Department of Chemistry

CHEM 203

Introductory Chemical Techniques Laboratory Manual

CONTENTS

Safety Rules by the Environmental Health, Safety, and Risk Management

BEING safe is smart, for a safe practice in laboratories follow these basic rules &regulations:

DO:

1. Wear lab coats (knee-length) and appropriate eye protection (minimum safety goggles).
2. Keep clean work places free of unwanted chemicals, biological specimens, radios, and idle equipment.
3. Keep exits and passageways clear at all time.
4. Become familiar with the locations and operation of safety and emergency facilities such as the fire extinguishers, first aid kit, emergency wash facilities, fire alarm pull stations, telephone, and emergency exits.
5. Wash hands before leaving the laboratory.
6. Leave behind protective clothing (lab coats, gloves, etc.) when leaving the laboratory to eat.
7. Remove contaminated cloths immediately.
8. Wash before eating, drinking, smoking, or applying make-up.
9. Pin or tie your hair (if long) up in a bun especially while working with chemicals, biohazards, radioisotopes, or moving machinery.
10. Work only with materials when you know their flammability, reactivity, toxicity, safe handling, storage and properly operating emergency procedures.
11. Perform all procedures involving the liberation of volatile materials or aerosols of a toxic or flammable nature in a fume hood.
12. Place sharp objects (syringe needles, broken glass, blades, etc.) in a labeled rigid container before disposal. Materials contaminated with bio-hazardous agents should first be autoclaved.
13. Keep wet hands and water away from electrical equipment.
14. Secure your compressed cylinders.
15. Perform a safety check at the end of each experiment - make sure that gas, water, electricity, vacuum lines, air and heaters have been turned off and decontaminate any equipment or work areas which may have been in contact with hazardous materials.
16. Lock laboratory when unoccupied.
17. Store coats, packs, etc., in areas provided, not around the lab bench.
18. Pay strict attention to all instructions before undertaking an experiment. If you do not understand, ask.
19. Clean up apparatus and work areas at the end of the lab period.
20. Set up apparatus so that it is not necessary to reach through the assembly to turn water, gas or electricity off.
21. Assemble apparatus so that control valves and switches will remain accessible if a fire should occur.
22. Be aware of what neighboring laboratory personnel are doing.

DO NOT:

1. Wear open shoes (such as sandals, ballerinas, ballerinas with socks) in the lab.
2. Wear shorts, skirts and anything that shows the feet.
3. Block access to emergency equipment (eyewashes, safety showers and fire extinguishers).
4. Pipette by mouth.
5. Pour water into acid
6. Return unused chemicals to stock bottles.
7. Run, walk in the lab.
8. Carry hazardous chemicals between the lab and storage rooms by hand. Use secondary containers.
9. Place chemicals where they will cause trip hazards, or are liable to cause personal injury. Reagent bottles, empty or full should not be left on the floor.
10. Place chemicals near incompatible substances that may cause them to react.
11. Leave chemicals or experiments unattended.
12. Store food, food containers and drinking glasses in the laboratory.
13. Keep food in refrigerators at the laboratory.
14. Sniff or taste chemicals.
15. Smoke, eat, or drink, food, beverages or tobacco in laboratories.
16. Apply cosmetics or lip-balm in the laboratory.
17. Engage in horseplay or other act or mischief in the lab.
18. Perform unauthorized experiments.
19. Remove chemicals from the lab unless directed otherwise from the instructor/supervisor.
20. Use damaged or broken equipment when handling or experimenting with chemicals.

***EHSRM:* ext.2360**

N.B: In case of violation of any of the above safety rules, you will be asked to leave the lab and you will receive a zero grade on your report.

Environmental Health, Safety, and Risk Management Procedures

Read carefully, it may save your life!

In Case of Fire

1. **Remain calm** – Do not shout "Fire".
2. **Rescue: Rescue** personnel who are in immediate danger. This step is usually performed simultaneously with step 3 Alarm.
3. **Alarm:** Give the **alarm** – Dial 5555 and inform operator of exact location of fire.
4. **Contain:** Close doors and windows to isolate fire and smoke from rest of the building.
5. **Evacuate:** Evacuate the building using the nearest exit (Do not use elevators). Do not reenter the building until the alarm is silenced and you are told that it is safe to reenter
6. **Extinguish:** You may fight the fire if you have been trained to do so, your exit is assured and that the alarm has been given.
7. Once the ERT / Beirut Fire Brigade arrives, they will be in charge until they declare the area safe and leave the scene.

Hazardous Materials Emergencies: *Chemical, biological and radioactive materials are present in laboratories. If a hazardous material is spilled or released the following precautions or actions are recommended:*

If you are unsure about the danger of the material:

1. Do not approach the spill and avoid contact with the material. Avoid breathing gases, fumes or smoke that may be generated. Vapours may be harmful even if there is no odour.
2. If others may be in danger, activate alarm or inform personnel to evacuate the area. Close doors to contain the area of the spill.
3. From a safe location call the EHSRM x 2360 (during working hours) or the protection office x 2400 (24 hours/day), describe the nature of the emergency.
4. Stay in a safe area near the vicinity so that you can assist emergency response personnel.

If you are certain that the spill or leak poses no immediate danger or personal injury report it as in 3 above and:

1. Use absorbent material to keep the contamination from spreading or entering drains. Absorbents such as sand, vermiculite, towel papers etc … may be used.
2. Working from the outside in, absorb the spilled material; and using a shovel or dust pan place the spilled material inside a plastic bag or container.
3. EHSRM personnel will advise on further actions.

If the spill is in a lab, shop or chemical storeroom:

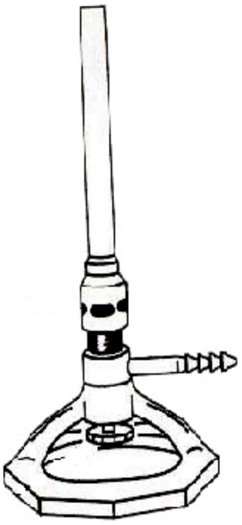
1. Evacuate all personnel from the room.
2. Be sure hood/local exhaust is on.
3. If flammable liquids are spilled, disconnect the electricity to sources of ignition if possible.
4. Call EHSRM @ ext. 2360 to request additional assistance if you cannot manage the clean up yourself.

If spill is in a corridor or other public passageway:

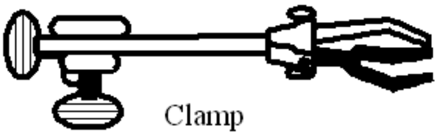
1. Evacuate all people from the area. Close off area to keep others out.
2. Call the EHSRM at ext. 2360
3. Call Physical Plant @ ext. 2015 to request to have the air system in the area shut down (to prevent contamination of other areas) and to request additional assistance.

Common Laboratory equipment

Hardware



Bunsen Burner

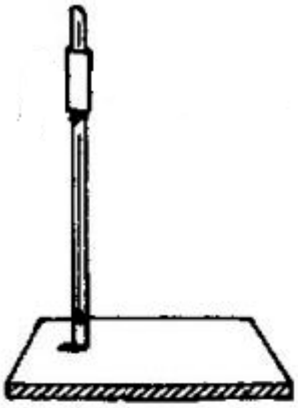


Clamp

Tong

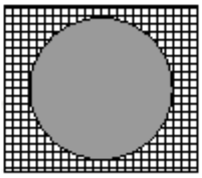
Spatula

Test tube holder



Stand

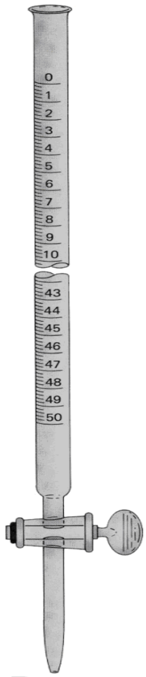
Washing bottle



Wire Gauze

Clay
Traingle

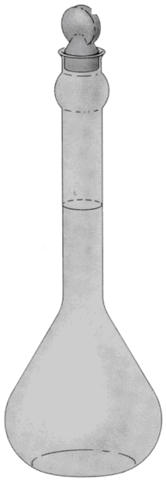
Glassware



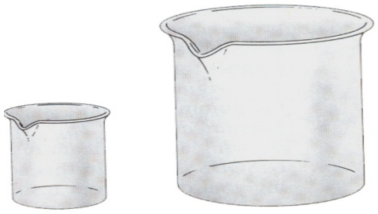
Buret

Graduated pipet

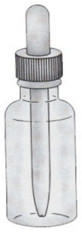
Volumetric pipet



Volumetric flask



Beakers

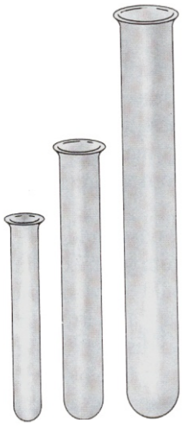


Dropping bottle

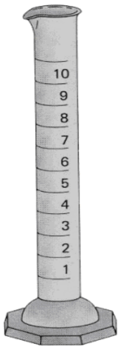
Florence flask

Funnel

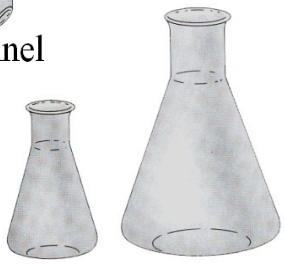
Watch glass



Test Tubes



Graduated cylinder



Erlenmeyer flasks

<u>**Precision of Chemical Measurements**</u>

A. Uncertainty on a Measurement

In every measurement, there is a possibility of experimental error. The margin of error in a given measurement is called the **uncertainty** on that measurement. The uncertainty depends on the measuring tool or instrument.

Examples:

1. Analytical Balances

Instrument	**Uncertainty**
Mettler model PB 302	± 0.01 g ← **least precise**
Mettler model PE 160	± 0.001 g
Mettler model AB 104/204	± 0.0001 g ← **most precise**

2. Volumetric Glassware

Tool	**Uncertainty**	**Correct expression of volume**
10 mL graduated cylinder	± 0.1 mL	8.3 mL (for example)
50 mL buret	± 0.02 mL	24.85 mL (for example)
25 mL volumetric pipet	± 0.06 mL	25.00 mL
500 mL volumetric flask	↓ ± 0.25 mL	↓ ± 500.0 mL

A. Significant Figures

- **Definition:** In a given number, each digit that appears to the right of the first non-zero digit, including that latter digit, is a significant digit (or significant figure: *Sig. Fig.*).

- **Examples:**

0.0032	*2 Sig. Fig.*
1.2100	*5 Sig. Fig.*
5.00	*3 Sig. Fig.*
5	*1 Sig. Fig.*

- **Note:** Zeroes to the left of the first non-zero digit and exponents are **NOT** significant.

Thus:

5.0×10^{2}	*2 Sig. Fig.*
0.01×10^{-4}	*1 Sig. Fig.*

- **Physical Significance:** A given number (measurement) contains significant figures that are all certain, **except one** (the last one) that is uncertain.

C. Significant Figures in Mathematical Operations

1. Addition and Subtraction:

The result must be expressed to the same degree of precision as that of the least precise component in the operation.

Example:

$$\begin{array}{r l} 245.1 & \leftarrow \textbf{least precise} \\ +\quad 6.713 & \\ 10.02 & \\ \hline 261.833 & \qquad \text{Result: 261.8} \end{array}$$

↑ *we round off here*

2. Multiplication and Division:

Keep as many *significant figures* in the result as there are in the component with the *least number* of significant figures.

Example: $$\frac{541 \times 2.067}{39} = 28.673$$ least number of Sig. Fig. is 2

↑ *we round off here, thus* Result= 29

D. Comprehensive Example from the Chemistry Lab:

We want to prepare 500 mL of a standard solution of $KMnO_4$ ~ 0.2 M.

- Let us calculate roughly the amount of $KMnO_4$ needed to have approximately a 0.2 M solution:

$$\mathbf{m}_{KMnO4} \text{ - } \mathbf{Molar\ mass}_{KMnO4} \times \mathbf{Molarity} \times \mathbf{V}_{soln}$$
$$\cong 158\ (g/mol) \times 0.2\ (mol/L) \times 0.5\ (L)$$
$$= 16\ g$$

- Now weigh accurately about 16 g of $KMnO_4$ on a four decimal balance:

Mass of beaker	19.346 g
Mass of beaker + permanganate sample	35.297 g
Mass of permanganate sample	15.951 g

- Transfer this accurate amount of $KMnO_4$ **quantitatively** into a 500 mL volumetric flask. The uncertainty on the volumetric flask is marked ± 0.25 mL. Thus, the volume is reported as 500.0 mL ≡ 0.5000 L (4 Sig. Fig.).

- Now, I can calculate the accurate **Molarity** of my **standard solution:**

$$\mathbf{Molarity} = \frac{\mathbf{m}_{KMnO4}}{\mathbf{Molar\ mass}_{KMnO4} \times \mathbf{V}_{soln}} = \frac{15.951\ (g)}{158.04\ (g/mol) \times 0.5000\ (L)}$$

$$= 0.201860288\ M \longrightarrow \underline{0.2019\ M}\ (4\ \text{Sig. Fig.})$$

Experiment 1

Determining the Hardness of Different Water Samples

A. Purpose

1. To learn the concept and technique of titration
2. To learn the concepts of complexometric titration.
3. To standardize an EDTA solution.
4. To determine the total hardness of different water samples
5. To determine the total hardness of an unknown water sample

B. Theory

Hard water is, in general, water that has a high mineral content. Water's hardness is determined by the concentration of multivalent cations in water, mainly calcium (Ca^{2+}) and magnesium (Mg^{2+}). As the concentration of these ions in water increases, as the water becomes harder. Although both of these cations contribute to the hardness of water, however, since most hardness is caused by carbonate mineral deposits, hardness is usually reported as parts per million (ppm) of calcium carbonate (by weight).

A single-number scale does not adequately describe hardness; however, the United States Geological Survey uses the following classification into hard and soft water.

Classification	hardness in mg/L
Soft	0–60
Moderately hard	61–120
Hard	121–180
Very hard	≥ 181

There are many methods in determining the concentrations of these ions in water. Complexometric titration is one of these methods. In a simple complexometric titration, the equivalence point is detected visually by the formation of a colored complex in the presence of a metal ion indicator. A metal ion indicator is a compound whose color changes when it binds to a metal ion.

Complexometric titrations are particularly useful in determining the concentration of a mixture of different metals ions in solution. The titration is performed with a complexing entity, also known as a chelating agent, ethylene diamine tetraacetic acid (EDTA). In buffered solution at pH = 10, EDTA is fully ionized and has the formula:

$$(^{-}OOCCH_2)_2NCH_2CH_2N(CH_2COO^{-})_2.$$

Both N atoms and four of the O atoms can act as ligands (EDTA is thus a hexadentate complexing agent: hexa = 6, dentate = "toothed"- reference to the fact that it surrounds the metal ion like a mouthful of teeth surrounding a pistachio nut) and EDTA can therefore form an immensely stable 1:1 complex with Mg^{2+} and with Ca^{2+}:

$$Mg^{2+} + EDTA^{4-} \longrightarrow [Mg\,(EDTA)]^{2-} \qquad K_f = 4.9 \times 10^{8}$$

$$Ca^{2+} + EDTA^{4-} \longrightarrow [Ca\,(EDTA)]^{2-} \qquad K_f = 5.0 \times 10^{10}$$

The criteria needed to allow a reaction to be used for titrimetric analysis are the following:

1. It goes to completion,
2. It is stoichiometric
3. It proceeds rapidly
4. It allows for easy end-point detection.

EDTA satisfies the first three of these very well, but an indicator must also be sought. Another complexing agent, Eriochrome T (or Erio T or E), forms metal complexes and changes color when it does so. The form of the indicator and its color changes are pH dependent, since Erio T is in fact a triprotic organic acid. At pH = 10, the red complex Metal-E^- exists at metal concentrations greater than 10^{-8} M, whereas at lower concentrations, the blue uncomplexed acid anion HE^{2-} is the stable from. Thus, as the cation is titrated by EDTA at pH = 10, in the presence of Erio T, the free cation concentration steadily decreases, and at the equivalence point, the solution color changes from *red* to *blue*. Using this method, one can determine the amount of magnesium and calcium in a solution, and thus the hardness.

The hardness of water is important because it affects numerous aspects of our life. Water hardness has an effect on the way water tastes, on cleaning/washing, and it creates problems with plumbing and industries. The problem of water hardness in the use of industrial water boilers/plumbing systems is that the water evaporates leaving behind rocklike deposits consisting mostly of calcite crystals. This is a problem because the calcite crystals build up and clog pipes, block jet engines, etc. and are very expensive and difficult to remove, if removable at all. The problem of water hardness in cleaning/washing is when hard water is used to wash away soap, the soap anions react with the calcium and magnesium cations to produce a greasy scum.

Wherever water hardness is a concern, softening methods, such as precipitation, ion exchange and others, can be applied to reduce hard water's adverse effects.

In this experiment, the hardness of different types of water will be determined via complexometric titration using EDTA as the ligand and Erio-T as the indicator.

C. Chemicals and Setup

$MgSO_4.7H_2O$, EDTA solution, Erio T indicator, NH_3/NH_4Cl buffer (pH 10), sea water, an unknown solution, a 250 mL volumetric flask, 50 mL buret, 25 mL volumetric pipet, three clean 125 mL (or 250 mL) Erlenmeyer flasks, 50 mL beaker, polyethylene dropping bottle and buret stand.

D. Procedure

- **Preparation of Standard Solution of $MgSO_4$ (0.020*M*)**
  1. Weigh by difference using a glazed weighing paper around 0.5020*g* of $MgSO_4.7H_2O$ and record the data in the report sheet
  2. Transfer the weighed $MgSO_4.7H_2O$ to a 100.0 mL volumetric flask
  3. Dissolve and dilute to the mark with distilled water
  4. Calculate the molarity of $MgSO_4.7H_2O$ solution that you have just prepared.

- **Preparation of Reference Solution A**
  1. Put 50 mL of distilled water in a 150 mL beaker.
  2. Add 10 mL of pH = 10 buffer and two drops of Erio-T indicator
  3. Add few drops of 0.01 M EDTA in order to see the blue color that should be attained when a titration is performed.

- **Standardization of a 0.01 M EDTA Solution**
  1. Pipet 10.00 mL of $MgSO_4.7H_2O$ solution into a 250 mL Erlenmeyer flask
  2. Add 10 mL of distilled water
  3. Add 10 mL of pH = 10 buffer and two drops of Erio-T indicator
  4. Titrate the solution with EDTA rapidly until the color changes from pink-red (wine-red) to blue.
  5. Repeat the titration with three new samples to find an accurate value of the EDTA concentration. You will be able to detect the change of color by referring to reference solution A (identical in hue but not necessarily in intensity).
  6. Record data in Table 1.

- **Total Hardness Determination of Distilled Water (Blank)**
  1. Pipet 25 mL of distilled water into an Erlenmeyer flask

2. Add 10 mL of a pH=10 buffer solution and 3 drops of the Erio-T indicator
3. Titrate the solution with EDTA rapidly to a color change from wine-red to blue.
4. Repeat if needed one more time.
5. Record data in Table 2.

- **Total Hardness Determination of an Unknown Water Sample**
  1. Pipet 10 mL of your unknown into an Erlenmeyer flask
  2. Add 10 mL of a pH=10 buffer solution
  3. Add 10 mL of distilled water and 3 drops of the Erio-T indicator
  4. Titrate the solution with EDTA rapidly to a color change from wine-red to blue.
  5. Repeat the titration with three new samples to find an accurate value of the EDTA concentration.
  6. Record data in Table 3.

- **Total Hardness Determination of Sea Water**
  1. Pipet 5 mL of sea water into an Erlenmeyer flask.
  2. Add 10 *mL* of a pH=10 buffer solution.
  3. Add 5 drops of Erio-T indicator
  4. Add 20 mL of distilled water.
  5. Titrate the solution with EDTA rapidly to a color change from wine-red to blue.
  6. Record data in Table 4.

- **Total Hardness Determination of Tap Water**
  1. With a 100 mL graduated cylinder, deliver 100 mL of tap water to be tested into a 250 mL Erlenmeyer flask.
  2. Add 10 mL of the pH=10 buffer solution and 2-3 drops of Erio-T indicator.
  3. Titrate the solution with EDTA rapidly to a color change from wine-red to blue.
  4. Record data in Table 4.

E. CHEM. 203 Lab Report

NAME : ______________________________ **EXPERIMENT No.** : ________

TITLE : ______________________________ **DATE :** ____________________

SECTION #: __________________________

- **Preparation of a Standard $MgSO_4.7H_2O$ Solution**

$m_{MgSO4.7H2O}$ = _________________

V of solution = _________________

$M_{MgSO4.7H2O}$ = _________________

Table 1: Standardization of the EDTA solution

	Trial 1	**Trial 2**	**Trial 3**
Upper EDTA reading (mL)			
Lower EDTA reading (mL)			
Volume (mL)			

Average volume, $\bar{v}_{EDTA}$ = _________________

M_{EDTA} = _____________________________

- **Total Hardness Determination of Distilled Water**

Volume of aliquot =

Table 2: Titration of distilled water.

	Trial 1	**Trial 2**
Upper EDTA reading (mL)		
Lower EDTA reading (mL)		
Volume (mL)		

Average volume, $\bar{v}_{EDTA}$ = _____________________________

Total hardness of sample (in ppm) = ____________________

Hardness classification = _____________________________

- **Total Hardness Determination of an Unknown Water Sample**

Unknown # =

Volume of aliquot =

Table 3: Titration of the unknown solution

	Trial 1	**Trial 2**	**Trial 3**
Upper EDTA reading (mL)			
Lower EDTA reading (mL)			
Volume (mL)			

Average volume, $\bar{v}_{EDTA}$ =__________

Corrected Average volume, $\bar{v}_{EDTA}$ =__________

$M_{unknown}$ = _____________________

- **Total Hardness Determination of Sea Water and Tap Water**

Table 4: Titration of sea water and tap water.

	Sea water	**Tap water**
Volume of aliquot (mL)		
Upper EDTA reading (mL)		
Lower EDTA reading (mL)		
Volume (mL)		
Corrected volume (mL)		
Total hardness of sample (in ppm)		
Hardness classification		

Sample calculation for determining the hardness of sea water or tap water

Questions

1. Convert the result obtained for the unknown (in molar units) to mg Mg/100 mL solution.

2. Write out the formulas of the following metal-ligand complexes *(coordination compounds)*: diammine silver (I) ion, tetraammine copper (II) ion, hexaaqua cobalt (II) ion, tetrachloro platinate (II) ion, tris(ethylenediamine) cobalt (III) ion.

3. A sodium carbonate (Na_2CO_3) primary standard solution is prepared by dissolving 10.587 g of the substance in enough distilled water, then transferring it quantitatively to a 250 mL volumetric flask and finally making up to the mark with distilled water. The volumetric flask is labeled T.C. ± 0.12 mL. Calculate the molarity of the standard Na_2CO_3 solution.

4. Explain why we run a blank titration.

5. The equivalence point of the titration of a weak base with a strong acid occurs at pH 5.32. Which of the following indicators is the best to detect the end-point of the titration?

Indicator	Color change	**pH range**
Bromophenol blue	yellow – blue	3.1 – 4.6
Methyl orange	red – yellow	3.3 – 4.5
Methyl red	pink – yellow	4.2 – 6.3
Bromocresol green	Yellow – blue	3.8 – 5.4

Sketch the titration curve for this titration.

Experiment 2

Factors Affecting Reaction Rates

A. Purpose

1. To introduce the basic principles of Chemical Kinetics
2. To study the various factors affecting the rates of chemical reactions.
3. To determine the rate order of two different reactions and the rate constant of one of these reactions.

B. Theory

Chemical Kinetics is the area of chemistry concerned with the speeds, or rates, at which a chemical reaction occurs. The **reaction rate** is the change of the concentration of reactant (or product) with time.

In general, the rate of a chemical reaction depends on several factors: the nature of the reaction, the concentrations of reactants, the temperature of the chemical system, the surface area in heterogeneous reaction involving reacting solids and liquids, and the presence of a catalyst. For the given reaction,

$$a\,A + b\,B \longrightarrow c\,C$$

The rate can be expressed as the rate of change of the concentration of any of the participating species (reactant or product) in the reaction, and defined as follows:

$$\text{rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t}$$

Note that the rate of product formation does not require the minus sign because $\Delta[C]$ is a positive quantity. In addition, "a" moles of A and "b" moles of B must be destroyed for the formation of "c" moles of C.

The measured rate of a reaction is often found to be proportional to the concentrations of the reactants raised to some power. Thus, a general form of this dependence of the rate on concentration can be written as:

$$\text{rate} = k\,[A]^m\,[B]^n$$

where k is the rate constant, and [A] and [B] are molar concentrations of reactants A and B. m and n are numbers that can be integers or fractions, and are called the orders of the reaction with respect to A and B respectively. We say that the reaction is m^{th} order in A, n^{th} order in B, and $(m+n)^{th}$ order overall. The above equation is known as the **rate law**, an expression relating the rate of a reaction to the rate constant and the concentrations of the reactants. Thus the overall order is defined as the sum of the exponents that appear in the rate law. The rate law is a relation arrived at by experiment, and can not be inferred by simply looking at the reaction equation.

In this experiment, two out of the five factors affecting rate will be investigated. These are the nature of the reactants and the concentration of the reactants. The effect of temperature on a reaction will be studied in experiment 3.

For the effect of concentration of reactants on the rate, the reaction that will be studied is the iodination of acetone:

$$CH_3COCH_{3\,(aq)} + I_{2\,(aq)} \xrightarrow{H^+} CH_3COCH_2I_{\,(aq)} + 2H^+_{(aq)} + I^-_{\,(aq)}$$

The rate law is expressed as

$$\text{rate} = k\,[\text{acetone}]^m\,[I_2]^n\,[H^+]^p$$
$$\text{rate} = k\,[A]^m\,[I_2]^n\,[H^+]^p$$

The reaction of acetone with iodine, in the vicinity of room temperature, proceeds at a moderate, relatively easily measured rate. This reaction can be very easily investigated experimentally because of two reasons. First, iodine has a color so that one can readily follow changes in iodine concentration visually. Second, this reaction turns out to be zero order in I_2 concentration, i.e. the rate of the reaction does not depend on $[I_2]$ at all. $[I_2]^0 = 1$, no matter what the value of I_2 is, as long as it is not itself zero.

Since the reaction rate does not depend on $[I_2]$, one can study the rate by mixing a known $[I_2]_0$, used as limiting reagent, with a large excess of acetone and H^+ ion. Then, we measure the time required for the known initial $[I_2]_0$ to be used up completely. Note that acetone and H^+, being present at much higher concentration than that of I_2, their concentrations will not change during the course of the reaction. Therefore,

$$\text{rate} = -\frac{\Delta [I_2]}{\Delta t} = -\frac{\text{change in } I_2 \text{ concentration}}{\text{time interval required for the change}}$$

The minus sign is to make the rate positive, keeping in mind that $\Delta[I_2]$ is negative.

$$\text{rate} = -\frac{\Delta [I_2]}{\Delta t} = \frac{[I_2]_o}{t}$$

Although the rate of the reaction is constant during its course under the conditions set, one can vary it by changing the initial concentrations of acetone and H^+ ion. For example, keeping $[H^+]$ and $[I_2]$ at the same values they had previously, and doubling [acetone] will make the new rate of the reaction equals to rate 2:

rate 2 = $k\,[2A]^m\,[I_2]^n\,[H^+]^p$, compared to

rate 1 = $k\,[A]^m\,[I_2]^n\,[H^+]^p$.

rate 2 / rate1 = $[2A]^m / [A]^m = 2^m$, since $[H^+]$ and $[I_2]$ are kept constant.

Therefore, by measuring rate 1 and rate 2, getting their ratio and then solving for m, one can find the order of the reaction with respect to acetone. Similarly, one can find the order of the reaction with respect to H^+ and also confirm the fact that the reaction is zero order with respect to I_2. Having determined m, n and p, the rate constant k can be evaluated.

C. Chemicals and Setup

3 M H_2SO_4, 6 M HCl, 5 M HCl, 4M HCl, 3 M HCl, 2 M HCl, 1 M HCl, 6 M CH_3COOH, and 6 M H_3PO_4, zinc strip, magnesium strip, copper strip, test tubes, beakers, 125 mL Erlenmeyer flask, stop watch and digital thermometer.

D. Procedure (work in pairs throughout the experiment)

- **Nature of the reactants**

  i. Reactivity of Different Acids with Magnesium Metal

  1. Half fill a set of four labeled small test tubes with 3 M H_2SO_4, 6 M HCl, 6 M CH_3COOH, and 6 M H_3PO_4.
  2. Insert a 1 cm strip of magnesium ribbon into each test tube at once.
  3. Compare the reaction rates and record your observations in the report sheet.

  ii. Reactivity of Different Metals with the Same Acid

  1. Half fill a set of three labeled small test tubes with 6 M HCl.
  2. Insert 1 cm strips of zinc, magnesium and copper separately into the test tubes.
  3. Compare the reaction rates of each metal and record your observations in the report sheet.

  Note: If any metal remains unreacted, do not discard in the sink. Decant the liquid and discard the metal in the specified waste container.

- **Concentration of Reactants:** ***Iodination of Acetone***

  1. Take 50 mL of each of the following solutions and place each solution in a clean 100 mL beaker. Cover each beaker with a watch glass. Keep the solutions on your bench for use throughout the experiment:

     4.00 M acetone
     0.00500 M iodine
     1.00 M HCl

2. Pipet 10.00 mL of 4.00 M acetone into a 125 mL Erlenmeyer flask.
3. Using a buret, transfer 10.0 mL of 1.00 M HCl to the flask used in step 2.
4. Using a buret, transfer 20.0 mL of distilled water to the flask used in step 2.
5. Pipet 10.0 mL of 0.00500 M iodine solution and add to the flask. Mark the time t = 0 with a stop-watch at the time of addition of the iodine.
6. Mix the obtained solution (mixture I) by swirling the flask vigorously. The yellow color of iodine will fade gradually.
7. Fill two thirds of a 15 cm long test tube with the reaction mixture (while it is still yellow), and another similar test tube with distilled water.
8. By looking vertically through the two tubes (for comparison), determine the time at which the yellow color just disappears. Measure and record the temperature of the reaction mixture.
9. Repeat the above experiment by using the colorless reaction mixture as a reference instead of distilled water. The times of the two runs must agree within 20 seconds. Record data in Table 1.
10. Calculate the rate of the reaction by dividing the initial concentration of iodine by the measured time (Why?). Note that acetone and H^+ are present in great excess. Find initial concentrations of acetone, iodine and H^+. Record the values in Table 2.
11. Repeat steps 2 to 10 (mixture II) using 20.0 mL of acetone and 10.0 mL of distilled water. This should keep the total volume constant (50.0 mL). Determine the order of the reaction in acetone (m).
12. Repeat steps 2 to 10 (mixture III) using 20.0 mL of HCl and 10.0 mL of distilled water. This should keep the total volume constant (50.0 mL). Determine the order of the reaction in H^+ (n).
13. Change the reaction mixture (mixture IV) composition in such a way as to make the volume of iodine 5 mL and the total volume of solution 50 mL in order to allow you to show that the order of the reaction is zero in I_2. Repeat steps 2 to 10 using the new mixture composition.
14. From the measured rates and the rate law of the reaction, calculate the rate constant k.

E.CHEM 203 Lab Report

NAME: ________________________________ **EXPERIMENT # :** ________________

TITLE: ________________________________ **DATE:** ___________________________

PARTNER: ______________________________ **SECTION #:** ______________________

- **Nature of the reactants**

-List the acids in order of decreasing reaction rate with magnesium.

-List the metals in order of decreasing reaction rate with 6M HCl.

- **Concentration of Reactants:** ***Iodination of Acetone***

Table 1: Reaction rate data @ T=

Mixture	Volume of of acetone	Volume of HCl	Volume of H_2O	Volume of of I_2	Time for 1st Run	Time for 2nd Run	Av.Time
I							
II							
III							
IV							

Table 2: Determination of reaction orders

Mixture	Initial Conc. of Acetone	Initial Conc. of H^+	Initial Conc. of I_2	rate=$[I_2]_0$/av.time
I				
II				
III				
IV				

Rate Law of the Iodination of Acetone,

$$\text{rate} = k\,[\text{acetone}]^m\,[I_2]^n\,[H^+]^p$$

rate I =

rate II =

rate III =

rate IV =

rate II / rate I = m=

rate III / rate---= p=

rate IV / rate----= n=

Table 3: Determination of the rate constant k

Mixture	**I**	**II**	**III**	**IV**	**Average**
k					

Questions

1. In the study of the rate of the chemical reaction **a A + b B** $\longrightarrow$ **c C** at 27°C, the following data were obtained:

Reaction mixture	**1**	**2**	**3**	**4**
$[A]_0$	0.200	0.400	0.200	0.100
$[B]_0$	0.200	0.200	0.400	0.300
Initial rate (Ms^{-1})	0.750	3.00	1.50	0.280

   a. What is the order of the reaction in A?
   b. What is the order of the reaction in B?
   c. Calculate the rate constant for this reaction at 27°C.

2. What volumes of the following stock solutions are necessary to prepare 50.0 mL of the following reaction mixture: 0.800 M acetone; 0.200 M HCl; 0.00100 M iodine?

   Stock solutions:
   4.00 M acetone: $V_{acetone}$ = ____________________.

   1.00 M HCl: V_{HCl} = ____________________.

   0.00500 M I_2: V_{I2} = ____________________.

   Distilled water: V_{water} = ____________________.

3. Derive the integrated rate law for a chemical reaction of the form
   A $\longrightarrow$ **P,** given that the reaction is first order in the reactant **A.**

Experiment 3

Chemical Kinetics: Hydrolysis of Ethyl Acetate

A. Purpose

1. To study experimentally the kinetics of a chemical reaction: hydrolysis of ethyl acetate.
2. To determine the rate constant and the activation energy, E_a, for the base-catalyzed hydrolysis of ethyl acetate

B. Theory

As mentioned in the previous experiment, chemical Kinetics is the area of chemistry concerned with the speeds, or rates, at which a chemical reaction occurs. The **reaction rate** is the change of the concentration of reactant (or product) with time.

Temperature, as mentioned previously, is one of the factors affecting reaction rates. The rate of a reaction most of the time increases with temperature. An often cited rule, but only approximately correct is: "a 10°C rise in temperature will double the rate". The quantitative relation between reaction rate and temperature is given by the so-called **Arrhenius equation:**

$$\ln k = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \text{constant}$$

where k is rate constant, E_a is called the **activation energy**, R is the gas constant , and T is the absolute temperature.

This relation is based on the fact that, in order to react, the reactant species must have a certain minimum amount of energy present at the time the reactants collide in the reaction step. This energy is called the **activation energy E_a.**

By measuring k at different temperatures, then plotting ln k versus 1/T, the activation energy can be determined from the slope of the line.

In this experiment, the basic hydrolysis of ethyl acetate will be studied. Hydrolysis is the breaking down of an ester to its corresponding organic acid and alcohol (in basic media, to its corresponding sodium salt of the acid and to the alcohol). The equation of the basic hydrolysis of ethyl acetate is given by:

$$CH_3COOC_2H_5 + NaOH \longrightarrow CH_3COO^-Na^+ + C_2H_5OH$$

This reaction is often called saponification. An application of saponification is the manufacture of soaps. The position of equilibrium lies far to the right. This hydrolysis is a second order reaction (bimolecular) in which the rate is directly proportional to the concentration of both reactants (whose initial concentrations are the same). The equation for this second order reaction is:

$$\frac{1}{A} - \frac{1}{A_o} = k.\,t$$

Where A is the concentration of the reactant at time t and k is the second order rate constant ($M^{-1}.time^{-1}$). Plotting 1/A versus time will produce a linear function with the slope equal to the rate constant.

When the experiment is performed at two different temperatures, the activation energy of the reaction can be obtained by the following formula:

$$\ln\frac{k_1}{k_2} = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

In the procedure, equal amounts of ethyl acetate and NaOH will be mixed at two different temperatures. At different time intervals, certain volume of the reaction will be pipetted out of the solution into an Erlenmeyer flask filled with HCl, which will quench the reaction by reacting with the remaining NaOH and thus, no more NaOH will be available for the hydrolysis to continue. The excess HCl will be titrated with a standardized NaOH solution using phenolphthalein as an indicator. By plotting and calculations, the two rate constants as well as the activation energy of the reaction can be determined.

C. Chemicals and Setup

0.04 M ethyl acetate solution, 0.04 M standardized NaOH, 0.04 M standardized HCl, phenolphthalein, distilled water, 50 mL volumetric flasks, 10 mL graduated pipet, 25 mL graduated pipet, pipet filler, beakers, buret, stop-watch, heaters, digital thermometers and Erlenmeyer flasks (125 mL and 250 mL).

D. Procedure (Work in pairs throughout this experiment)

1. Fill your 150 mL beakers with the following solutions; cover each with a watch glass and keep the solutions on your bench for use throughout the experiment:
   0.04 M ethyl acetate solution (~110 mL)
   0.04 M standardized NaOH (~ 160 mL)
   0.04 M standardized HCl (~ 100 mL)
2. Label 8 clean and dry Erlenmeyer flasks (125 or 250 mL) with 5, 10, 15, 20, 25, 30, 35, and 40 minutes.
3. Pipet into each flask 5 mL of 0.04 M HCl.
4. Fill a buret (after cleaning it) with 0.04 M NaOH to the mark.
5. Fill a ¾ of a container (that you will be provided with) with water and regulate the temperature of the water to 20ºC using ice or hot water. Record the exact temperature in Table 1.
6. Fill a 50.0 mL volumetric flask with 0.04 M ethyl acetate to the mark.
7. Using the buret, deliver 50.00 mL of 0.04 M sodium hydroxide into an Erlenmeyer flask (different than the ones labeled).
8. Place the flasks of steps 6 and 7 (after closing them) in the water bath for 10 minutes keeping the bath temperature constant.
9. In the mean time, re-fill the buret with 0.04 M NaOH.
10. After 10 minutes, pour the solution of ethyl acetate to the solution of sodium hydroxide while keeping the Erlenmeyer flask containing NaOH in the water bath. Start timing.
11. After 5 minutes, pipet 10 mL of the reaction mixture (while keeping the flask in the bath) to the corresponding Erlenmeyer flask containing the 5 mL HCl (do not stop timing till all the samples are pipetted).
12. Add to the flask labeled 5 minutes 2 drops of phenolphthalein indicator and titrate carefully with NaOH from colorless to light pink (only one trial is possible). Record data in Table 1. (It is possible to perform the titration after all the samples are pipetted since HCl stops the hydrolysis reaction).
13. Repeat steps 9 and 10 every 5 minutes seven more times (in the 10th, 15th, 20th, 25th, 30th, 35th, and 40th min. from the moment of mixing).
14. Repeat the same experiment at 30°C and record data in Table 2.
15. Discard the solutions in the sink.

Note: If one of the results seems incorrect, do not include it in the calculation.

E.CHEM 203 Lab Report

NAME: ______________________________ **EXPERIMENT # :** _______________

TITLE: ______________________________ **DATE:** _________________________

PARTNER: ______________________________ **SECTION #:** ______________________

Table 1: Hydrolysis of ethyl acetate at 20°C

Molarity of NaOH =

Molarity of HCl =

Time (minutes)	NaOH upper reading (mL)	NaOH lower reading (mL)	Volume of NaOH used (mL)	Concentration of unreacted Ethyl acetate (A)	1/Concentration (1/A)
5					
10					
15					
20					
25					
30					
35					
40					

Plot 1/A versus time. Attach graph to the report.

Show sample calculation for the concentration calculation.

Table 2: Hydrolysis of ethyl acetate at 30°C

Molarity of NaOH=

Molarity of HCl=

Time (minutes)	NaOH upper reading (mL)	NaOH lower reading (mL)	Volume of NaOH used (mL)	Concentration (A)	1/Concentration (1/A)
5					
10					
15					
20					
25					
30					
35					
40					

Plot 1/A versus time. Attach graph to the report.

Table 3: Determination of the rate constant k

	At 20°C	**At 30°C**
k		

E_a = ______________________.

Show calculation for finding the activation energy.

Questions

1. The rate constant for the second order reaction:

$$2\ NOBr\ (g) \longrightarrow 2\ NO\ (g) + Br_2\ (g)$$

is 0.80 $M^{-1}s^{-1}$ at 10°C. Starting with a concentration of 0.086 M NOBr, calculate its concentration after 22 s.

2. Given the same concentrations, the reaction:

$$CO\ (g) + Cl_2\ (g) \longrightarrow COCl_2\ (g)$$

at 250°C is 1.50×10^3 times as fast as the same reaction at 150°C. Calculate the activation energy of this reaction. Assume the frequency factor remains constant.

Spectrophotometry-Beer's Law in Chemical Analysis

A. Background

The concentration of a colored constituent can be determined by measurement of the relative intensity of a light beam before and after passage through a solution. Let I_o be the intensity of the incident light, and I_t the intensity of the transmitted light ($I_o > I_t$), and b is the length of the path of light through the solution.

The laws describing this absorption can be readily formulated. The first law relates the intensity of the light to the path length when working with a fixed concentration of the colored constituent. It is evident that if radiation with intensity I passes through a thin layer of the solution and is partly absorbed, the intensity of solution will be less and will in turn be decreased by the next thin layer of solution. The cumulative effect can be expressed as

$$-\frac{dI}{db} \; \alpha \; I \quad \text{or} \quad -\frac{dI}{db} = k_1 I$$

The constant k_1 depends on the wavelength of the radiation, and also on both the nature and concentration of the colored substance. Rearrangement, followed by integration, gives

$$\int_{I_o}^{I_t} \frac{dI}{I} = -\int_{o}^{b} k_1 db \quad \Rightarrow \quad \ln\left(\frac{I_t}{I_o}\right) = -k_1 b \qquad (1)$$

This is often called Lambert's law, and there are no known deviations from this law with homogeneous materials. The quantity I_t/I_0 is known as the transmittance (T).

The second law relates the intensity of the light to the concentration of the colored constituent when working with a fixed path length. The effect is expressed by the equation

$$-\frac{dI}{dc} \; \alpha \; I \qquad \text{or} \qquad -\frac{dI}{dc} = K_2 I$$

Here the constant k_2 depends on the wavelength of the radiation, the path length, and the nature of the colored substance. Rearrangement, followed by integration, gives:

$$\int_{I_o}^{I_t} \frac{dI}{I} = -\int_{o}^{c} k_2 dc \qquad or \qquad \ln\left(\frac{I_t}{I_o}\right) = -k_2 c \qquad (2)$$

This is known as Beer's law. If a solution is sufficiently dilute, the law is obeyed exactly for monochromatic light; however, some systems do show deviations as the concentration is increased. These deviations come about as the colored ions or molecules come closer and closer together and modify each other's light-absorbing characteristics. There are also apparent deviations when the colored constituent is involved in a chemical equilibrium.

If both relations (1) and (2) are obeyed, then:

$$In\left(\frac{I_t}{I_o}\right) = -k' b c_x \qquad or \qquad \log\left(\frac{I_t}{I_o}\right) = -kbc_x \qquad (3)$$

where k is a constant depending on the wavelength of the radiation and the nature of the absorbing species. It is convenient to define the absorbance (A) of the solution such that:

$$-\log\left(\frac{I_t}{I_o}\right) = kbc_x \qquad (4)$$

The absorbance is an experimentally measured quantity and it is directly proportional to concentration. The concentration can be expressed in any convenient unit, (that is, grams per liter, molarity, and so forth), but the value of k will depend upon the units chosen for c. If the concentration is expressed in moles per liter and the path length in centimeters, then the constant is given the special symbol ε (epsilon) and is known as the molar absorptivity (or extinction coefficient) of the absorbing substance.

$$\boxed{A = \varepsilon\, b\, c} \qquad \textbf{\textit{Beer-Lambert's law}}$$

B. Absorbance Measurements

The absorbance of a solution can be determined by eye, relative to some visual scale, but absorbance measurements are more accurately made by using a **spectrophotometer.**

The usual instrument employs a tungsten lamp and a grating or prism monochomator to give light of the wavelength desired for the measurement. The measurement involves two steps:

1. Filling the cell with a reference blank solution and adjusting the instrument so it reads 100 percent transmittance (zero absorbance).
2. Filling the cell with the unknown solution containing the colored substance and again reading the percent transmittance (or, the absorbance).

The percent transmittance corresponds to:

$$\left(\frac{I_t}{I_o}\right) x\ 100$$

so that absorbance is:

$$A = -\log\left(\frac{I_t}{I_o}\right) x\ 100 = -\log(T) = -\log\left(\frac{Percent\ T}{100}\right) = Kbc_x$$

C. Calibration Line

When we determine the concentration of an unknown solution of a certain substance, we measure the absorbance in a spectrophotometer. If we know ($\varepsilon\ b$), we can readily determine c, from the Beer-Lambert law. To determine $\varepsilon\ b$, we normally perform more than one absorbance measurement on a set of solutions of accurately known concentrations (standards). A plot of absorbance (A) versus concentration (c), should yield a straight line of slope $\varepsilon\ b$, called a **calibration line**. We thus take the best fit (see Fig. 1) and compute the slope. In Figure 1, the calculated slope is 1,364 M^{-1}, and can be used in the determination of any unknown concentration from the absorbance, measured in the same cuvettes (same path length).

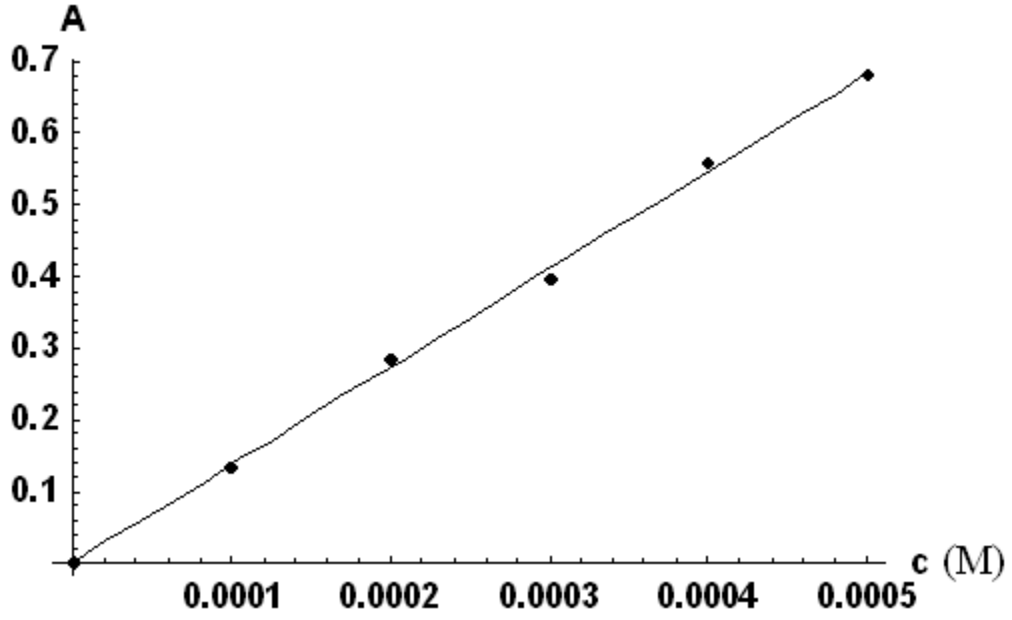


Figure 1. An example of a plot of absorbance versus concentration

Experiment 4

Chemical Equilibrium

A. Purpose

1. To review the concepts and principles of chemical equilibrium.
2. To learn the principles of spectrophotometry and the use of a spectrophotometer.
3. To learn the principles of chemical analysis by spectrophotometric means.
4. Determination of λ_{max} of $FeSCN^{2+}$
5. To determine, spectrophotometrically, the equilibrium constant for the reaction between iron (III) ion and thiocyanate ion (SCN^-) at a given temperature.

B. Theory

When chemical substances react, the reaction typically does not go to completion. Rather, the system goes to some intermediate state in which both the reactants and the products have concentrations which do not change with time: **Chemical Equilibrium** is reached.

Once an equilibrium state has been reached by a chemical system it is possible to stress the system and establish a new state of equilibrium. Le Chatelier's principle summarizes the effect of stressing a chemical system at equilibrium as follows:

When a stress is applied to a system at equilibrium the system will shift in such a direction to relieve the stress and establish a new state of equilibrium.

Some of the factors that affect equilibrium are:

1. Change in temperature
2. Change in concentration

At equilibrium, a reaction mixture obeys the Law of Chemical Equilibrium which imposes a condition on the concentrations of reactants and products. This condition is expressed in the **Equilibrium Constant K_c** for the reaction at a given temperature.

In this experiment, we study the equilibrium reaction:

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

The equilibrium constant is defined as:

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

K_c is constant at constant temperature; this means that mixtures containing Fe^{3+} and SCN^- will react until this equilibrium is satisfied, so that the same value of K_c will be obtained no matter what initial amounts of Fe^{3+} and SCN^- are used.

This reaction is particularly suitable for study because K_c has a convenient magnitude and the color of the $FeSCN^{2+}$ ion allows for easy spectrophotometric analysis of the equilibrium mixture. $FeSCN^{2+}$ is a deep, blood-red complex. K_c will be determined for several mixtures made up in different ways, and it can thus be shown that K_c has indeed the same value in each mixture.

The **Beer-Lambert's Law** will be applied, in this experiment, to determine the $FeSCN^{2+}$ concentration at equilibrium. **$A = \varepsilon bc$**, where **A** is the absorbance of the substance, **ε** is the molar absorptivity coefficient (it is constant at a given wavelength for a particular absorbing substance), **b** is the width of the light path that passes through the absorbing substance in centimeters, and **c** is the molar concentration of the absorbing species.

In the first part of the experiment, a set of standard solutions of the $FeSCN^{2+}$ complex is prepared using a concentration of Fe^{3+} that far exceeds the SCN^- concentration. This huge excess of Fe^{3+} pushes the equilibrium far to the right, nearly consuming all the original SCN^- concentration. The reaction is thus assumed to go to completion. The absorbance of each solution is measured, then plotted versus the molar concentration of $FeSCN^{2+}$; this establishes a calibration curve from which the concentrations of $FeSCN^{2+}$ are determined for the chemical systems in the second part.

In the second part of the experiment, you will prepare a set of various solutions using nearly the same concentration of Fe^{3+} and SCN^- ions, and thus have a number of equilibrium systems. By knowing the initial concentrations of Fe^{3+} and SCN^-, and by determining the equilibrium concentration of $FeSCN^{2+}$ spectrophotometrically, the equilibrium concentrations of Fe^{3+} and SCN^- can be calculated. Using these equilibrium concentrations, the K_c for the system is calculated.

Step-by-step Calculation:

	$Fe^{3+}(aq)$ +	$SCN^-(aq)$ $\rightleftharpoons$	$FeSCN^{2+}(aq)$	
Initially	$n_{0\,Fe^{3+}}$	$n_{0\,SCN^-}$	0	
Change	$-x$	$-x$	x	But $x = n_{FeSCN^{2+}}$
At equil.	$(n_{0\,Fe^{3+}} - n_{FeSCN^{2+}})$	$(n_{0\,SCN^-} - n_{FeSCN^{2+}})$	$n_{FeSCN^{2+}}$	

Where: $n_{0\,Fe^{3+}} = M_{0\,Fe^{3+}}\ V_{0\,Fe^{3+}}$
$n_{0\,SCN^-} = M_{0\,SCN^-}\ V_{0\,SCN^-}$
$n_{FeSCN^{2+}} = x = [FeSCN^{2+}]\,V_{tot} = (A/\varepsilon b)\,V_{tot}$; A is the measured absorbance for that particular solution.

<u>Note</u>: In preparing the mixtures for this experiment, the H^+ ion concentration will be maintained at 0.5 M; H^+ does not participate directly in the reaction, but its presence is necessary to avoid the formation of brown color species such as $Fe(OH)^{2+}$, which interferes with the analysis of $FeSCN^{2+}$.

C. Solutions and Setup

2.00×10^{-3} M $Fe(NO_3)_3$ in 1.0 M HNO_3 (**solution A**), 2.00×10^{-3} M KSCN **(solution B),** 0.20M $Fe(NO_3)_3$ (**solution C**) in 1.0 M HNO_3, 0.20M KSCN, 6M NaOH, 0.1 M $AgNO_3$**,** 0.20 M $Fe(NO_3)_3$ (**solution C**) in distilled water, distilled water, test tubes, cuvettes, spectrophotometer, beakers, labels and parafilm paper.

D. Procedure (Work in pairs throughout this experiment)

1. Determination of the Equilibrium Constant for a Chemical Reaction

Place 30 mL of **solution A** (2.00×10^{-3} M $Fe(NO_3)_3$ in 1.0 M HNO_3) in a clean 100 mL beaker. Then in another clean 100 mL beaker, place 20 mL of 2.00×10^{-3} M KSCN (**solution B**). Finally, in a third beaker, put 40 mL of 0.200 M $Fe(NO_3)_3$ in 1.0 M HNO_3 (**solution C**).

I. Determination of λ_{max} of $FeSCN^{2+}$

1. Pipet 5.00 mL of solution C into two test tubes labeled 0 and 5.
2. Into test tube 5, pipet 3.00 mL of solution B.

3. Add distilled water to each test tube so that the final volume is 20.00 mL. Deliver the necessary volume of water by means of a buret.
4. Cover the tube with parafilm paper and homogenize.
5. Use test tube 0 as the blank.
6. Measure (using a spectrophotometer) the absorbance of solution 5 at 25 nm intervals between 350 and 600 nm. Record your data in Table 1. **<u>Note:</u>** Whenever the wavelength is changed, zero the absorbance of the blank before reading the absorbance of the solution.
7. Select, from the spectrum, the best wavelength for Beer's law application (λ_{max}).

II. Absorbance Measurements of FeSCN $^{2+}$ Standard Solutions.

1. Obtain from the storeroom 10 clean test tubes. Label them 1 to 10.
2. Pipet 5.00 mL of solution C into each of the tubes 1 to 4.
3. Into tubes 1 to 4, pipet 0.50, 1.00, 1.50, and 2.00 mL of solution B respectively. Then add distilled water to each of the tubes so that the final volume is 20.00 mL in each of them. Deliver the necessary volume of water by means of a buret.
4. Cover the tubes with parafilm paper and mix the solutions well to make them homogeneous.
5. Measure the absorbance of each of the prepared solutions at λ_{max}. Record your data in Table 2. Use the blank prepared in part I (test tube 0) as the blank.
6. Plot absorbance versus concentration (do not forget to include the result of solution 5 in the plot) and find the slope.

III. Absorbance Measurements of Different Systems at Equilibrium

1. Pipet 5.00 mL of solution A into each of test tubes 6 to 11.
2. To the test tubes 6 to 11, add 0.00, 1.00, 2.00, 3.00, 4.00 and 5.00 mL of solution B respectively. Then add distilled water to each of the tubes so that the final volume is 10.00 mL in each of them. Deliver the necessary volume of water by means of a buret.
3. Cover the tubes with parafilm paper and mix the solutions well to make them homogeneous.
4. Determine the absorbance of each of the five prepared solutions, at the previously selected wavelength using test tube 6 as the blank. Record your data in Table 3.

E. CHEM. 203 Lab Report

NAME: ______________________________ **EXPERIMENT # :** _______________

TITLE: ______________________________ **DATE:** _________________________

PARTNER: ______________________________ **SECTION #:** _____________________

Table 1: Absorption Spectrum of an $FeSCN^{2+}$ Solution

λ (nm)	A	% T
350		
375		
400		
425		
450		
475		
500		
525		
550		
575		
600		

λ_{max} =

Table 2: Absorbance measurements of $FeSCN^{2+}$ standard solutions

Mixture	**Volume of $Fe(NO_3)_3$**	**Volume of KSCN**	**Volume of H_2O**	**% Transmittance**	**Absorbance**	**$[FeSCN^{2+}]$**
0	**5.00**	**0.00**	**15.00**			
1	**5.00**	**0.50**	**14.50**			
2	**5.00**	**1.00**	**14.00**			
3	**5.00**	**1.50**	**13.50**			
4	**5.00**	**2.00**	**13.00**			
5	**5.00**	**3.00**	**12.00**			

Slope of Calibration Curve: εb (M^{-1}) = ___________________

Table 3: Composition of different mixtures and their absorbance measurements at λ_{max}

Mixture	Volume of $Fe(NO_3)_3$	Volume of KSCN	Volume of H_2O	% Transmittance	Absorbance	$[FeSCN^{2+}]$
6	**5.00**	**0.00**	**5.00**			
7	**5.00**	**1.00**	**4.00**			
8	**5.00**	**2.00**	**3.00**			
9	**5.00**	**3.00**	**2.00**			
10	**5.00**	**4.00**	**1.00**			
11	**5.00**	**5.00**	**0.00**			

Table 4: Equilibrium concentrations and equilibrium constant

Mixture	$n_{0\ Fe^{3+}}$	$n_{0\ SCN^-}$	$n_{Fe^{3+}}$	n_{SCN^-}	$n_{FeSCN^{2+}}$	$[Fe^{3+}]$	$[SCN^-]$	$[FeSCN^{2+}]$	K_c

Show one sample calculation for each calculated quantity (for one mixture only).

Questions

1. Write an expression for the equilibrium constant of the chemical reaction:

$$Fe^{3+}{}_{(aq)} + H_2O \rightleftharpoons Fe(OH)^{2+}{}_{(aq)} + H^+{}_{(aq)}$$

2. Consider the chemical reaction:

$$HClO_{2(aq)} \rightleftharpoons H^+{}_{(aq)} + ClO_2^-{}_{(aq)}$$

What are the equilibrium concentrations of H^+, ClO_2^- and $HClO_2$ in an aqueous solution with initial concentration $[HClO_2]_0 = 0.260$ M, given that the reaction has an equilibrium constant $K_c = 1.1 \times 10^{-2}$?

3. Back to the chemical reaction studied in this experiment:

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

We mix 2.00 mL of a 1.00×10^{-3} M $Fe(NO_3)_3$ with 3.00 mL of a 1.75×10^{-3} M KSCN solution. What are the equilibrium concentrations of Fe^{3+}, SCN^- and $FeSCN^{2+}$? (Use the value $K_c = 1.15 \times 10^2$)

Experiment 5

Spectrophotometric Determination of the pKa of Bromothymol Blue

A. Purpose

1. To learn about indicators and buffers.
2. To learn how to use a pH meter.
3. To determine the pK_a of Bromothymol Blue using the spectrophotometer and the pH-meter.

B. Theory

An acid-base indicator is a substance that displays different colors at different pH because of the differences between the electronic spectra of its conjugated acid and base. Such indicators are weak acids or bases depending on whether they are present in solution as their acidic form (HIn) or as their basic form (In^-) according to the equation below:

$$HIn_{(aq)} \rightleftharpoons H^+_{(aq)} + In^-_{(aq)} \qquad (1)$$

As the pH of a solution containing the indicator changes, the equilibrium shown above will be driven either towards reactants (HIn) or products (In^-), causing the solution color to change depending on the concentration of each form present. At low pH values most of the indicator will be present in its acidic form, causing the solution color to correspond to that of HIn. At high pH values, most of the indicator will be in the In^- form, causing the solution color to correspond to that of In^-. At intermediate pH values, the solution color will be a mixture of both colors depending on the relative amounts of HIn and In^- present.

In addition to the above, since such indicators are colored, they can be studied using the visible spectrophotometer where λ_{max} of the acidic solution (spectrum (a) in the figure1) will be different than the λ_{max} of the basic solution (spectrum (b) in the figure 1). At intermediate pH, the two wavelengths will be observed (spectrum (c) in the figure1).

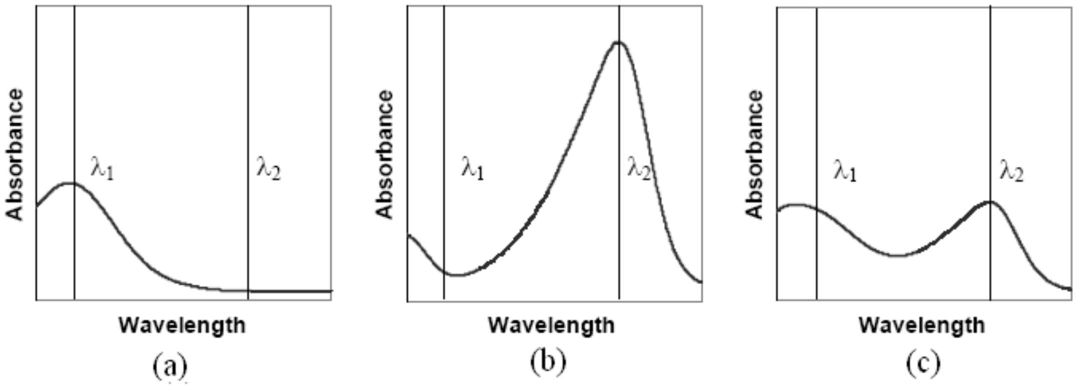


Figure 1: *Example absorbance spectra of an acid base indicator in (a) acidic solution, (b) basic solution, and (c) solution of intermediate pH.*

The acid base indicator to be studied in this experiment is Bromothymol blue, also called 3, 3'-dibromothymolsulfone-phthalein. This indicator is yellow in acidic solution and blue in basic. As the pH increases, the intermediate color that will be observed before the solution turns blue is the green.

The acid dissociation constant for BTB is given in eqn. (2), in terms of the concentrations of the hydrogen ion, In^- and HIn.

$$K_a = \frac{[H^+][In^-]}{[HIn]} \qquad (2)$$

Taking the negative logarithm of both sides yields eqn. (3)

$$-\log K_a = -\log [H^+] - \log \frac{[In^-]}{[HIn]} \qquad (3)$$

which can be written as eqn. (4),

$$pK_a = pH - \log \frac{[In^-]}{[HIn]} \qquad (4)$$

An examination of eqn. (4) suggests that if we are able to monitor the relative concentrations of HIn and In^-, it should be possible to determine the K_a for the indicator. Also, from eqn. (4), we note that when the concentrations of HIn and In^- in solution are equivalent, pH will be equal to the pKa of the indicator. Experimentally, this corresponds to the pH where the absorbance of each form is half of its maximum absorbance. At this point, half of the initial number of moles of HIn has been converted to an equivalent number of moles of In^- as shown by the dotted line in the figure 2.

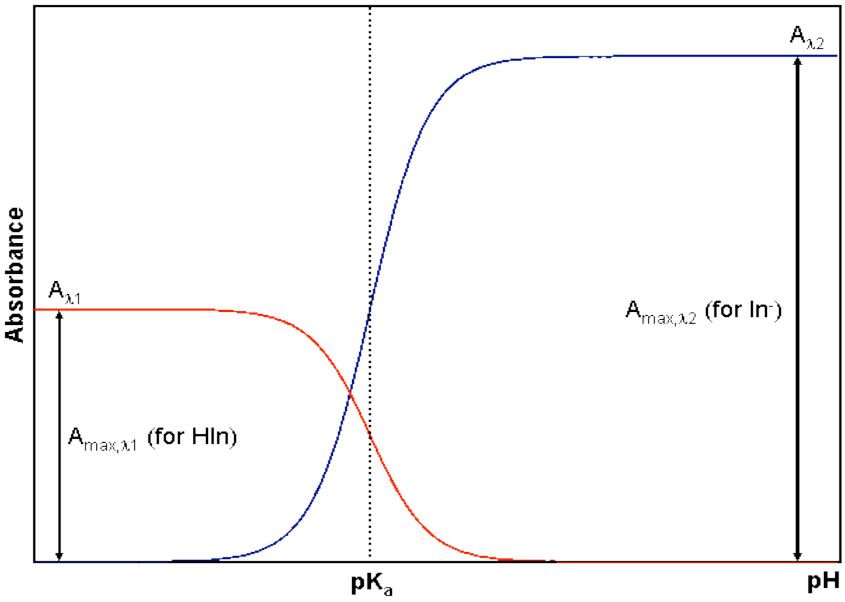


Figure 2: *A plot of absorbance as a function of pH for an indicator.*

Rearranging eqn. (4) results in the most common form of the Henderson-Hasselbalch equation (eqn. 5) for the indicator.

$$pH = pK_a + \log \frac{[In-]}{[HIn]} \qquad (5)$$

This expression provides an alternative way to determine the pKa of an indicator by plotting pH (y axis) as a function of log($[In^-]/[HIn]$). As shown in Figure 3, the resulting straight line intersects the pH axis when pH equals pK_a.

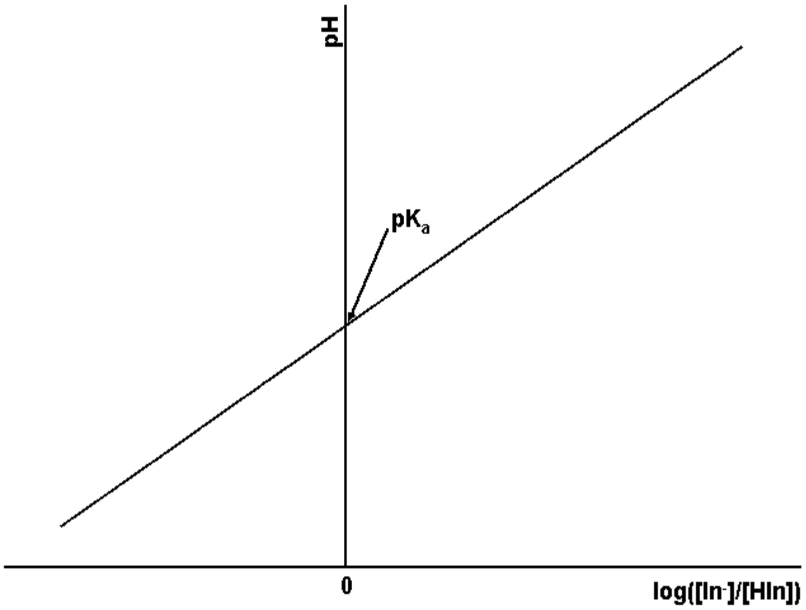


Figure 3. *A plot of pH as a function of log([In$^-$]/[HIn]).*

The ratio [In$^-$]/[HIn] can be obtained from spectrophotometric measurements which are made at two wavelengths. The first wavelength (λ_1) is chosen where the acidic (HIn) but not the basic form (In$^-$) of the indicator strongly absorbs radiation. The second wavelength (λ_2) is chosen where the basic but not the acid form strongly absorbs radiation. If Beer's law is obeyed, the absorbance at λ_1 and λ_2 are:

$$A_{\lambda 1} = \varepsilon_{(HIn,\ \lambda 1)}\ b\ [HIn]$$

$$A_{\lambda 2} = \varepsilon_{(In-,\ \lambda 2)}\ b\ [In^-]$$

where A is absorbance, ε is molar absorptivity and b is cell pathlength.

At any pH, the total concentration (C_T) of both forms of the indicator is constant and is the sum of the individual concentrations of each species.

$$C_T = [HIn] + [In^-]$$

In solutions of low pH, essentially all the indicator is in the acid form. Consequently, in highly acid solutions (lowest pH), $C_T = [HIn]$, and in highly basic (highest pH) solutions essentially all the indicator is in the basic form and $C_T = [In^-]$. By substitution, taking ratios and rearrangements, we can write eqn. (6)

$$\frac{[In^-]}{[HIn]} = \frac{A_{\lambda 2} \cdot A_{\lambda 1}(lowest\ pH)}{A_{\lambda 1} \cdot A_{\lambda 2}(highest\ pH)} \qquad (6)$$

Till now it has been assumed that at λ_1 the measured absorbance is due only to any HIn present and at λ_2 all absorbance is due to In$^-$. In fact, the basic form may absorb somewhat at λ_1 and the acidic form may absorb at λ_2. Because of this, the values of absorbance used in these equations must be corrected to take into account the amount of the absorbance that is due to the other species. However, this correction will be neglected sine it is very small.

C. Chemicals and setup

Bromothymol blue solution, conc. HCl, KH_2PO_4 solution (0.1M), Na_2HPO_4 solution (0.1M), 4 M sodium hydroxide solution, 10 mL graduated cylinder, beakers (50 and 100 mL), 10 mL graduated pipet, pipet filler, 12 volumetric flasks (25 mL), pH-meter, cuvets, and spectrophotometer.

D. Procedure (Work in pairs throughout this experiment)

1. Using a 10 mL graduated pipet, deliver 0.5 mL of the bromothymol blue solution to each of two, labeled, 25-ml volumetric flasks. Add 5 ml of distilled water and 4 drops of conc. hydrochloric acid to one of the flasks (labeled **A**). Dilute the solution to the mark with water. The resulting solution should have a pH of about 1. To the second flask (labeled **B**) add 12 drops of 4 M sodium hydroxide solution and fill the flask to the mark with water. **B** should have a pH of about 12-13.

2. Using the spectrophotometer measure the absorbance of each of solution A and solution B at 430 and 615 nm and record data in Table 1.
   Note: 430 nm is the λ_{max} of solution A while 615 nm is the λ_{max} of solution B.

3. Measure the pH of solutions **A** and **B.** Record data in Table 1.

4. Label 10, 25-mL volumetric flasks with numbers 1 through 10. Use a pipet to deliver 0.5 mL of the bromothymol blue solution to each of the flasks. Using the 10 mL graduated pipet, add the volumes of the 0.10 M Na_2HPO_4 solution and the 0.10 M KH_2PO_4 solution to each flask that are indicated in the table below. Dilute each solution to the mark with distilled water.

Solution Number	**Volume of KH_2PO_4 (mL)**	**Volume of Na_2HPO_4 (mL)**
1	5	0
2	10	0.5
3	5	1
4	10	5
5	5	5
6	5	10
7	1	5
8	1	10
9	0.5	10
10	0	5

5. Measure the pH of the 10 prepared solutions. Record data in Table 1.

6. Measure the absorbance of each of the 10 solutions at the two wavelengths given above. Record data in Table 1.

7. Determine the pKa of bromothymol blue via two ways of calculation discussed in the theory.

Note: - Use distilled water as blank for all your absorbance measurements.
- In case the specified number of volumetric flasks is not available, prepare solutions in the available flasks, transfer the prepared solutions to clean and dry beakers or Erlenmeyer flasks, clean the used volumetric flasks and re-use them.

E.CHEM 203 Lab Report

NAME: ______________________________ **EXPERIMENT # :** _______________

TITLE: ______________________________ **DATE:** _________________________

PARTNER: ______________________________ **SECTION #:** _____________________

Table 1:

i- Data and calculation (via method 1)

Solution #	**pH**	**Absorbance at λ_1**	**Absorbance at λ_2**
A (acidic)			
1			
2			
3			
4			
5			
6			
7			
8			
9			
10			
B (basic)			

Plot Absorbance versus pH of the solutions at λ_1 and λ_2 (a similar graph to figure 2).

Attach the graph to the report. Find the pK_a of bromothymol blue and record data in Table 2.

ii- Data and calculation (via method 2)

Solution #	**pH**	**Absorbance at λ_1**	**Absorbance at λ_2**	**$[In^-]/[HIn]$**	**log ($[In^-]$ / $[HIn]$)**
A (acidic)					
1					
2					
3					
4					
5					
6					
7					
8					
9					
10					
B (basic)					

Plot pH versus log ($[In^-]/[HIn]$) (Attach the graph to the report) and show the equation and regression of the curve.

Find the pK_a of bromothymol blue and record data in Table 3.

Table 2: pK_a results

	method 1	**method 2**
pKa		
% error		

Questions

1. The pKa of the indicator methyl orange is 3.46. Over what pH range does this indicator change from 90% HIn to 90% In^-?

2. Two drops of indicator HIn (K_a=1.0 x 10^{-9}), where HIn is yellow and In^- is blue, are placed in 100.0 mL of 0.10 M HCl.
   a) What color is the solution initially?
   b) The solution is titrated with 0.10 M NaOH. At what pH will the color change (yellow to greenish) occur?
   c) What color will the solution be after 200.0 mL of NaOH has been added?

3. You have 75.0 mL of 0.10 M HA. After adding 30.0 mL of 0.10 M NaOH, the pH is 5.50. What is the K_a value of HA?

Experiment 6

Thermodynamics of the Dissolution of Borax

A. Purpose

1. To learn about the laws of thermodynamics.
2. Determine the tetraborate concentration at 5 different temperatures by titration against standardized HCl .
3. To determine the solubility product of borax as a function of temperature.
4. To determine the standard free energy change (ΔG), the standard enthalpy change (ΔH), and the standard entropy change (ΔS) for the dissolution of borax in an aqueous solution.

B. Theory

Most physical and chemical changes are affected by temperature. Many years ago, via observations of temperature effects on everyday phenomena, the thermodynamic laws, which are mathematical descriptions of these observations, were formulated. When the thermodynamic laws are applied to chemical reactions, they relate the chemical equilibrium condition and the temperature of a given reaction to the thermodynamic quantities, ΔH^o, ΔS^o, and ΔG^o, which specify respectively the change in enthalpy, entropy and free energy for the system under standard conditions.

The free energy change of a reaction, $\Delta G°$, is proportional to the equilibrium constant for the reaction according to equation 1, and is related to the enthalpy and entropy changes during the reaction according to equation 2:

$$\Delta G° = -RT \ln K \qquad (1)$$

where R is the gas constant (is equal to $8.314 * 10^{-3}$ kJ/mol.K)
and T is the temperature in Kelvin.

$$\Delta G° = \Delta H° - T\Delta S° \qquad (2)$$

The reaction is thermodynamically favored if $\Delta G° < 0$; this means that $K > 1$. If K is significantly larger than 1, the reaction should proceed primarily to products.

Combining equations 1 and 2 gives the general relationship between K, $\Delta H°$, and $\Delta S°$:

$$-RT \ln K = \Delta H° - T\Delta S°$$

Dividing both sides by –RT gives a particularly useful form of this relationship:

$$\ln K = -\frac{\Delta H°}{R}\left(\frac{1}{T}\right) + \frac{\Delta S°}{R}$$

This represents a linear equation of the form $y = mx + b$. In this case, $y = \ln K$ and $x = 1/T$; a plot of ln K against 1/T will therefore be linear. In addition, the slope of this line (m) will be equal to $-(\Delta H°/R)$, and its y-intercept (b) will be equal to $(\Delta S°/R)$. It is therefore possible to determine $\Delta H°$ and $\Delta S°$ by simply measuring the equilibrium constant at two different temperatures, graphing ln K against 1/T, and measuring the slope and intercept of the resulting line. In practice, K is measured at several temperatures, so that the effect of any experimental error in one measurement will be minimized.

It is also possible to determine ΔH° and ΔS° by simply measuring the equilibrium constant K values at two temperatures. Thus:

$$\ln \frac{K_1}{K_2} = \frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

For slightly soluble salts with a solubility product constant, ksp, the equation can be written as:

$$\ln \frac{Ksp_1}{Ksp_2} = \frac{\Delta H^o}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Knowing ΔG° at each temperature from equation 1, ΔS° can be calculated from equation 2.

The reaction that will be studied in this experiment is the dissolution of the slightly soluble salt borax (sodium tetraborate octahydrate), a weak base, in water. "Borax" is a naturally occurring compound; it is in fact the most important source of the element boron, and it has been used for many years as a water softening agent. Borax is a rather complicated ionic salt which has the chemical formula $Na_2B_4O_5(OH)_4 \cdot 8\ H_2O$. When it dissolves, it dissociates as follows:

$$Na_2B_4O_5(OH)_4 \cdot 8\ H_2O_{(s)} \rightleftharpoons 2\ Na^+_{(aq)} + B_4O_5(OH)_4^{2-}{}_{(aq)} + 8\ H_2O\ (l) \quad (3)$$

The K expression for this reaction is:

$$K = [Na^+]^2[\ B_4O_5(OH)_4^{2-}]$$

Note that the borax solvation reaction equilibrium constant is the solubility product K_{sp} for borax:

$$K = K_{sp} = [Na^+]^2\ [B_4O_5(OH)_4^{2-}].$$

By the stoichiometry of the reaction $[Na^+] = 2\ [B_4O_5(OH)_4^{2-}]$

$$\Rightarrow\ K_{sp} = [(2\ [B_4O_5(OH)_4^{2-}]\ )\ ]^2\ [B_4O_5(OH)_4^{2-}]$$
$$= 4\ [B_4O_5(OH)_4^{2-}]^3$$

$$\Rightarrow \quad \ln K = \ln \mathrm{Ksp} = -\frac{\Delta H^\circ}{R}\left(\frac{1}{T}\right) + \frac{\Delta S^\circ}{R}$$

K_{sp} will be measured by analyzing a saturated solution of borax. Tetraborate is a weak base, so it can be titrated with a strong acid according to the equation:

$$B_4O_5(OH)_4^{2-}{}_{(aq)} + 2\ H^+_{(aq)} + H_2O_{(l)} \rightarrow 4\ H_3BO_{3\,(aq)} \quad (4)$$

By titration, the number of moles of tetraborate can be calculated. Thus, the number of moles of sodium ion can also be calculated by using the stoichiometry of reaction 3. Then, you can calculate the molar concentrations of the two ions and, finally, the value of K_{sp}.

The literature values for **enthalpy** and **entropy** of the dissolution of **borax** in water are 110 kJ/mol and 380 J/mol K, respectively.

C. Chemicals and setup

Solid borax, standardized HCl solution (~ 0.5M), bromocresol green indicator, distilled water, beakers

(100 mL, 150 mL and 400 mL), Erlenmeyer flasks, 10 mL graduated cylinder , 10 mL graduated pipet, pipet filler, digital thermometer, heater and buret.

D. Procedure (Work in pairs throughout this experiment)

1. Label 6 Erlenmeyer flasks (100 mL) with the following temperatures: 25, 30, 35, 40, 45, and 50°C. Add to each, using a graduated cylinder, 5 mL of distilled water.

2. Fill a 400 mL beaker labeled B1 with around 200 mL distilled water, place the beaker on the hot plate and heat at a rate of around 7.

3. Weigh around 17g borax in a 100 mL beaker and add on top, using a graduated cylinder, 50 mL distilled water. Place the beaker on the hot plate where B1 is placed and heat till 58°C. During heating, stir the solution gently with the digital thermometer. If all of the borax dissolves before the solution reaches 58°C, add more borax (1-2 g) while the solution remains on the hot plate until some of the salt remains undissolved. Keep heating at 58°C for 5 minutes.

   Note: Do not let the temperature of the solution exceed 60°C to avoid decomposition of borax.

4. When the temperature reaches 58°C, remove the borax solution from the hot plate, place it on the bench and leave it to cool to 50°C. (Do not keep the thermometer in the beaker while cooling; just measure the temperature of the solution (not borax) from time to time).

5. When the temperature is almost 50°C, pour some of the hot distilled water from B1 to a 50 mL beaker. Rinse your 10 mL graduated pipet (**note:** the graduated pipet to be used needs to be graduated till volume = 9 and not 10 mL) with some of this water so that the pipet becomes hot or else while the borax solution is pipeted, borax will precipitate in the pipet and the pipet will be sealed.

6. When the temperature is 50°C, pipet 5 mL (try to be accurate from the first time) of the borax solution using the heated pipet quickly and transfer to the corresponding Erlenmeyer flask (Note: do not pipet any solid borax). Rinse the pipet with at least 5 mL of the hot water placed in the 50 mL beaker and place the rinse in the Erlenmeyer flask (do not discard). Repeat three more times.

7. Clean your pipet and the 50 mL beaker with distilled water and proceed similarly as you reach the other temperatures.

8. Add to each flask 5 drops of bromocresol green indicator and titrate slowly (you only have one sample) with standardized 0.5 M HCl solution from light blue to pale yellow. Record data in Table 1.

9. Discard the saturated borax solution in the specified waste bottle while all the other solutions in the sink.

Note:

1- In case you pipet at different temperatures than the ones mentioned, record the exact temperature you read. Besides, if a mistake were committed in one of the samples, an extra sample can be pipeted at a different temperature than the ones mentioned above but again the exact temperature needs to be recorded.

2- You may find that it is difficult to obtain samples at the lower temperatures, because of the large amount of solid that forms. If this happens, you can decant the liquid into a smaller flask or beaker and allow it to cool in this new container. This allows you to remove most of the solid, so it is easier to pour samples of the solution which are uncontaminated by solid borax

E. CHEM. 203 Lab Report

NAME: ______________________________ **EXPERIMENT # :** _______________

TITLE: ______________________________ **DATE:** _________________________

PARTNER: ______________________________ **SECTION #:** _____________________

Table 1: Titration of borax solutions with HCl

	50°C	**45°C**	**40°C**	**35°C**	**30°C**	**25°C**
HCl upper reading (mL)						
HCl lower reading (mL)						
Volume (mL)						

Calculation:

Molarity of HCl =

i-The graph method:

	50°C	**45°C**	**40°C**	**35°C**	**30°C**	**25°C**
Temperature (kelvin)						
Volume of sample (mL)						
Moles of HCl						
Moles of tetraborate						
Concentration of borax						
Ksp						
ln Ksp						
1/T						

Plot ln Ksp versus 1/T. Attach graph to the report.

Slope =

y-intercept =

ΔH° =

ΔS° =

$\Delta G° =$

% error on $\Delta H°$ =

% error on $\Delta S°$ =

ii-<u>The calculation method:</u>

	50°C	**45°C**	**40°C**	**35°C**	**30°C**	**25°C**
Temperature (kelvin)						
Concentration of borax						
Ksp						
ln Ksp						
$\Delta G°$						
ln (Ksp_1/Ksp_2)						
($1/T_2-1/T_1$)						
$\Delta H°$						
$\Delta S°$						

$\Delta G°_{\text{average}} =$

$\Delta H°_{\text{average}} =$

$\Delta S°_{\text{average}} =$

% error on $\Delta H°$ =

% error on $\Delta S°$ =

Questions

1- Is the dissolution of borax in water an exothermic or endothermic process? What experimental evidence supports your answer?

2-Complete the table below.

	Reaction Conditions	**Sign of ΔH**	**Sign of ΔS**	**Sign of ΔG**	**Spontaneous Reaction? (Yes or No)**
(a)	at high *T*	+	+		
(b)	at low *T*	+	+		
(c)	at high *T*	–	–		
(d)	at low *T*	–	–		
(e)	at all *T*	+	–		
(f)	at all *T*	–	+		

Experiment 7

Impurities in Natural Water

A. Purpose

1. To learn some techniques for the purification of natural water.
2. To test for the contaminants of natural water (mostly ions in this experiment).
3. To learn the technique of water "softening" using ion-exchange resins.
4. To learn about the properties of phosphate salts and their role as contaminants of natural water.
5. To determine quantitatively (by spectrophotometric means), the phosphate content in a number of water samples and in an unknown.

B. Theory

Water covers nearly three-quarters of the earth and is the most abundant substance on the planet surface. Less than 3% of the earth's water is actually "fresh water". There is no such thing as "pure" spring water. If it has been in contact with earth, it holds minerals and, frequently gases in solution. Impurities in natural water consist of any substances other than the H_2O molecule. Today, the production of ultrapure water that is both sterile and free of dissolved and suspended impurities, is carried out in research laboratories using different techniques such as distillation, reverse osmosis (RO), deionization, carbon adsorption and membrane filtration.

Drinking water must be free of harmful bacteria (sterile), suspended matter, odor, color and objectionable taste. Dissolved minerals and gases, unless present in large amounts, usually do not need to be removed. Sometimes they can even be beneficial. If water is to be used for industrial purposes, appreciable concentrations of minerals, which are chiefly the salts of calcium or magnesium, must be removed. The removal of such ions by chemical means is usually referred to as "softening".

There are two ways to test for the presence of ions in water. Either qualitatively, which involves chemical reactions that produce visible colored products or precipitates, or quantitatively via titrations or use of spectrophotometers.

An application of the spectrophotometer use for the quantitative determination of an ion in a sample is the determination of phosphate ion such as phosphate determination via complexation with a reagent. Under acidic conditions, the orthophosphate ion, PO_4^{3-}, reacts with ammonium molybdate to form molybdophosphoric acid. A yellow compound vanadomolybdophosphoric acid is formed in the presence of vanadium. The color intensity produced depends on the amount of phosphate present, and the acidity of the solution. By maintaining the same acidity in all solutions and by adding the same large excess of vanadate/molybdate reagent to each solution, we can ensure that the amount of phosphate present controls the intensity of color developed. It is of course possible to get a rough idea of the relative amount of phosphate in the solutions by visually comparing their color intensities. By use of the spectrophotometer, however, we can obtain a more accurate quantitative measurement. The importance of quantitative determination of phosphates, which are essential nutrients for plant life, lies behind the fact that they contribute to the growth of algae and premature aging or eutrophication of lakes. Among the sources of phosphate in water are household detergents and fertilizers. Although it is possible that other factors such as nitrate content or dissolved carbon dioxide (CO_2) are limiting factors in the growth of algae, ecologists advise lowering the amounts of phosphates in surface water.

C. Chemicals and Setup

Solid $CoCl_2$, 14 M aqueous ammonia (NH_4OH), phenolphthalein indicator, 6 M HNO_3, 6 M HCl, 0.05 M $AgNO_3$, 0.5 M $BaCl_2$, 5.0 mg/L phosphate standard, tap water, sea water, 3.230 mM phosphate solution and an unknown phosphate sample, beakers, Erlenmeyer flasks, 50.0 mL volumetric flasks, cuvette and spectrophotometer.

D. Procedure *(with Setup and Theoretical Explanations)* (Work in pairs throughout this experiment)

- **Purification of Water by Distillation:**
  1. Fill an Erlenmeyer flask with 100 mL of tap water using the graduated cylinder. Add a few crystals of $CoCl_2$ to the water to give the water a slight pink color. Put in a few boiling chips. Clamp this flask on top of a hot plate (as shown in figure 1 below). Close the flask with a rubber stopper having a glass U-tube inserted in it with one sides of the u-tube being longer than the other. The longer side should be inserted in a test tube placed in an ice bath (the test tube should not be stoppered). Turn on the flame and distill slowly until about 2 cm of distillate has accumulated in the test tube.

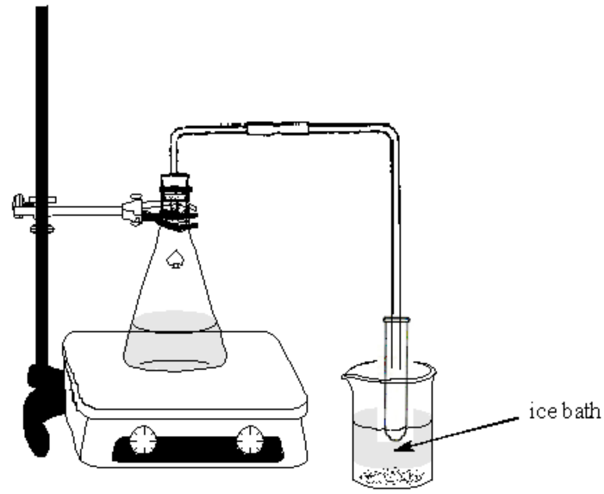


Figure 1 *Distillation apparatus*

Note the color of the distillate as compared with the initial mixture. Is the pink-colored impurity present in the distillate? Cover the test tube with parafilm paper and save the collected distillate (label A1) for parts 3 and 4.

  2. Empty the Erlenmeyer flask, rinse it well with distilled water then add 5 mL of concentrated aqueous ammonia, and 25 mL of distilled water. Set-up the distillation apparatus again using a new test tube. Distill slowly. Note the odor of the distillate as compared with that of the solution being distilled.
     Pour a few drops of the distillate into a clean test tube. Add one drop of phenolphthalein indicator. Note the color. Now add one drop of phenolphthalein to the original solution. Compare the color with that of the distillate test.
     Save the remainder of the distillate (label A2) for parts 3 and 4.

- **Minerals in Water:**
  1. **Indication of Carbonates in Tap Water:** Fill a 150 mL beaker with about 125 mL of tap water. Add a few boiling chips (3-4) and start boiling gently on a hot plate (proceed to part 3 while boiling). When the volume has been reduced to about half, withdraw a 25 mL sample (call it B1) and place it into a large test tube (to be used in parts 2 and 3). Boiling away some of the water concentrates ions that may be present in a very small amount of tap water.
     Continue boiling of the remaining contents of the beaker to dryness. Remove the flame as soon as the water is gone (to avoid cracking of the glass). A residue will be observed. It consists for the most part of $CaCO_3$ and $MgCO_3$ produced by the reactions:

$$Ca(HCO_3)_2\ (aq) \rightarrow CaCO_3\ (s) + H_2O\ (l) + CO_2\ (g)$$

$$Mg(HCO_3)_2\ (aq) \rightarrow MgCO_3\ (s) + H_2O\ (l) + CO_2\ (g)$$

Put a few drops of HCl solution on the residue and tilt the beaker so as to let it flow slightly. A slight bubbling at the leading edge indicates the carbonate ion CO_3^{2-}. A typical equation is:

$$2\ HCl\ (aq) + CaCO_3\ (s) \rightarrow H_2O\ (l) + CO_2\ (g) + CaCl_2\ (aq)$$

2. **Chloride Ion Test:** Divide the 20-mL sample of tap water (B1) into two parts and to the first one, add a few drops of HNO_3 and 1 mL of $AgNO_3$ solution (provided in a dropping bottle). A precipitate or cloudiness is AgCl, which indicates that Cl^- ion was present in the sample. Write the equation. Nitric acid, HNO_3, need not be included in the equation because it merely serves to prevent a false test. Try the test on water directly from the tap.
   Then repeat the test on the distillates A1 and A2, and on the resin-softened tap water. Record your conclusions.

3. **Sulfate Ion Test (Qualitative):** To the other half of the sample (B1), add a few drops of HCl and about 1 mL of $BaCl_2$ solution. What do you observe? The substance (precipitate or cloudiness) is $BaSO_4$ and indicates that SO_4^{2-} ion was present. Write the equation. The HCl need not be included in the equation. Try the test directly on tap water.
   Then repeat the test on the distillates A1 and A2, and on the resin-softened tap water. Record your conclusions.

- **Water Softening Using Ion-exchange Resins:**
  Household Type (cation-exchange resin in which cations are replaced by Na^+). Pour 50 mL of tap water from a beaker through a column of single resin (DOWEX 50W-X8) water softener like the model shown in Figure 2.

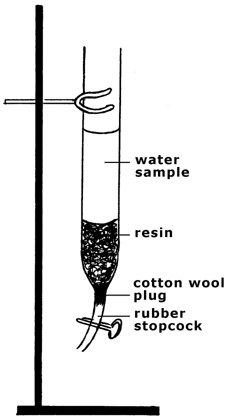


Figure 2 *Set-up of the cation exchange column*

By ion exchange, the resin captures all metal ions and releases Na^+ ions in their place. Hence the water (resin-softened tap water) now contains increased concentrations of sodium salts such as NaCl. A typical equation for this ion exchange process is:

$$Na_2R + CaCl_2 \rightarrow CaR + 2NaCl$$

In this equation, the symbol "R" represents the negatively charged site of the cation exchange resin. Test the resin-softened tap water for hardness (presence of calcium and magnesium cations) according to the procedure below; as well as for chloride and sulfate ion. Record your result in the report.

a- Hardness of Tap Water Test (qualitative):

1. Using a 10 mL graduated cylinder, transfer ~2.5 ml of tap water into a test tube.
2. Using a 10 mL graduated cylinder, add 1-2 mL of pH= 10 buffer.
3. Add one drop of Erio-T indicator.
4. Observe the color of the solution (refer to experiment 1).

b- Hardness of Resin-softened Tap Water (qualitative):

1. Using a 10 mL graduated cylinder, transfer ~2.5 ml of resin-softened tap water into a test tube.
2. Using a 10 mL graduated cylinder, add 1-2 mL of pH= 10 buffer.
3. Add one drop of Erio-T indicator.
4. Observe the color of the solution (refer to experiment 1).

- **Phosphate Determination Using the Spectrophotometer:**

I. Preparation of a Set of Standard Phosphate Solutions:

1. Obtain from the stock room a sample of standard phosphate solution (3.230×10^{-3} M KH_2PO_4), in a clean and dry 50 mL beaker.
2. Pipet a 1.00 mL aliquot of this standard solution into a clean and dry 50.0 mL volumetric flask (free of phosphate contaminants).
3. Using a graduated cylinder, add 10 mL of ammonium vanadate/molybdate reagent and dilute to the mark with distilled water. Stopper the flask and mix well. You must observe a yellow color whose intensity depends on the concentration of phosphate in the solution.
4. Repeat steps 2 and 3 using 2.00, 3.00, 4.00 and 5.00 mL aliquots of the original standard solution. Make sure to rinse the volumetric flask very thoroughly with distilled water, each time before use.
   You have thus prepared five phosphate standards of different known concentrations.
   Wait for 10 min before measuring the absorbance of the prepared solutions to ensure complete complexation of the ion with the reagent.
5. Prepare a blank by adding 10 mL of ammonium vanadate/molybdate reagent to a 50.0 mL volumetric flask and diluting to the mark with distilled water.
6. Measure the absorbance of each of the five solutions (treated with vanadate/molybdate reagent) at 420 nm in a spectrophotometer as demonstrated by your instructor and record data in Table 1.
7. Construct a calibration curve (Absorbance ***A*** versus concentration ***C***). Determine the slope of this curve.

Note: In case you are provided with 100.0 mL volumetric flasks instead of the 50.0 mL, then double all the volumes used in the experiment.

II. Measurement of Phosphate in Sea Water and in an Unknown:

1. Pipet 5.00 mL of sea water into a 50 mL volumetric flask.
2. Add 10 mL of ammonium vanadate/molybdate reagent and dilute to the mark with distilled water. Stopper the flask and mix well.
   Wait for 10 min before measuring the absorbance of the prepared solution.
3. Measure the absorbance of the solution at 420 nm and record data in Table 2.
4. Repeat steps 1 to 3 with your unknown sample. Record the number of your unknown in Table 2.
5. From the slope of the calibration curve (Part A), determine the concentration of phosphate in sea water and your unknown water sample expressed in ppm and in molar units.

Note: Discard all the solutions containing vanadiam/molybdate reagent in a waste bottle (not in the sink).

E. CHEM 203 Lab Report

NAME: ________________________________ **EXPERIMENT # :** ________________

TITLE: ________________________________ **DATE:** ___________________________

PARTNER: ________________________________ **SECTION #:** ______________________

- **Distillation**

1. Distillation of a solution containing a dissolved solid ($CoCl_2$)

Is $CoCl_2$ impurity present in the distillate? ________________________
Explain from your observations.

2. Distillation of a solution containing a dissolved gas (NH_3)

Is NH_3 impurity present in the distillate? ________________________
Explain from your observations.

- **Minerals in Water**

3. Indication of Carbonates in Tap Water

Is the CO_3^{2-} ion present in the residue? ____________

How do you know?

Write a balanced equation for the reaction of HCl with any $MgCO_3$ that may have been present.

____

4. Chloride Ion Test

Evaporated water (B1) _____________ Tap water _______________

Distillate A1 ________________ Distillate A2 ________________

Equation for test: ____

5. Sulfate Ion Test

Evaporated water (B1) ______________ Tap water ______________

Distillate A1 ________________ Distillate A2 ________________

Equation for test: ____

- **Water Softening Using Ion-exchange Resins**

6. Household Type

Is calcium/magnesium ions present in tap water? Explain.____________________________

____

Is calcium/magnesium ions present in the resin-softened tap water? Explain._____________

____

Is chloride ion present? ____________ Is sulfate ion present? _____________

- **Phosphate Determination Using the Spectrophotometer**

  Concentration of standard KH_2PO_4 =

Table 1: Calibration curve

Sample	Volume of phosphate standard solution (mL)	Concentration of phosphate (M)	Concentration of phosphate (ppm)	Absorbance (at 420 nm)
Blank				
1				
2				
3				
4				
5				

Slope of Calibration Curve: εb (M^{-1}) = __________________

Correlation coefficient (R^2) of the Calibration Curve = __________________

Table 2: Phosphate in sea water and in an unknown (# ____________)

Water sample	Absorbance	Concentration of phosphate (M)	Concentration of phosphate (ppm)
1.			
2.			

Show a sample calculation for finding concentrations in M and ppm.

Calculation for finding concentrations of phosphate in sea water and in unknown (in M and ppm)

Questions

1. What reaction between soil, water and limestone rock accounts for the relatively large amounts of $Ca(HCO_3)_2$ and $Mg(HCO_3)_2$ found in ground water. Where does the necessary CO_2 come from?
2. "Boiler scale" forms in kettles, consisting mainly of calcium carbonate. Write a chemical equation for the corresponding reaction. Explain why the scale forms much more heavily at high temperature (like the boiling point of water).
3. In the phosphate analysis part, if H^+ ion, VO_3^- ion, and $Mo_7O_{24}^{6-}$ ion, as well as PO_4^{3-} ion, are required to produce the yellow color, why does the analysis measure phosphate ion content of the water sample?
4. If a given water sample contains 10 parts per million phosphorous, how many grams of phosphorous would a liter contain?
5. Why are phosphates used in household detergents? What are some of the substitutes that have been suggested for use instead of phosphates for cleaning purposes?

Experiment 8

Turbidimetric Determination of Sulfate in Water

A. Purpose

1. To understand the concept of turbidimetry.
2. To determine quantitatively (by spectrophotometric means), via turbidimetry, the sulfate content of different water samples.

B. Theory

Turbidimetry is the measurement of light-scattering species in solution by means of a decrease in intensity of the incident beam of a spectrophotometer after it has passed through solution. Turbidimetry is a method that can be used to determine the concentration of sulphate in water. In turbidimetry, the principle of absorption chemistry can be used wherein transmittance, and not absorbance, due to suspended particles is measured because the particles scatter most of the light without ever absorbing it. Turbidimetry can be measured by an instrument such as a colorimeter or Spectrophotometer and it obeys Beer's Law. Percent transmission can be mathematically converted into turbidance (S) according to the following equation:

$$S = -\log T = 2 - \log \%T$$

Where T is the transmittance and %T refers to percent transmittance.

The correlation of concentration of dispersed particle to that of transmission or scattered light will hold provided that there is no settling of particles (precipitate must be very fine not to settle) , no coagulation of dispersed particles and no nucleation and crystal growth. The particles should have a uniform shape and size to allow uniform scattering of light.

Sulfate is the second most abundant anion in seawater. Its high concentration owes to the high to moderate solubility of the salts that it forms with the major cations in seawater, namely, Na^+, Mg^{2+}, and Ca^{2+}. Sources of sulfate in water include the dissolution of sulfur-bearing compounds found in rocks on the continents, volcanic emissions, and, lately, from sulfur released into the atmosphere, primarily as SO_2, by the combustion of fossil fuel. The latter two lead to the formation of acid rain. Acid rain has as its main constituent sulfate ion and its principal contributor to pollution is sulfur dioxide, which is oxidized in the atmosphere to sulfate and converted into an environmentally harmful strong acid (H_2SO_4). Sulfate may also be discharged in numerous industrial wastes such as those from tanneries, pulp mills, textile mills, and other industries that use sulfate compounds. Although sulfate is not particularly toxic, if the concentration is too high it may cause other problems, such as build up in high-pressure boilers, the taste of the water being bitter, and at concentrations above 1000ppm, the water may cause diarrhea.

The sulfate determination in this experiment uses the barium sulfate turbidimetric method. In highly acidic solutions, the only common ion which forms a precipitate with sulfate is barium. The percent transmittance of the precipitate is the determined by a spectrophotometer, which is then converted to turbidance and compared to a curve prepared from standard sulfate solutions. This reaction is performed in a sodium chloride-hydrochloric acid solution *(NaCl-HCl) and Glycerol-ethanol solution. NaCl-HCl solution* is added to acidify the medium in order to favor the precipitation reaction, to eliminate the possibility of precipitation of barium carbonate that may form in highly alkaline waters and to inhibit the growth of micro crystal of barium sulfate. As to the *Glycerol-ethanol solution*, the glycerin in this solution favors the dispersion of the colloidal precipitate formed in the liquid medium, allowing a better turbidimetry measurement.

C. Chemicals and Setup

Barium chloride, sodium sulphate solution (~ 10^{-3} M), NaCl-HCl solution, glycerol-ethanol solution, beakers, Erlenmeyer flasks, beakers, 25 mL volumetric flasks, stopwatch, stirrer, magnetic bar, cuvette and spectrophotometer.

D. Procedure (Work in pairs throughout this experiment)

I. Preparation of a Blank Solution

1. Pipet 25 mL of distilled water to a 100 mL beaker.
2. Add 0.3g of barium chloride and stir to homogenize.

II. Preparation and Turbidance Measurement of a Set of Standard Sulfate Solutions

1. Obtain from the stock room around 50 mL of standard sodium sulfate solution (~ 1×10^{-3} M) and record the exact concentration in the report form.
2. Pipet 25.00 mL of this standard solution into a clean and dry 125 mL Erlenmeyer flask (standard 1). Add a magnetic bar and place the flask on the stirrer.
3. Using a graduated cylinder, add 5 mL of NaCl-HCl solution and 2 mL of glycerol-ethanol solution.
4. Weigh around 0.3 g of barium chloride.
5. While the solution is being stirred add to it the weighed barium chloride and start timing immediately.

Note: Keep the stirring rate constant throughout the experiment.

6. Stir for a minute, then stop and continue timing for one more minute. During this minute, zero the absorbance of the blank solution at 420 nm wavelength.
7. Transfer part of the solution to a cuvette and place the cuvet in the spectrophotometer. Measure the transmittance of the solution after a total of 7 minutes from the time barium chloride was added. Record data in Table 2.
8. Prepare another standard (std 2) by pipetting 10 mL of sodium sulfate to a 25 mL volumetric flask and diluting it to the mark with distilled water.
9. Transfer std 2 to a 125 mL Erlenmeyer flask. Add a magnetic bar and place the flask on the stirrer. Stirring rate should be the same as the rate used for standard 1.
10. Repeat steps 3 to 7 and record data in Table 2.
11. Prepare three other standards similarly to step 8 but using 7.5 mL, 4 mL and 2 mL of sodium sulfate respectively instead of the 10 mL.
12. Repeat steps 3 to 7 for every standard and record data in Table 2.
13. Plot a calibration curve of turbidance versus concentration.

III. Preparation and Turbidance Measurement of Tap Water

1. Pipet 25.00 mL of tap water into a clean and dry 125 mL Erlenmeyer flask. Add a magnetic bar and place the flask on the stirrer.
2. Using a graduated cylinder, add 5 mL of NaCl-HCl solution and 2 mL of glycerol-ethanol solution.
3. Weigh around 0.3g of barium chloride.
4. While the solution is being stirred add to it the weighed barium chloride and start timing immediately.

Note: Keep the stirring rate constant throughout the experiment.

5. Stir for a minute, then stop and continue timing for one more minute. During this minute, zero the absorbance of the blank solution at 420 nm wavelength.
6. Transfer part of the solution to a cuvette and place the cuvette in the spectrophotometer. Measure the transmittance of the solution after a total of 7 minutes from the time barium chloride was added. Record data in Table 2.

IV. Preparation and Turbidance Measurement of Sea Water

1. Pipet 1 mL of sea water into a 25 mL volumetric flask and dilute to the mark with distilled water.
2. Transfer this solution to a 125 mL Erlenmeyer flask
3. Add a magnetic bar and place the flask on the stirrer.
4. Repeat steps III. 2 to III.6 and record data in Table 2.
5. Calculate the concentration of sulfate in sea water.

Note: *Discard all solutions prepared in in the proper waste bottle.*

E. CHEM 203 Lab Report

NAME: ______________________________ **EXPERIMENT # :** _______________

TITLE: ______________________________ **DATE:** _________________________

PARTNER: ______________________________ **SECTION #:** _____________________

Table 1 Preparation of sulfate standards

Concentration of sodium sulfate stock (M) =

Concentration sodium sulfate stock (ppm) =

Concentration of sulfate stock (ppm) =

Sample	Volume of sulfate standard solution (mL)	Concentration of sulphate (ppm)

Table 2 Transmittance measurements of sulfate in the standards and the different water samples

Sample	Concentration of sulphate (ppm)	Transmittance	Turbidance

Plot Turbidance versus concentration and find the equation of the curve and correlation coefficient.

Concentration of sulfate in tap water (ppm) =

Concentration of sulfate in sea water (ppm) =

Questions

1. Why is it important to use the same stirring rate and time for the samples and standards?

2. Many natural waters have a slight color and may contain suspended matter. Explain why these might interfere with the analysis for sulfate. For each interferent, suggest a method for minimizing its effect on the analysis.

3. What is the significance of high sulphate concentration in water supplies and in wastewater disposal?

Periodic Table of the Elements

Key:

element name
atomic number
symbol
atomic weight

hydrogen 1 **H** 1.00794																	helium 2 **He** 4.002602
lithium 3 **Li** 6.941	beryllium 4 **Be** 9.012182											boron 5 **B** 10.811	carbon 6 **C** 12.0107	nitrogen 7 **N** 14.00674	oxygen 8 **O** 15.9994	fluorine 9 **F** 18.9984	neon 10 **Ne** 20.1797
sodium 11 **Na** 22.98977	magnesium 12 **Mg** 24.3050											aluminum 13 **Al** 26.981538	silicon 14 **Si** 28.0855	phosphorus 15 **P** 30.97376	sulfur 16 **S** 32.065	chlorine 17 **Cl** 35.453	argon 18 **Ar** 39.984
potassium 19 **K** 39.0983	calcium 20 **Ca** 40.078	scandium 21 **Sc** 44.95591	titanium 22 **Ti** 47.867	vanadium 23 **V** 50.9415	chromium 24 **Cr** 51.9961	manganese 25 **Mn** 54.93805	iron 26 **Fe** 55.845	cobalt 27 **Co** 58.9332	nickel 28 **Ni** 58.6934	copper 29 **Cu** 63.546	zinc 30 **Zn** 65.409	gallium 31 **Ga** 69.723	germanium 32 **Ge** 72.64	arsenic 33 **As** 74.9216	selenium 34 **Se** 78.96	bromine 35 **Br** 79.904	krypton 36 **Kr** 83.798
rubidium 37 **Rb** 85.4678	strontium 38 **Sr** 87.62	yttrium 39 **Y** 88.90585	zirconium 40 **Zr** 91.225	niobium 41 **Nb** 92.90638	molybdenum 42 **Mo** 95.94	technetium 43 **Tc** [98]	ruthenium 44 **Ru** 101.07	rhodium 45 **Rh** 102.9055	palladium 46 **Pd** 106.42	silver 47 **Ag** 107.8682	cadmium 48 **Cd** 112.411	indium 49 **In** 114.818	tin 50 **Sn** 118.710	antimony 51 **Sb** 121.760	tellurium 52 **Te** 127.60	iodine 53 **I** 126.9045	xenon 54 **Xe** 131.293
cesium 55 **Cs** 132.90545	barium 56 **Ba** 137.327	lutetium 71 **Lu** 174.967	hafnium 72 **Hf** 178.49	tantalum 73 **Ta** 180.9479	tungsten 74 **W** 183.84	rhenium 75 **Re** 186.207	osmium 76 **Os** 190.23	iridium 77 **Ir** 192.217	platinum 78 **Pt** 195.078	gold 79 **Au** 196.96655	mercury 80 **Hg** 200.59	thallium 81 **Tl** 204.3833	lead 82 **Pb** 207.2	bismuth 83 **Bi** 208.980	polonium 84 **Po** 209	astatine 85 **At** 210	radon 86 **Rn** 222
francium 87 **Fr** 223	radium 88 **Ra** 226	lawrencium 103 **Lr** 262	rutherfordium 104 **Rf** 261	dubnium 105 **Db** 262	seaborgium 106 **Sg** 266	bohrium 107 **Bh** 264	hassium 108 **Hs** 269	meitnerium 109 **Mt** 268	darmstadtium 110 **Ds** 271	roentgenium 111 **Rg** 272	ununbium 112 **Uub** 285		ununquadium 114 **Uuq** 289				

lanthanum 57 **La** 138.9055	cerium 58 **Ce** 140.116	praseodymium 59 **Pr** 140.90765	neodymium 60 **Nd** 144.24	promethium 61 **Pm** 145	samarium 62 **Sm** 150.36	europium 63 **Eu** 151.964	gadolinium 64 **Gd** 157.25	terbium 65 **Tb** 158.9253	dysprosium 66 **Dy** 162.50	holmium 67 **Ho** 164.930	erbium 68 **Er** 167.259	thulium 69 **Tm** 168.934	ytterbium 70 **Yb** 173.04
actinium 89 **Ac** 227	thorium 90 **Th** 232.038	protactinium 91 **Pa** 231.0359	uranium 92 **U** 238.0289	neptunium 93 **Np** 237	plutonium 94 **Pu** 244	americium 95 **Am** 243	curium 96 **Cm** 247	berkelium 97 **Bk** 247	californium 98 **Cf** 251	einsteinium 99 **Es** 252	fermium 100 **Fm** 257	mendelevium 101 **Md** 258	nobelium 102 **No** 259