OH^-]$ of each solution that you investigated with **<u>pH meter</u>**.

		1.0 M	0.10 M	0.010 M
HCl	pH			
	$[H_3O^+]$			
	$[OH^-]$			
HC$_2$H$_3$O$_2$	pH			
	$[H_3O^+]$			
	$[OH^-]$			
NH$_3$(aq)	pH			
	$[H_3O^+]$			
	$[OH^-]$			

Name_____**Department**_____**Group**_____

Using your data, calculate the value of K_a or K_b and the degree of ionization, **α**, for each of the solutions you investigated.

		1.0 M	0.10 M	0.010 M
HCl	K_a			
	α			
HC₂H₃O₂	K_a			
	α			
NH₃(aq)	K_a			
	α			

Name_____**Department**_____**Group**_____

REPORT QUESTIONS

1. A solution of carbon dioxide in water is slightly acidic. Show how this can occur by using a balanced chemical equation for the reaction of CO_2 and water.

2. In water, the K_a of phenol, C_6H_5OH, is equal to 1.3×10^{-10} at 25 °C. Calculate the value of K_b for the conjugate base of phenol, the phenolate ion, $C_6H_5O^-$.

3. NH_3 is a stronger base than water. Which of their conjugate acids is stronger, NH_4^+ ion or H_3O^+ ion? Support your answer with an explanation.

4. A 0.100 M solution of a weak mono-functional base, $NaNO_2$, has a pH = 8.18. Calculate the value of K_a for the conjugate acid of this system, HNO_2.

Name_____**Department**_____**Group**____

PRELAB QUESTIONS

1. Classify each of the following according to their pH behavior in water (acidic, basic, neutral)

a. KNO_3 _____

c. N_2H_4 _____

b. NH_4Cl _____

d. $NaNO_2$ _____

2. A solution has a pH of 8.75. Calculate the

a. $[H_3O^+]$

b. pOH

c. $[OH^-]$

3. What must be done if strong base solution is spilled on your skin?

4. Why do we avoid leaving glass electrodes immersed in solutions of bases for more than a brief time?

5. A 0.100 M solution of a weak mono-protic acid, HX, has a pH = 3.25. Calculate the acid ionization constant, K_a, of HX.

9. An Investigation of Voltaic Cells: The Nernst Equation

INTRODUCTION

This experiment investigates the electrical potential (voltage) produced by an oxidation-reduction reaction and the effect of concentration on that potential. **Oxidation** is that process in which the oxidation state of an element increases; the element also loses electrons. In **reduction**, the oxidation state of an element decreases; the element gains electrons. In oxidation-reduction reactions, an oxidation must always accompany a reduction; neither process can occur alone.

The objectives of this experiment are to:
1. Measure the potentials of cells formed with a variety of different solutions and electrodes.
2. Calculate half reaction potentials using the Cu^{2+}/Cu half reaction as a reference.
3. Measure the effect of changes in concentration on cell potential.
4. Use the Nernst Equation to relate concentration and cell potential.

When an iron nail is placed in a copper (II) nitrate solution and left to stand, the blue color of the solution fades and a brown-red deposit forms on the nail. If the brown-red deposit is scraped away, the nail is found to be somewhat smaller and to have an uneven surface. Chemical analysis reveals that the brown-red deposit is copper metal and Fe^{2+} ions are in solution. Some elemental iron, Fe, has become Fe^{2+} ions, and some Cu^{2+} ions have become elemental copper, Cu. These changes are summarized by the following two half-equations.

$$Fe(s) \rightarrow Fe^{2+}(aq) + 2\ e^- \hspace{4cm} (1)$$
$$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s) \hspace{4cm} (2)$$

Equation [1] represents an oxidation half-reaction, and equation [2] represents a reduction half-reaction. Another way of stating this is that Fe has been oxidized to Fe^{2+} and Cu^{2+} has been reduced to Cu.

Yet another way to summarize the results of the observation described above is to write an overall equation. Two different types of equations may be written.

$$Fe(s) + CuSO_4(aq) \rightarrow FeSO_4(aq) + Cu(s) \hspace{2.5cm} (3)$$
$$Fe(s) + Cu^{2+}(aq) \rightarrow Fe^{2+}(aq) + Cu(s) \hspace{2.8cm} (4)$$
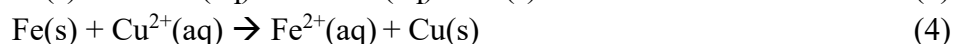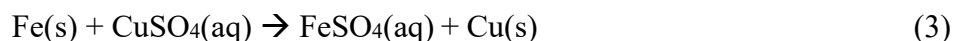
Equation [3] represents the complete reaction for these observations. If the colorless solution by the reaction were gently evaporated, solid $FeSO_4$ and Cu would be obtained; little or no $CuSO_4$ would be found in the now colorless solution. Equation [4] summarizes the essential features of the reaction and eliminates the ion that is changed in the process (SO_4^{2-} in this case). Equation [4] is called the **net ionic equation** for this reaction.

One benefit of using half-equations is now evident; if electron gain and loss are balanced, two half-equations can be added to yield the net ionic equation for the overall reaction. Since the net ionic equation can be separated into two-half equations on paper; it is not surprising that they can be run almost independently in practice.

oxidation: $Fe(s) \rightarrow Fe^{2+}(aq) + 2\ e^-$ **reduction:** $Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$
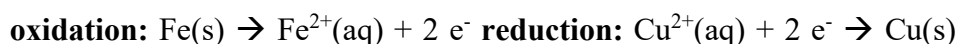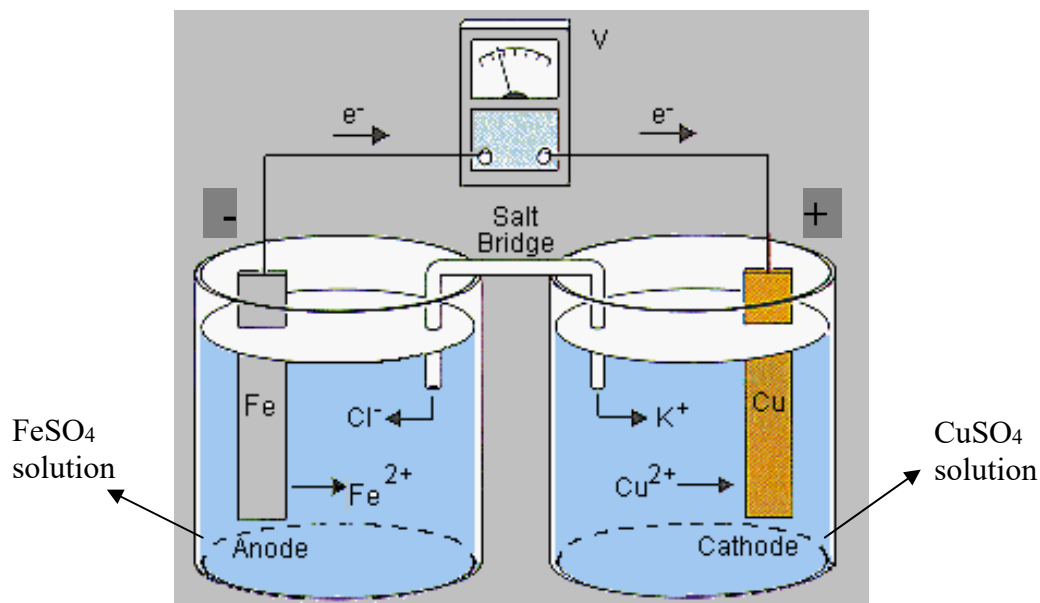
Figure 1. Apparatus for Measurement of Cell Potentials

The experimental setup is shown in Figure 1. The salt bridge is necessary to complete the electric circuit by allowing electrical contact between the two solutions. The setup of Figure 1 can be used to measure the voltage, or potential, of the cell reaction [4]. As seen from the figure, oxidation occurs at the anode and reduction occurs at the cathode. The potential changes if a zinc strip is used in place of the iron nail and $ZnSO_4$ solution is used in place of the $FeSO_4$ solution. Each half-reaction has distinct potential associated with it and the potential of a cell is the sum of these half-cell potentials.

The Nernst Equation

The concentration of the ions in solution also affects the potential of the half-cell. For the reaction;

$Fe^{3+}(aq) + e^- \rightarrow Fe^{2+}(aq)$ [5]

The half-cell potential is given by the Nernst equation;

$$E_{red} = E^o_{red} - \frac{0.0592}{n} \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$ [6]

Where E^o_{red} is the standard reduction half-cell potential (the voltage measured when $[Fe^{2+}] = [Fe^{3+}] = 1.00$ M) and n is the number of electrons transferred in the half-reaction. In the case of reaction [5], n=1. For half-reaction [2], the Nernst equation is;

$$E_{red} = {}^o_{red} - \frac{0.0592}{2} \log \frac{1}{[Cu^{2+}]}$$ [7]

Frequently, it is easier to use the Nernst equation for the entire cell. For reaction [4], the Nernst equation is (where $E^o_{cell} = E^o_{ox} + E^o_{red}$);

$$E_{cell} = E^o_{cell} - \frac{0.0592}{2} \log \frac{[Fe^{2+}]}{[Cu^{2+}]}$$ [8]

Concentration Cells

The Nernst equation also may be used to determine the potential of a cell in which the net reaction is one of simple dilution.

$$Cu^{2+} (1.0M) \rightarrow Cu^{2+} (0.050M)$$ [9]

For this reaction $E^o_{cell} = 0.00$ V (since $E^o_{ox} = E^o_{re}$) and the cell voltage depends only on concentration.

$$Ecell = 0.00 - \frac{0.0592}{2} \log \frac{0.050}{1.0} = 0.0385V$$

In general, the Nernst equation contains the molar concentrations of the concentrated and dilute solutions, which are physically separated in the cell by a porous cup or a salt bridge.

$$Ecell = - \frac{0.0592}{2} \log \frac{[M^{n+}(dil.)]}{[M^{n+}(conc.)]}$$ [10]

Equation [10] is the Nernst equation for the reaction and cell shown below;

$$M^{n+}(conc.) \rightarrow M^{n+}(dil.) \qquad M \mid M^{n+}(dil.) \parallel M^{n+}(conc.) \mid M$$ [11]
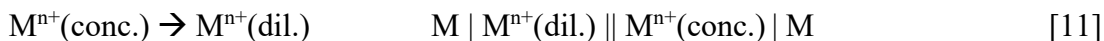
SAFETY PRECAUTIONS

Be very careful in handling chemicals. Wipe all spills promptly with a damp sponge or towel. If any chemicals get on your hands or clothing, wash immediately with soap and large volumes of running water. If more than a few drop of chemical solution spill on you, tell your instructor while you are washing off the spill. Wash your hands carefully and thoroughly at the end of the experiment before leaving the laboratory.

PROCEDURE

A. Oxidation-Reduction Reactions

1. Add 1.0 M $CuSO_4$ solution into two small test tubes to a depth of 1 cm. Partially immerse a clean iron nail in one test tube and a strip of zinc in the other. Observe the color of the solutions and the metals immediately after the metals are immersed.
2. Allow the two test tubes to stand while you setup the apparatus shown in Figure 1 for the measurement of cell potentials. Note the color of the solutions every five minutes during the following 15 minute period.
3. Remove the metals and gently scrape and wash off the metallic deposit. Describe the color and the texture of the metallic deposit as well as the surface of iron nail and the zinc strip. Especially note any differences between the part of the metal that was immersed in the $CuSO_4$ solution and the part that was not.

B. Cell Voltages

1. Place approximately 20 mL of 1.0 M $CuSO_4$ solution in a 50 mL beaker.
2. Place approximately 20 mL of 1.0 M $FeCl_2$ solution in another 50 mL beaker.
3. Prepare a salt bridge by soaking a strip of porous paper in a solution of saturated KCl. The two ends of this salt bridge are dipped into the beakers.
4. Place the iron nail in the $FeCl_2$ solution and a copper strip in the $CuSO_4$ solution. Each electrode should be long enough (at least 8 cm) so that it is not completely immersed in the solution. (The electrodes should not be in contact with the paper salt bridge). Connect the lead from the positive terminal of the voltmeter to the copper electrode using the alligator clip at the end of the lead. Connect the black lead to the iron nail electrode. Do not allow the alligator clips to come into contact with the solutions. **You will use the same copper electrode and $CuSO_4$ solution throughout the experiment.**
5. Allow the electrodes to sit in solution until the voltmeter reading is stable to ±0.1 V (fluctuation in the third digit after the decimal will not be significant in this experiment). Read the voltage to the nearest 0.01 V.
6. A voltaic cell undergoes a spontaneous reaction and will therefore always have a positive potential. The alligator clips should be connected to the electrodes such that a positive potential reading is obtained on the voltmeter. The electrode connected to the positive terminal of the voltmeter is positive and is therefore the cathode. In this first case the

copper electrode is the positive cathode. The other electrode is negative and is therefore the anode.

7. Disconnect the alligator clip from the iron nail.

8. Repeat steps 2-7 with each of the solution-electrode pairs given in Table.

Table 1. Electrodes to be investigated

Solution	Electrode
1.0 M $FeCl_2$	Iron nail
1.0 M $Zn(NO_3)_2$	Zn metal
1.0 M $Pb(NO_3)_2$	Pb metal

C. Effect of Concentration

1. Place approximately 20 mL of 1.0 M $CuSO_4$ solution in a 50 mL beaker. This beaker and solution will be used throughout this part.

2. Place approximately 20 mL of 0.10 M $CuSO_4$ solution in another 50 mL beaker.

3. Dip the two ends of the salt bridge into the beakers.

4. Place a copper strip in the both of solutions and record the potential of the cell.

5. Repeat steps 2-4 with a 0.01 M and 0.001 M $CuSO_4$ solutions.

Disposal of solutions:
Dispose the solutions in a waste bottle labeled heavy metals-solutions.

Name _____ **Department** _____ **Group** ____

DATA & CALCULATIONS

A. Oxidation-Reduction Reactions

Describe the appearance of the metals and solutions and the deposit with respect to time.

	initial	5 min	10 min	15 min
Zn immersed solution				
Fe immersed solution				
Zn metal				
Fe metal				

B. Cell Voltages

1. For each cell you constructed, record the potential (voltage) of the cell. Write the half cell equations and the net ionic equation for the reaction that occurred.

Cell	Potential (V)	Half Reactions	Net Ionic Equation
Cu^{2+}/Fe^{2+}			
Cu^{2+}/Zn^{2+}			
Cu^{2+}/Pb^{2+}			

Name_____**Department**_____**Group**_____

2. Use the known standard potential (0.34 V) of the copper half reaction to calculate the oxidation half cell potential of the studied half reactions.

$Cu^{2+}(aq) + 2\ e^- \rightarrow Cu(s)$ 0.34 V

$\underline{M(s) \rightarrow M^{2+}(aq) + 2\ e^-}$? E°ox

$Cu^{2+}(aq) + M(s) \rightarrow Cu(s) + M^{2+}(aq)$ measured potential
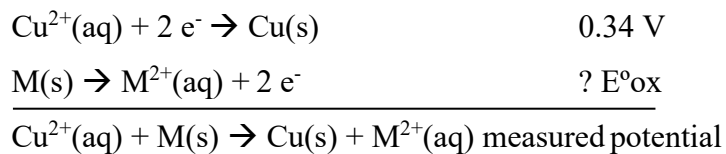
Half-Cell	E°ox (V)	E°red (V)	%Relative Error
Fe^{2+}/Fe			
Zn^{2+}/Zn			
Pb^{2+}/Pb			

Name_____**Department**_____**Group**_____

C. Effect of Concentration

1. For each part, record the potential of the cell. Calculate the diluted Cu^{2+} concentration using the measured cell potentials and the Nernst Equation.

Assumed [Cu^{2+}] (M)	Cell Potential (V)	Experimental [Cu^{2+}] (M)	% Relative Error
0.10 M Cu^{2+}			
0.010 M Cu^{2+}			
0.0010 M Cu^{2+}			

Experiment 9: An Investigation of Voltaic Cells-The Nernst Equation

Name_____**Department**_____**Group**____

PRELAB QUESTIONS

1. Why is it important to keep half of the electrodes out of the solutions when making measurements in Part A, oxidation-reduction reactions?

2. Calculate the E_{cell} between two Cu^{2+}/Cu half-cells, one of which contains 0.00100 M Cu^{2+} and the other contains 1.00 M Cu^{2+}.

3. A Voltaic cell undergoes a_____cell reaction and has a_____cell potential.

4. A voltaic cell is constructed in which a copper wire is placed in a 1.0 M $Cu(NO_3)_2$ solution and a strip of gold is placed in a 1.0 M $AuNO_3$ solution. The measure potential of the cell is found to be 1.36 V and the copper electrode is negative. Given that the E^o for the Cu^{2+}/Cu half cell is +0.34 V, calculate the E^o for the Au^+/Au.

Scores of the General Chemistry Laboratory II Experiments

Experiment 1: Determination of Water Hardness

	CHEM 102	CHEM 114
Title Page	5	5
Purpose	5	10
Introduction	15	-
Procedure	5	10
Data & Results	5	5
Calculation	25	30
Questions	20	20
Conclusion	20	20

Experiment 2: Synthesis of Soap

	CHEM 102	CHEM 114
Title Page	5	5
Purpose	10	10
Introduction	40	40
Procedure	15	15
Conclusion	25	25
Tidy	5	5

Experiment 3: Molecular Models and Covalent Bonding

	CHEM 102	CHEM 114
Purpose	10	10
Calculation	48 (each 1p)	48 (each 1p)
Questions	20 (each 4p)	20 (each 4p)
Conclusion	5	17
Tidy	5	5

Experiment 4: Steam Distillation

	CHEM 102	CHEM 114
Title page	5	5
Purpose	5	5
Introduction	10	-
Procedure	5	5
Data & Results	5	5
Questions	20	20
Calculation	20	30
Conclusion	25	25
Tidy	5	5

Experiment 4: Molecular Weight Determination From Freezing Point Depression

	CHEM 102	CHEM 114
Title Page	5	5
Purpose	10	10
Introduction	10	-
Procedure	5	5
Data & Results	5	5
Calculation	25	30
Conclusion	15	20
Tidy	5	5
Graph	20	20

Experiment 6: Kinetic Study of the Reaction Between Ferric and Iodide Ions

	CHEM 102	CHEM 114
Title Page	5	5
Purpose	5	10
Introduction	10	-
Procedure	5	5
Data & Results	10	10
Calculation	25	25
Graph	15	15
Conclusion	15	15
Questions	5	10
Tidy	5	5

Experiment 7: Chemical Equilibrium

	CHEM 102	CHEM 114
Title page	5	5
Purpose	5	5
Introduction	10	-
Procedure	10	10
Data & Results	5	10
Calculations	30	30
Questions	15	20
Conclusion	20	20

Experiment 8: Weak acids, Weak bases and Their Salts

	CHEM 102	CHEM 114
Title Page	5	5
Purpose	10	10
Introduction	10	-
Procedure	10	10
Data & Results	10	10
Calculation	30	35
Conclusion	20	25
Tidy	5	5

Experiment 9: An Investigation of Voltaic Cells-The Nernst Equation

	CHEM 102	CHEM 114
Title Page	5	5
Purpose	5	10
Introduction	10	-
Experimental	5	10
Calculation	35	35
Conclusion	25	25
Tidy	5	5