Chemistry 104

The City College of New York

Prepared by Scott S. Berlant

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Introduction to Safety Rules

The City College Chemistry Department wants you to learn chemistry safely. That means that certain rules of operation in the lab must be followed. Please note: your laboratory instructor will reduce your grade or ask you to leave the lab if the safety rules are not followed!

1.You should bring no food or drink into the laboratory, to avoid possible contamination.

2.Keep your hands away from your face, while working in the lab, and do not put anything in your mouth.

3.Wash your hands as often as possible, especially before leaving the lab.

4.Keep your workstation neat and clean.

5. No horseplay, practical jokes or tricks, which may lead loss of concentration or worse to serious injury.

6. Be well prepared before you come to the lab.

7. Do not pour chemicals into the sink drain. Dispose of all hazardous waste in the appropriate container provided in the lab.

8. Know what to do in case of emergency.

Dress Code

If you come to the lab dressed inappropriately, you will be asked to leave, and you will receive a grade of "0" for the day's work.

1. Wear splash-proof goggles at all times in the lab. State and federal law requires the use of splash-proof goggles by anyone working in a chemical laboratory. The goggles must have a rubber or plastic seal, which fits snugly against your face, an elastic strap that holds the goggle in

place, and baffled indirect ventilation. Indirect ventilation means that there are covered vents, which allow for ventilation and no chemical splash. The Chemistry Department will provide one pair of approved goggles for each student.

2. Do not wear contact lenses!

Contact lenses pose several dangers. First, contact lenses can absorb and react with chemical fumes. No goggles can protect you from fumes! Second, if you were to get liquid or solid chemical into your eye, the chemical would get under the contact lens. A contact lens would hamper efforts to wash the chemical out of your eye, thus making the damage much more severe.

3. Tie back long hair

Long hair can accidentally fall into flames or chemicals. Many hair sprays, gels, mousse, etc. are flammable. Think about this! Loose long hair can block your vision, which may lead to an accident.

4. Do not wear clothing, which is loose enough to knock over containers on the bench or dip into flames or chemicals.
5. Wear clothing (shirt, blouse, or dress) which covers and protects your full front and back, including shoulders, and upper arms
6. Wear clothing (pants, long skirt or dress), which covers and protects your body all the way down to and including your ankles.
7. Wear shoes, which cover and protect your feat completely.

Safety Equipment

1. First Aid

If an injury occurs, a student will normally be escorted to the Student Health Services Office (J-15) to receive treatment from the health care professional there, or can wait in the lab for an EMS team from the NYC Fire Department if the injury is severe.

2. Brush and Dust Pan

In the Chemistry Lab we use a lot of glassware. It is unsafe to pickup broken glass with your hands. Instead, use a table brush and dustpan to collect the broken glass. The broken glass should be disposed of in the specially marked box in the lab.

3. Fume Hoods

These are large metal cabinets, which have sliding glass doors in front. Fume hoods are used to protect you from harmful fumes gases and odors. Use the fume hood when working with concentrated ammonium hydroxide or evaporating liquids.

4. Know the location of the eyewash and safety shower in the lab. Also, on the first day of lab, learn the location of the appropriate fire exit. (See the evacuation route placard at the entrance to the lab.)
5. Organic vapors can flare up when brought into contact with a hot surface. Avoid using alcohol/ and or acetone, which are very flammable, in the presence of a hot plate or flame.
6. Accidents happen! Even with the greatest care, something will sometimes go wrong.
    a. If you get a corrosive chemical on your skin, go to the large sink and wash it off with lots of water. If this is not sufficient, and you still feel a stinging sensation, ask your lab instructor for the acid neutralizing powder. What ever you do, don't try to neutralize a strong acid with a strong base on your skin, or vice versa—This turns a mere accident into a major disaster.
    b. Corrosive chemicals that you will use in the lab include: Nitric Acid, Sulfuric Acid, Hydrochloric Acid, Ammonium Hydroxide, and Sodium Hydroxide.
    c. If there is a fire, the lab instructor will alert you to evacuate the lab room in an orderly manner and proceed to the appropriate exit. If you clothing is on fire go to the safety shower at once to extinguish the flame.

d. For serious injury or illness in the lab

1.Use the lab phone to call security at #7777.

2.Call NYC EMS at #9-911.

3.If the lab phone is not available proceed to call at the security phone located adjacent to the bank of elevators.

The City College
Department of Chemistry
Laboratory Syllabus for Chemistry 10401

Week 1 Check in; Introduction to other solution units.
Week 2 Freezing point, Freezing point depression and molecular mass determination.
Week 3&4 Determination of the order of a chemical reaction from literature rate data. Kinetics of the dimerization of 2,5-dimethyl-3, 4-diphenylcyclopentadiene-1-one.
Week 5 Problem set on chemical equilibrium. Discussion on chemical equilibrium of solutions. Formation constant of a complex ion, $FeSCN^{2+}$ system (part a).
Week 6 Formation constant of a complex ion system continued. Discussion and calculation of experimental results.
Week 7 Discussion and problem set on pH of buffer solutions Discussion of a pH titration. Use and calibration of a pH meter, and analytical balance.
Week 8 Complete pH titration of ammonium phosphate known sample, and percent report.
Week 9 Titration Curves and pH Calculations for known phosphate data.
Week 10 Complete Unknown determination, and calculate phosphate percent in sample.
Week 11 Discussion of qualitative analysis theory and techniques. Preliminary test and flow diagram for analytical group 1. Discussion of K_{sp}. Separation and identification of known and unknown mixtures of silver, mercury, and lead ions.
Week 12 Electrochemistry I: Silver ion equilibria and calculation of equlibrium constants.
Week 13 Electrochemistry II: Determination of an unknown anion concentration in a silver system.
Week 14 Intermolecular Forces. Check out.

To: Students in Chemistry 10401
From: Simon Simms, Chair Department of Chemistry

Below you will find the formula for calculating the lab grade in chemistry 10401 labs. Note that for chem. 10401 the lab grade counts for 25% of the total course grade.

Experiment	% of the grade
Colligative properties	10
Kinetics	15
Equilibrium	15
pH	20
Analytical Group 1	15
Electrochemistry	20
Intermolecular forces	05

If you miss a laboratory session, you should make arrangements to make it up within the same week. Check the Chemistry Department schedule for the alternative times and days. See Mr. Berlant (j1014) to work out the details. You are responsible for turning in your lab results the day the experiment is completed. No "incomplete" grades will be given for the laboratory except for an extenuating medical reason and with my permission.

You are responsible for keeping your work area and balance clean. Up to 10% of your laboratory grade may be deducted for failure to meet your responsibility. Goggles must be worn in the lab at all times.

Equipment List For Chemistry

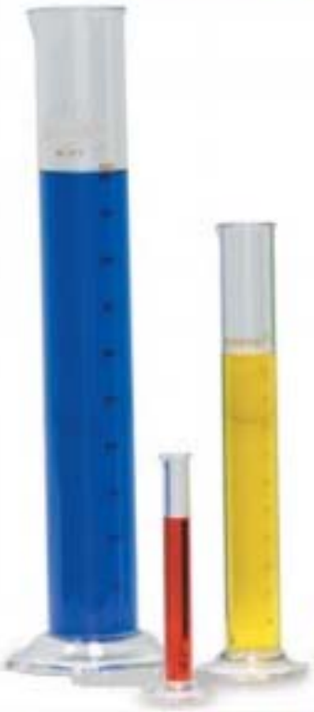
Beakers
1-600 ml
2-400 ml
3-150 ml
4-250 ml

3-250 ml
Erlenmeyer
Flasks

Dessicator
Jar

Funnels
1-4 cm
1-7.5 cm

Misc.
Equipment
14-Test
Tubes
Rack
Brush
3-Dropper
Pipettes
1-25 ml
pipette
2-5 ml
pipettes
2-10 ml



Graduated
Cylinders
10,50,100
ml

Plastic
Wash
Bottle

Amber
Bottle
250 ml

1000
ml

Weighing
Bottles
and
Covers -

Vials
with
plastic

Scoopula

Spatula

An Introduction to Alternative Solution Units

Objectives:

a. To learn about molar, molal, and mole fraction solutions and their appropriate application.
b. To learn how to convert between molar and molal units.
c. To perform an experiment which demonstrates solution properties.

Experimental Procedure

The type of balance available for this experiment is shown in figure 1. The Denver A-160 Analytical balance has a capacity of 160 grams and a sensitivity of 0.0001 grams. That is it weighs objects to the nearest 0.1 milligram. These balances are very convenient and easy to use.

To weigh an object:

- Check that the pan is clean and empty.
- Press the tare button and zero the balance. The display should show 0.0000 g.
- Place the object to be weighed in the center of the balance pan and read the mass to the nearest 0.0001g.

1. Determine the mass of an empty, clean, and dry 25 ml graduated cylinder. Record the mass on your data sheet.
2. From a plastic wash bottle deliver 10-11 ml of deionized water to the graduated cylinder. Record the volume to the proper number of significant figures on your data sheet.
3. Determine the mass of the graduated cylinder and water to the nearest 0.0001 gram and record on your data sheet.
4. Measure the temperature of the water with device provided by your lab instructor. Is this temperature colder than room temperature?
5. Calculate the density of the water contained in the cylinder.
6. Place a weighing boat on the balance and "tare" its mass. Remove the boat from the balance and with the aid of spatula add enough sodium nitrate crystals until the mass is more than 5.2 grams. Carefully transfer all of the crystals from the boat to the 25 ml graduated cylinder containing the water.

7. With a glass rod stir the water to dissolve all of the sodium nitrate. Measure and record the mass of the solution to the nearest 0.0001 gram. Measure the volume of the solution to the proper number of significant figures. Determine if the solution is colder than the water or room temperature.
8. Your lab instructor will discuss molarity, molality, and mole fraction for the data you have just measured. In addition a good review of conversion of concentration units can be found in Brown & Lemay sample exercise 13.5 and 13.6.

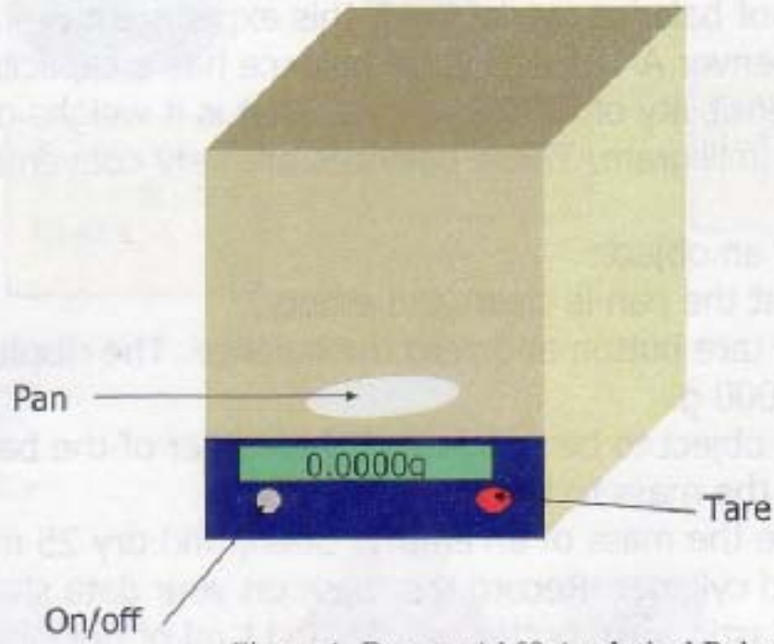


Figure 1. Denver A160 Analytical Balance

Data Sheet for Solution Chemistry Experiment

Mass of graduated cylinder and water	grams
Mass of graduated cylinder	grams
Mass of water	grams
Volume of water contained in cylinder	ml
Density of Water	g/ml
Mass of water and sodium nitrate	grams
Volume of sodium nitrate solution	ml
Density of sodium nitrate solution	G/ml
The molarity of sodium nitrate is:	Mole/L
The molality of sodium nitrate is:	Mole/Kg water
The mass percent of sodium nitrate is:	
The mole fraction of sodium nitrate is:	The mole fraction of water is:
Molar mass of sodium nitrate is 84.995 g/mole	Molar mass of water is 18.015 g/mole.

Freezing Point, Freezing Point Depression and Molar Mass Determination.

Introduction

The freezing point of a substance is the temperature at which the vapor pressures of the solid and liquid phases are the same. At that temperature and pressure the number of molecules, which exchange their places in the solid and liquid phases, is in equilibrium. The freezing point temperature is not affected significantly by a change in external pressure.

A more dramatic effect occurs with the addition of a non-volatile solid or liquid solute to a liquid solvent. If the solute is non-volatile, the vapor pressure of the solution is reduced in proportion to the mole fraction of the solute. This means that the temperature at which the solution and solid phase have the same vapor pressure is reduced. The original equilibrium established in the pure solvent at a particular temperature and pressure favors the liquid state. To restore the equilibrium the temperature must be lowered so as to favor formation of solid.

For dilute solutions, the freezing point depression varies linearly with the concentration of the solute, expressed as the number of moles of solute per 1Kg of pure solvent. This expression of concentration represents the molality, m, of the solution. Doubling the molality of the solution will increase the number of particles in solution and double the freezing point depression effect. The relationship of molal concentration to freezing point depression is:

$$\Delta T_F = K_F m \text{ or } \Delta T_F = T_F \text{ pure solvent} - T_F \text{ solution} = K_F m,$$

where T_F is the freezing point, K_F is the freezing point depression constant for pure solvent, and m is the molality in $gmole^{-1}$ per Kg solvent. Because K_F is a constant for a given solvent, the measurement of the change in freezing point, ΔT, for known masses of dissolved solute permits the experimental determination of the molecular mass of the solute.

The table below lists several solvents and their freezing point data. These solvents are typically used for freezing point determinations because of their convenient freezing point temperatures and their relatively large K_F values.

Solvent	T_F ^0C	K_F $^0C Kg$ Solvent $mole^{-1}$
Benzene	5.50	5.12
Biphenyl	70.00	8.00
Cyclohexane	6.50	20.00
Ethylene glycol	-11.5	1.91
Tertiary butyl alcohol	25.50	9.10
Water	0.00	1.86

Materials List

Two 25X200 test tubes, 100 ml graduated cylinder, 10 ml graduated cylinder, two 50 ml conical flasks with stoppers, 600 ml beaker, digital thermometer, clamp and stand, and magnetic stirrer.

Experimental Procedure

Part 1 Freezing point of pure solvent

It is first necessary to determine an experimental value for the freezing point of the solvent (tertiary butyl alcohol). This is done primarily to compare the experimental value obtained to the literature value given in table 1. In addition commercial thermometers are not always calibrated carefully and a reference temperature needs to be established for the solvent.

Note: The solvent may be solid at room temperature depending on the room temperature. A hot air dryer will be available to melt the solvent.

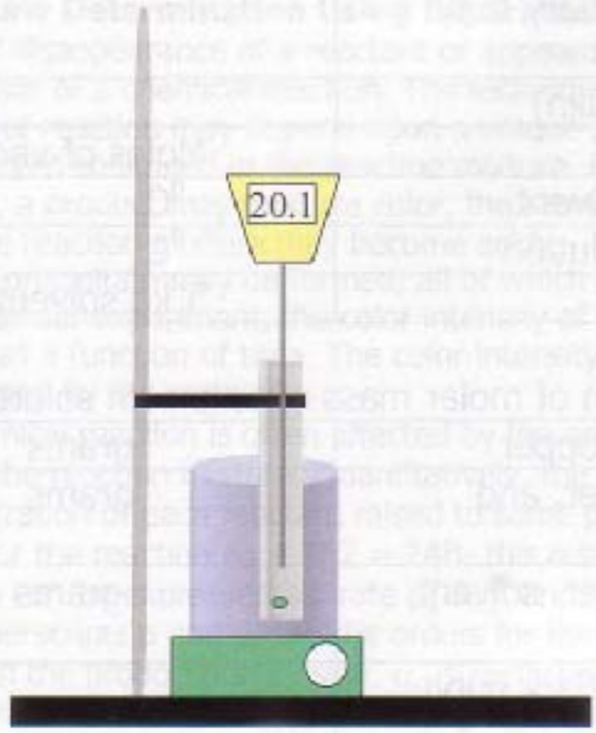
1. Add 30 ml of tertiary butyl alcohol to the large test tube. Place the tube in a 600 ml beaker containing warm tap water. Allow the temperature to return to room temperature and record the temperature every 30 seconds. Is the room very warm (above 27 degrees)? The freezing point is reached when crystals start to form and the temperature will remain constant. It may be necessary to cool the external water bath with a small amount of ice. At the freezing point the liquid will appear cloudy. Do not freeze the solvent until it is completely solid. In addition do not attempt to remove the thermometer from a frozen block of solvent. Melt the solvent in a warm water bath. The solvent should be able to be used for the next part of the experiment.

Part 2 Determination of the K_F for tertiary butyl alcohol using vanillin as a known solute.

1. Determine the mass of a 50 ml conical flask and stopper to the nearest0.1 mg and record the mass on your data sheet.
2. Pour 30 ml of pure solvent into the flask and determine the mass to the nearest 0.1 mg.
3. "Tare" a weighing boat and weigh 1.7500-2.000g of vanillin.
4. Transfer the entire solid to the flask and reweigh the flask to the nearest 0.1 mg. Stopper the flask and swirl to mix. Do not allow the solvent to come into contact with the stopper.
5. Pour the solution into a clean dry large test tube. Determine the freezing point of the solution as before. It will be necessary to add small amounts of ice to the large beaker in order to freeze the solution. The cooling curve temperature should be recorded every 30 seconds. The molar mass for vanillin is 152.15 g/mole. Determine the K_F for the solvent with the equation given in the introduction.
6. Discard the solution in the waste container provided in the laboratory.

Part 3 Determination of the molar mass of an unknown solute.

1. Determine the mass of a clean dry 50 ml conical flask and stopper to the nearest 0.1 mg.
2. Add 30 ml of tertiary butyl alcohol and determine the mass to the nearest 0.1 mg.
3. Add 2 ml of the liquid unknown and measure the mass of the solution to the nearest 0.1 mg.
4. Determine the freezing point of the unknown solution as before.
5. Calculate the molar mass of the solute to four significant figures.
6. Discard the solution in the designated chemical waste container.



Data Sheet For Freezing Point Experiment

Part 1. Experimental Freezing point for tertiary butyl alcohol. _____

Part 2 Determination of the freezing point depression constant K_F

Mass of flask and stopper	grams
Mass of flask, stopper, and solvent	grams
Mass of flask, stopper, solvent, and solute	grams
Mass of solvent (tertiary butyl alcohol)	
Mass of solute (vanillin)	
Molality of vanillin	Moles of vanillin/kg solvent
Freezing point of solvent	^{0}C
Freezing point of solution	^{0}C
K_F of solution	^{0}Ckg solvent/mole solute

Part 3 Determination of molar mass of unknown solute

Mass of flask and stopper	grams
Mass of flask, stopper, and solvent	grams
Mass of flask, stopper, solvent, and solute	grams
Mass of solvent (tertiary butyl alcohol)	
Mass of solute (unknown)	
Molality of vanillin	Moles of solute/kg solvent
Freezing point of solvent	^{0}C
Freezing point of solution	^{0}C
Molar mass of solute	g/mole

Determination of Rate Laws

Objectives:

To determine the rate law of a reaction experimentally
To determine the order of a reaction from literature rate data
To use different methods of graphical analysis

Preliminary Reading

Review appendix IV on the use of a Digital Spectronic 20 Spectrophotometer.
Review appendix II, and appendix III on CBL graph.
Review the 103.1 lab manual concerning Beer's Law relationships.
Chapter 14 in Brown and Lemay

Part a -Rate Law Determination Using Experimental Data

The rate of disappearance of a reactant or appearance of a product is indicative of the rate of a chemical reaction. The technique used to monitor and measure the rate of reaction may depend upon a unique property inherent in one of the substances contained in the reaction mixture. For example a reactant may lose its color, a product may produce color, the reaction products may generate heat, the reaction mixture may become acidic or basic, a gas or precipitate may be formed, all of which may be monitored as a function of time. In our experiment, the color intensity of the reaction mixture will be measured as a function of time. The color intensity will decrease as the reactant is consumed by the reaction.

The rate of a chemical reaction is often affected by the amount of reactant initially placed in the reaction mixture. Quantitatively, the rate is proportional to the molar concentration of each reactant raised to some power, called the order of the reactant. For the reaction $A_2 + 2B2 = 2AB_2$ this relationship between rate and concentration can be expressed as: rate $\alpha[A_2]^p$ and rate $\alpha[B_2]^q$ or rate $\alpha[A_2]^p[B_2]^q$. The superscripts p and q, are the orders for the reactants A and B respectively. When the proportionality sign, α, is replaced with a proportionality constant, κ(, the rate for the reaction is rate = $\kappa[A_2]^p[B_2]^q$. The value of κ, called the specific rate constant, is determined experimentally and varies with temperature and the presence of catalyst, but is independent of reactant concentrations.

The orders p and q are also determined experimentally. For example, suppose that on doubling the molar concentration of A (while holding the B constant) the reaction rate is observed to increase by a factor of four: to maintain proportionality between rate and $[A_2]$, p must equal 2.

The reaction studied in this experiment is the (reversible) dimerization of 2,5-Dimethyl- 3,4-diphenylcyclopentadiene-l-one.

$$2\ C_{19}H_{16}0 \rightarrow C_{38}H_{32}0_2$$

monomer dimer

The monomer reactant is colored, while the dimer product is not. The experiment is conducted on a previously prepared sample of 50 mg of the dimer dissolved in 10 ml of toluene. Prior to the lab session your lab instructor in a hot water bath will warm the sample in order to regenerate the monomer. The monomeric solution may be preserved in an ice bath. Although the solution is highly colored we will assume the "'Zero time" for the start of the experiment, is at an absorbance value of 1.20 at 460 nm. The absorptivity value for the monomeric material is 225.

Lab Procedure

I. Record absorbance data for your sample every 5 minutes for a total of 75 minutes.

2. Use Beer's Law to convert the absorbance values obtained to concentration units of mole/liter of the monomer.

3. Use CBL Graph to plot your data for [monomer] versus time. Set up time as the x-axis. Remember to use the proper number of significant figures.

4. Turn on the Tangent Line function of the program and record the slope for each data point.

Please note: some features of CBL Graph may have been automated for facility of data entry by large classes. Please consult your lab instructor.

5. To directly determine the kinetic order we assume that the rate of the monomer dimerization is proportional to the concentration of reactant raised to some power.

$$\text{Rate} = \kappa[\text{monomer}]^n$$

If we take the log of the expression; log rate = logκ + nlog[monomer], the new equation predicts that plotting the log of the calculated rates against the log of the monomer concentration should produce a straight line with a slope of n.

6.Enter your values for the log of the individual slopes and the log[monomer].

7. Use CBL graph to plot the log values.

8. Use the "Best Line" routine to find the slope of your second graph.

9. What is the order of this reaction.

10. Use three monomer concentrations and three values of the slope to calculate the κ for the reaction.

Part B Rate Law Determination from Literature Data

A less exact method of determining the order of a reaction is practical when the order is an integer between zero and two, using the reactant concentration versus time dependence equations, as given for first and second order reactions in Brown & Lemay chapter 14.

For a first order reaction, the equation is, $\ln [A] = -kt + \ln[A_o]$.

For a second order reaction, the equation is: $1/[A] = kt + 1/[A_o]$.

In addition, using the same sort of derivation given in the above reference, we can deduce the equation for a zero order reaction as: $[A] = -kt$.

Procedure

I. You will be given the literature data for two exercises; one is a "practice" exercise on a known zero order reaction; the other is a reaction of"unknown" order.

2. Using the literature data for the "practice" exercise, verify that the reaction is of zero order, by comparing the results of three separate graphs: [A] vs. t, ln[A] Vs. t, and $1/[A]$ vs. t.

3. Explain in a paragraph how the results of your three graphs verify the zero order reaction.

4. Using the data for the "unknown" exercise, determine the reaction order by comparing the results of the three separate graphs, as described in step 2. Explain how your results indicate the reaction order.

Practice Kinetics Computer Exercise

Most of the nitric acid used in industry comes in the form of approximately 16M aqueous solution. It is produced from ammonia by the three-step Ostwald process:

Step 1. Ammonia is burned in excess oxygen over a platinum/ rhodium catalyst to form NO.

$4\ NH_3(g) + 5O_2(g) \rightarrow 4\ NO(g) + 6\ H_2O(g)$

Step 2. Additional air is added to cool the mixture and oxidize NO to NO_2 :

$2\ NO(g) + O_2 \rightarrow 2\ NO_2(g)$

Step 3. The NO_2 gas is bubbled into warm water where it will disproportionate into nitric acid and nitrogen monoxide. The monoxide is recycled in step 2.

$3\ NO_2 + H_2O(l) \rightarrow 2\ HNO_3 + NO(g)$

Gas chromatography is used to monitor the ammonia concentration which remains during the reaction sequence. Typical data for the ammonia oxidation is shown in the table below.

Molarity of ammonia remaining [M^{-3}]	Time Seconds
2.00	0.00
1.82	50.0
1.63	100.0
1.49	150.0
1.30	200.0
1.20	250.0
1.00	300.0
0.83	350.0
0.66	400.0
0.47	450.0

Data Sheet For Kinetic Determination of Rate Law From Dimerization Reaction

Time Minutes	**Absorbance**	**[Monomer]**	**Rate** Mole/l/min	**Log [mono.]**	**Log Rate**

Slope for graph_____.
Reaction Order_____.

Calculations for Rate Constant

Student Name_____

Chemical Equilibrium
Formation Constant of a Complex Ion System

Adapted from Chemistry in the Laboratory- Jo A. Beran and Laboratory Manual for Chemistry- L. Epstein

Objectives

- To develop the techniques for the care and operation of a digital spectrophotometer.
- To determine the equilibrium constant for a soluble ionic system.

Principles

The magnitude of an equilibrium constant, K_c, expresses the equilibrium position for a chemical system. For example, a small K_c indicates large amounts of reactants at equilibrium conditions, whereas a large K_c indicates large amounts of products. The value of the K is constant for a system at constant temperature.

This experiment determines the constant for a system in which all-chemical species are ionic and water-soluble. The equilibrium involves the hydrated iron(III) ion, the thiocynate ion and the iron(III)-thiocyanate complex ion.

$$\mathbf{Fe(H_2O)_6^{3+}(aq) + SCN^-(aq) \leftrightarrow Fe(H_2O)_5NCS^{2+}(aq) + H_2O(l)}$$

The equilibrium expression for this process is: $\mathbf{K_c = [FeSCN^{2+}]/[Fe^{3+}]\,[SCN^-]}$.

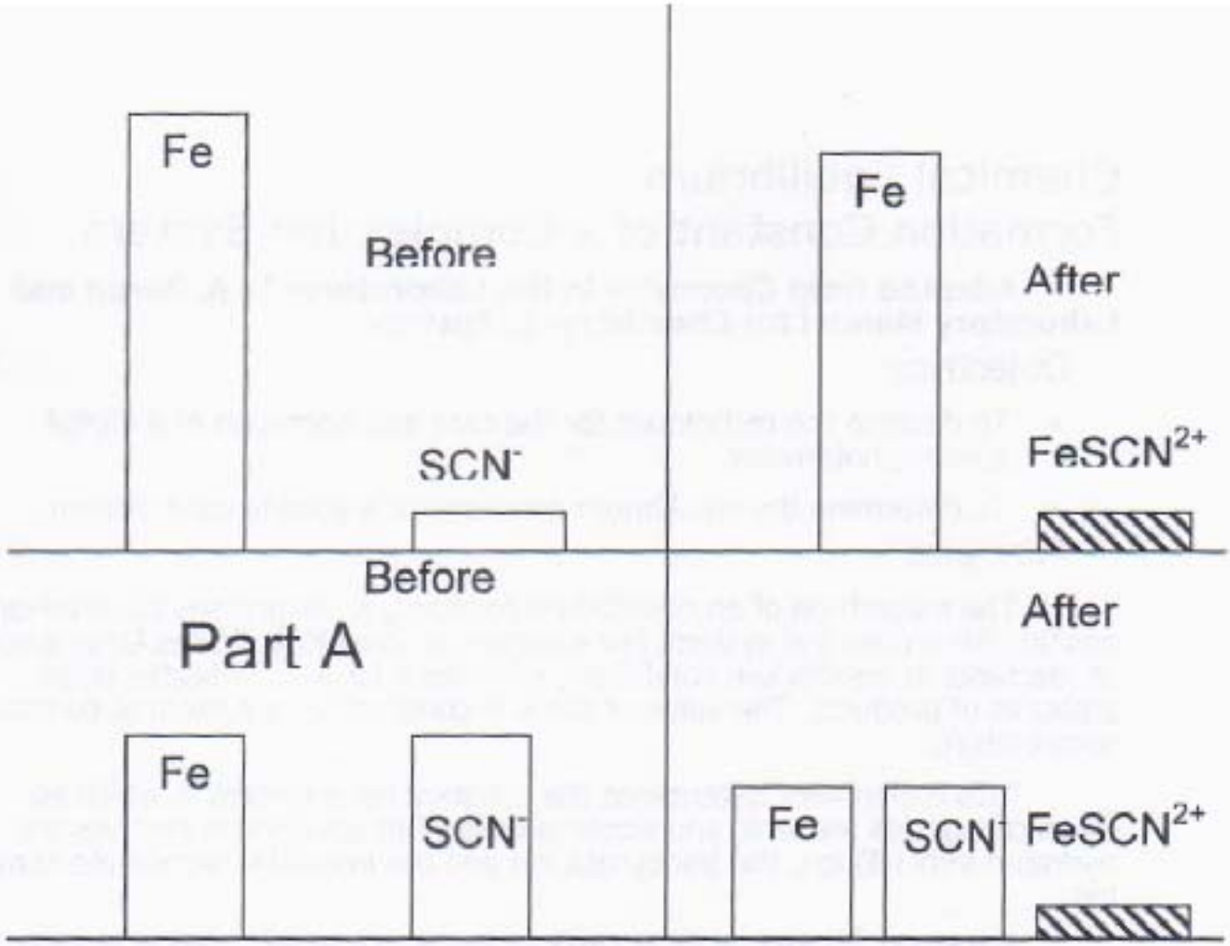
To determine the K for the system, known amounts of Fe^{3+} and SCN^- are mixed and react to form an equilibrium condition with $FeSCN^{2+}$, a deep, blood red complex ion with an absorption maximum at 470 nm. Because of its intense color the concentration of the complex ion is determined spectrophotometrically. Controlling the initial number of moles of Fe and SCN ions, and measuring the equilibrium number of moles of the complex ion spectrophotometrically can calculate the equilibrium moles of Fe and SCN ions.

$$\mathbf{Moles\ Fe^{3+}\ (eq) = moles\ Fe^{3+}\ (initial) - moles\ FeNCS^{2+}\ (at\ equil.)}$$

$$\mathbf{Mole\ SCN^-\ (eq) = mole\ SCN^-\ (initial) - mole\ FeNCS^{2+}\ (at\ equil.)}$$

The equilibrium molar concentrations of Fe^{3+}, SCN^-, and $FeNCS^{2+}$ can be calculated with the known volume of the test solution. Using the equilibrium molar concentrations of each ion in the equilibrium expression the K_c for the chemical system can be calculated.

In part A of the experiment, a set of standard solutions for the $FeNCS^{2+}$ ion is prepared and the absorbance of each solution is measured. The absorbance values are plotted on a graph against the known molar concentrations of $FeNCS^{2+}$. Because absorbance is directly proportional to concentration, a linear calibration curve is expected. This plot of data is used to determine the molar concentration of $FeNCS^{2+}$ in a non-controlled environment in part B.



Part B

To prepare the standard solutions for part A, the Fe ion concentration is added in large excess relative to the SCN ion concentration. The excess Fe^{3+} drives the equilibrium far to the right. We make the assumption that the number of moles of $FeSCN^{2+}$ that form at equilibrium approximates the number of moles of SCN^- initially placed in the system (figure A).

Data for the determination of K_c is collected in part B. In the chemical systems that are analyzed, the initial molar concentrations of Fe and SCN ions are nearly the same (figure B). In reaching equilibrium conditions, the molar concentrations of Fe and SCN ions decrease and the complex increases, all of which are present in the system and measurable.

Experimental Procedure

Each student will prepare their own solutions and perform spectrophotometric measurements. The experiment will be performed over a two-week period of time.

Part A- Set of Standard Solutions (week 1)

- For part A, the set of standard solutions, five large test tubes with stoppers, two 10 ml pipettes, one 5 ml pipette, 3-150 ml beakers and 1-600 ml beaker are needed.
- See appendix 1 for volume measurements, and appendix 4 for the use of a digital spectrophotometer.
- Prepare the solutions listed in table 1. Use a separate pipette for each solution. Stopper the tubes and mix well.

Table 1 A Set of Standard $NaNCS^{2+}$ Solutions			
Solution #	0.100M $Fe(NO_3)_3$	0.001M NaSCN	1.000M HNO_3
Blank	10.0 ml	0.0 ml	10.0 ml
1	10.0 ml	1.0 ml	9.0 ml
2	10.0 ml	2.0 ml	8.0 ml
3	10.0 ml	3.0 ml	7.0 ml
4	10.0 ml	4.0 ml	6.0 ml

- Your instructor will demonstrate the use of the spectrophotometer. Absorbance measurements should be made at 447 nm and data recorded on sheet A.
- After receiving approval from your lab instructor concerning your data, clean up your work area, dispose of all the solutions in the designated waste container, and complete the required calculations on data sheet A
- The class will proceed to the computer room to plot their results. Refer to appendix to learn how to plot data with CBL graph.
- Have your printout initialed by your lab instructor.

Part B- a set of equilibrium Solutions (week 2)

This set of solutions is independent of the solutions listed in Table 1. The concentrations of the reactants are different. Be sure to consult Table 2 for the exact amounts of each solution.

Table 2 A set of equilibrium solutions			
Solution #	0.003M $Fe(NO_3)_3$	0.003M NaSCN	1.00M HNO_3
Blank	10.0 ml	0.0 ml	10.0 ml
5	10.0 ml	2.0 ml	8.0 ml
6	10.0 ml	4.0 ml	6.0 ml
7	10.0 ml	6.0 ml	4.0 ml
8	10.0 ml	8.0 ml	2.0 ml
9	10.0 ml	10.0 ml	0.0 ml

Measure the absorbance of the six solutions you have prepared in part B. Record your results in data sheet B. Your lab instructor will discuss how to determine the equilibrium constant and calculations on data sheet C.

- # Data Sheet For Chemical Equilibrium

A Set of Standard Solutions

Exact Molar Concentration for NaSCN is given in table 1

Exact molar concentration for $Fe(NO_3)_3$ is also given in table 1

Standard Solutions	Blank	1	2	3	4
Volume of NaSCN, ml					
Moles of SCN^-					
$[SCN^-]$ for 20ml solution					
$[FeNCS^{2+}]$					
Absorbance					

Instructor approval_____

Data Sheet For Equilibrium Experiment

Part B Set of Equilibrium Solutions

The exact molar concentrations for Fe and SCN ion solutions is given in table 2

Solutions	5	6	7	8	9
Volume of Fe ion solution used, ml					
Moles of Fe^{3+}, initial					
Volume of NaSCN, ml					
Moles of SCN^-, initial					
Absorbance					

Data Sheet for Equilibrium Experiment
Sheet C. Determination of K_c

Solutions	5	6	7	8	9
$[FeNCS^{2+}]$ from calibration curve					
Moles of $FeNCS^{2+}$ in solution at equilibrium					
Moles of Fe^{3+} reacted					
Moles of Fe^{3+} unreacted (left over)					
$[Fe^{3+}]$, at equilibrium unreacted					
Moles SCN^-, reacted					
Moles of SCN^-, unreacted					
$[SCN^-]$, at equilibrium unreacted					
K_c					
Average K_c Take closest 4/5					

pH Titration of a Phosphate Base with HCl

Introduction to Titration Curves and Calculations

Although chemical indicators can be used for end point detection, a pH electrode system is the best way to monitor an acid-base titration. A typical setup for measuring pH during a titration is illustrated in figure 5. To understand why titration curves have characteristic shapes, we will examine the curves for three types of titrations.

Figure 1 shows a plot of a strong acid-strong base titration. This curve consisting of twelve data points depicts the pH change that occurs as 0.100 M NaOH is added to 25.00 ml of 0.100 M HCl.

As NaOH is added, the pH increases slowly at first and then rapidly in the vicinity of the equivalence point. The equivalence point itself is the point of inflection at the center of a steep portion of the curve; in this region, the addition of only a few drops of NaOH produces a pH change of several units.

Figure 2 shows a weak acid/strong base titration curve, which depicts the pH change that occurs as 0.100M NaOH is added to 25.00 ml of 0.100M acetic acid. The titration is a bit more complex than the previous curve, since we are concerned with conjugate acid/base pairs and their equilibrium. We can verify the experimental pH values at three points in the titration curve using the methods given in your lecture textbook.

Point #1 Beginning of the titration 0 ml NaOH

$$HC_2H_3O_2 \leftrightarrow H^+ + C_2H_3O_2^-$$

$$K_a=[H^+][C_2H_3O_2^-]/[HC_2H_3O_2] =1.8 \times 10^{-5}$$

Initial	0.100 M	0	0
Change	-XM	+XM	+XM
Equilibrium	(0.100-X)	XM	XM

$$K_a = X^2/0.100 =1.8 \times 10^{-5}$$

$$X^2 =(0.100)(1.8 \times 10^{-5}) = 1.8 \times 10^{-6}$$

$$X = 1.34 \times 10^{-3} =[H^+]$$

pH = 2.87 the experimental pH

An identical calculation may be performed to verify all of the data points from 1.0 ml through 24.99 ml. In this region, the pH is a function of the value of K and the ratio of the acid and its conjugate base. A common format for the equilibrium expression used in the buffer region is the Henderson-Hasselbalch equation.

$$pH = pK_a + \log [\text{conjugate base}]/[\text{acid}]$$

Point #2 When 12.5 ml of NaOH have been added half of the acetic acid has been converted to the acetate ion. The number of moles of acetic acid equals the number of moles of the acetate ion, and the buffer ratio is 1.

(.0125L)(0.100M)=1.25 mmole NaOH delivered→ 1.25 mmole acetate ion

(.02500L)(0.100) = 2.50 mmol acetic acid – 1.25 mmole NaOH

=1.25 mmole of acetic acid left over.

$pH = pK_a + \log [1] = -1 \log 1.8 \times 10^{-5} + \log 1 = 4.75$

Point #3 At the equivalence point 25 ml of 0.100 M NaOH has been delivered to the titration. This number of moles is equal to the initial number of moles of acetic acid. Since the titration produces the corresponding conjugate base, we expect the pH to be basic at the equivalence point.

(25.00 ml)(0.100)= 2.50 mmole NaOH used= 2.50 mmoles of acetic acid initially present. 2.5 mmoles of acetic acid also yields 2.50 mmoles of acetate ion.

$[C_2H_3O_2^-]$ =2.50 mmoles/100 ml =0.025 M

The acetate ion is weaker base and K_b can be calculated from the K_a.

$K_b = K_w/K_a$; $1 \times 10^{-14}/1.8 \times 10^{-5} = 5.6 \times 10^{-10}$

$K_b=[HC_2H_3O_2][OH^-] / [C_2H_3O_3^-]= (X)(X)/ 0.025 - X = 5.6 \times 10^{-10}$

$X^2 = (0.25)(5.6 \times 10^{-10}) = 1.4 \times 10^{-11}$

$X= 3.74 \times 10^{-6}= [OH^-]$

pOH=5.42; pH= 14-5.42= 8.58

A comparison of figure 2 with figure 3 shows several differences between the weak acid-strong base titration curve and the strong acid-strong base titration curve. The weak acid-strong base curve shows:

1. Low initial pH.
2. Short abrupt pH rise at the beginning of the titration because of lack of a buffer.
3. An equivalence point above 7.

Figure 3 shows the pH changes that occur when 0.100 M HCl is added to 25.00 ml of 0.100 M NH_3. This curve is a typical strong acid-weak base titration curve. The ammonia solution is initially basic (pH= 11.1), and the pH decreases as HCl is added and ammonium ion forms. The buffer region is centered near the half neutralization point where the pH equals the pK of the ammonium ion. The pH falls sharply between 7 and 4. The solution is acidic (pH=5.3) at the equivalence point.

Practice Problems

1. Five problems are found in the lab experiment on page 30.
2. Your lab instructor will make suggestions for additional problems from your lecture text.

Figure 1
A strong acid-strong base titration curve, showing how the pH increases as 0.100 M NaOH is added to 25.00 mL of 0.100 M HCl. The equivalence point pH is 7.00.

ml NaOH added		pH
0		1
1		1.04
12.5		1.48
24		2.69
24.5		3
24.9		3.7
24.95		4
24.99		4.7
25		7
25.05		10
26		11.29
27		11.31

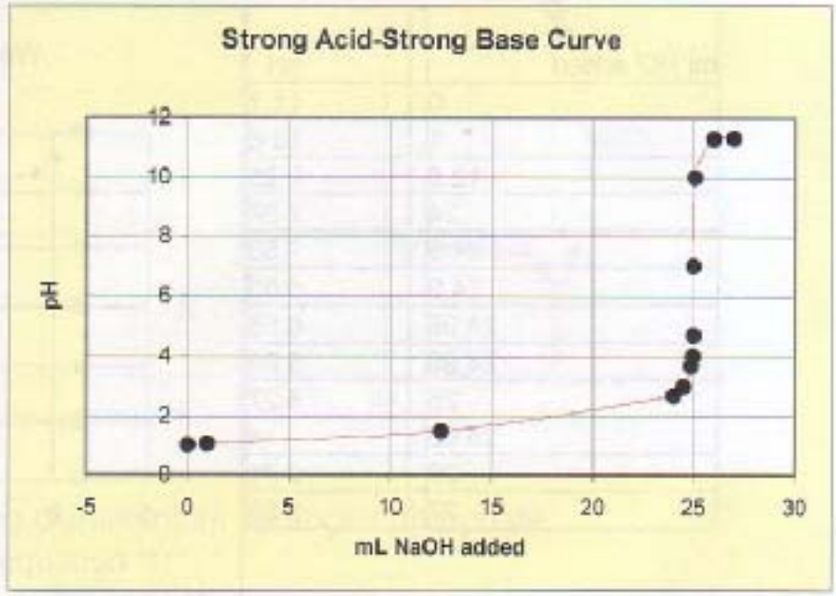


Figure 2
A weak acid strong base titration curve showing how the pH increases as 0.100 M NaOH is added to 25.00 mL of 0.100 M acetic acid

Equivalence point at pH 8.73

mL NaOH added pH		pH
0		2.88
1		3.38
12.5		4.75
24		6.13
24.5		6.45
24.9		7.15
24.95		7.45
24.99		8.15
25		8.73
25.05		10
26		11.29
27		11.31

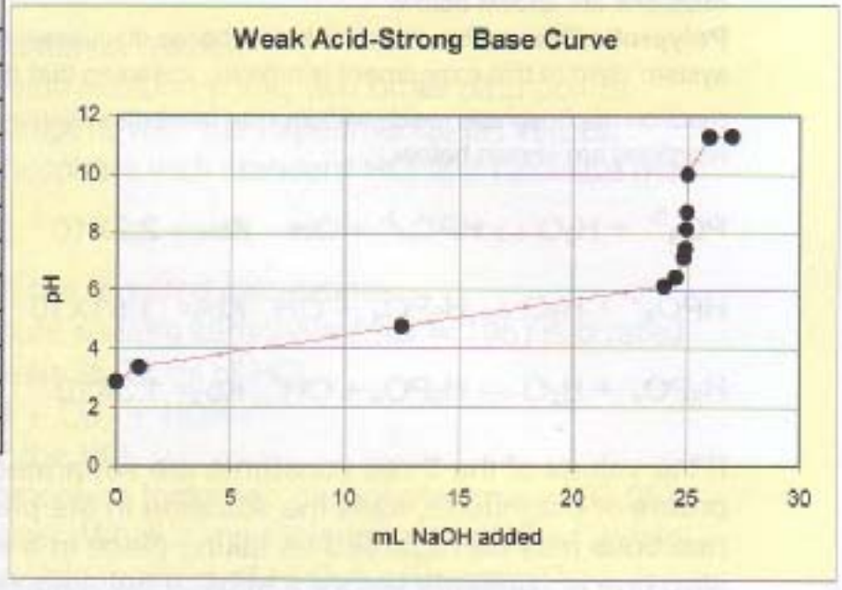
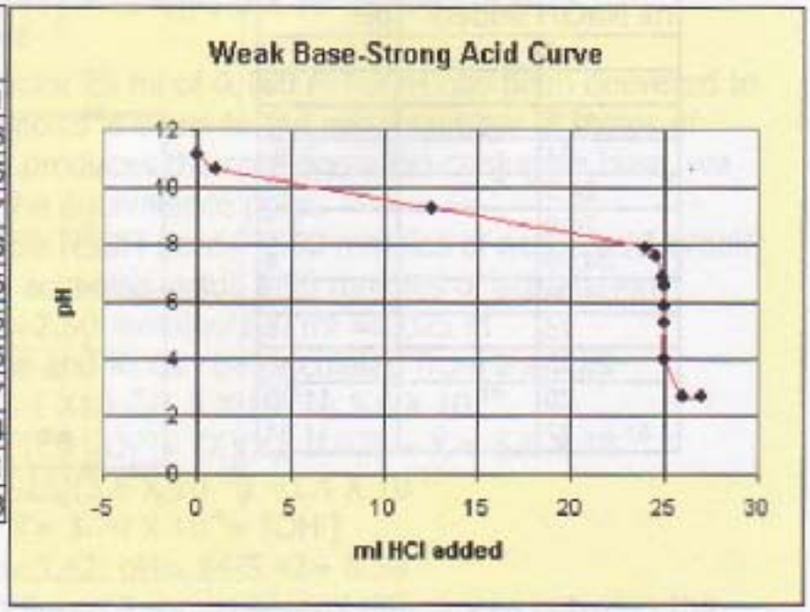


Figure 3
A weak base-strong acid titration curve, showing how the pH decreases as 0.100 M HCl is added to 25.00 ml of 0.100 M ammonia. The equivalence point pH is 5.27.

ml HCl added	pH
0	11.1
1	10.6
12.5	9.25
24	7.87
24.5	7.56
24.9	6.85
24.95	6.55
24.99	5.85
25	5.27
25.05	4
26	2.71
27	2.68



Polyprotic Bases-The weak acids and bases discussed above are monoprotic. The phosphate system used in this experiment is triprotic, meaning that there are three steps in the basic reaction of phosphate, each with its own base dissociation constant K_b. Thent K_b. The three basic reactions are shown below.

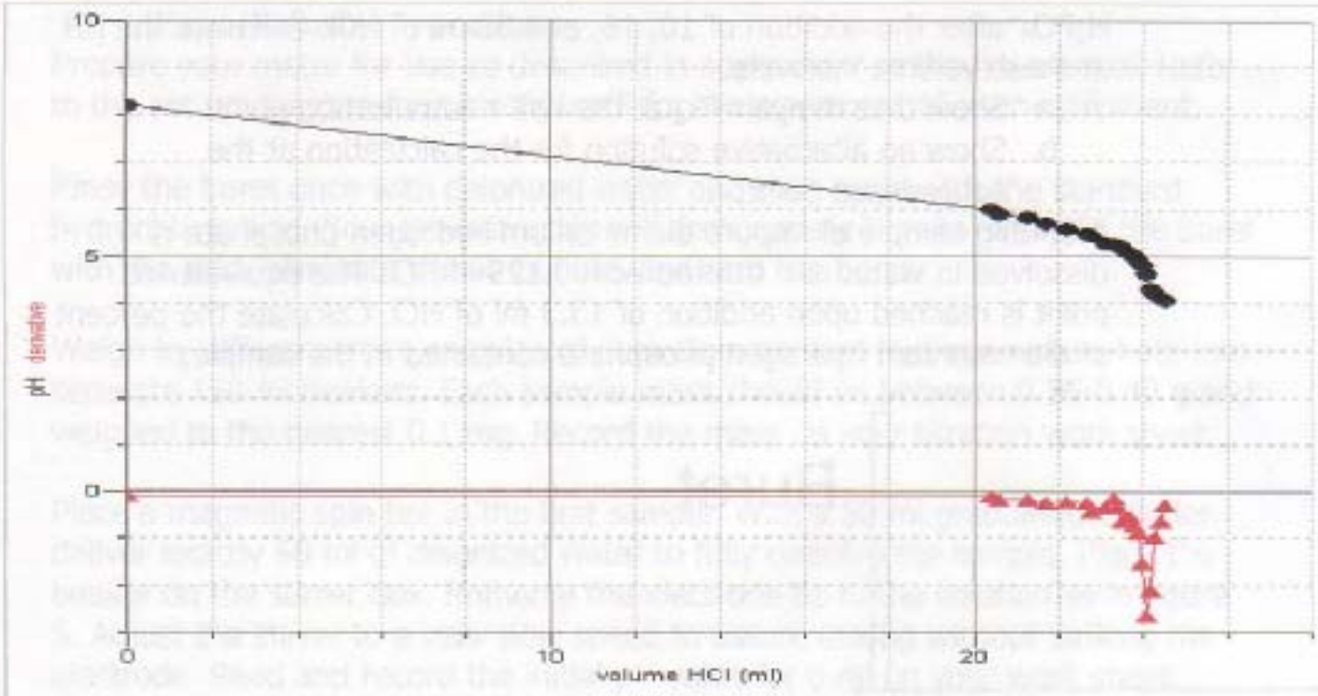
Polyprotic Bases-The weak acids and bases discussed above are monoprotic. The phosphate system used in this experiment is triprotic, meaning that there are three steps in the basic reaction of phosphate, each with its own base dissociation constant K_b. The reactions are shown below.

$PO_4^{3-} + H_2O \leftrightarrow HPO_4^{2-} + OH \quad Kb_1 = 2.2X10^{-2} \ [HPO_4^{2-}][OH^-]/[PO_4^{3-}]$

$HPO_4^{2-} + H_2O \leftrightarrow H_2PO_4^- + OH^- \quad Kb_2 = 1.61X10^{-7} \ [H_2PO_4^-][OH^-]/[HPO_4^{2-}]$

$H_2PO_4^- + H_2O \leftrightarrow H_3PO_4 + OH^- \quad Kb_3 = 1.3X10^{-12} \ [H_3PO_4][OH^-]/[H_2PO_4^-]$

If the values of the three constants are separated from each other by several orders of magnitude, as is the situation in the phosphate system, the three reactions may be regarded as taking place in a stepwise fashion. In other words, step one is complete before a substantial amount of step 2 takes place. As a result, the titration curve for the phosphate base with HCl, shown on the next page, resembles figure 3. The value of Kb_3 is so small that step 3 is not sufficiently complete to obtain a usable third step titration curve.



Experimental Outline

In this experiment we will be titrating diammonium hydrogen phosphate, $(NH_4)_2HPO_4$ with HCl. The net ionic equation is:

$$HPO_4^{2-} + H^+ \rightarrow H_2PO_4^-$$

As HCl is added to the HPO_4^{2-} solution and H_2PO_4 is produced, a buffer is formed from the two chemical species. The pH can be calculated at various points along the titration curve.

- Learn to use and calibrate a pH meter, analytical balance, and buret.
- Titrate an known mass of pure phosphate with standard HCl to an equivalence point
- Plot a curve of the best experimental results.
- Calculate the pH at the half neutralization point, two other data points, and the equivalence point. Compare with the experimental pH values.
- Titrate a sample of impure phosphate with standard HCl and calculate the percent purity of the sample.

The Following problems illustrate the required calculations.

1. A sample of 0.2231 g of pure sodium carbonate (mw = 106) is titrated to the equivalence point with 36.72 ml of HCl.
   $Na_2CO_3 + 2\ HCl \rightarrow 2\ NaCl + CO_2 + HOH$
   Determine the molarity of the HCl.
2. A 0.384 g sample of diammonium hydrogen phosphate (mw =132.06) is dissolved in 50 ml of water. What is the molarity of the HPO_4^{2-} ion in the solution (assume negligible reaction of HPO_4^{2-} with water)?
3. A 0.520 g sample of DAHP is dissolved in 50 ml water and titrated with 0.125 M HCl. Draw a chart and calculate the molarity of the HPO_4^{2-},

$H_2PO_4^-$ after the addition of 10, 16, and 32 ml of HCl. Calculate the pH at these volume intervals.

   a. Show that the pH=Pk_a at the half neutralization point.
   b. Show an alternative solution for the calculation at the equivalence point.

4. A 0.427g sample of impure diammonium hydrogen phosphate is dissolved in water and titrated with 0.125 M HCl. The equivalence point is reached upon addition of 13.3 ml of HCl. Calculate the percent of diammonium hydrogen phosphate contained in the sample.

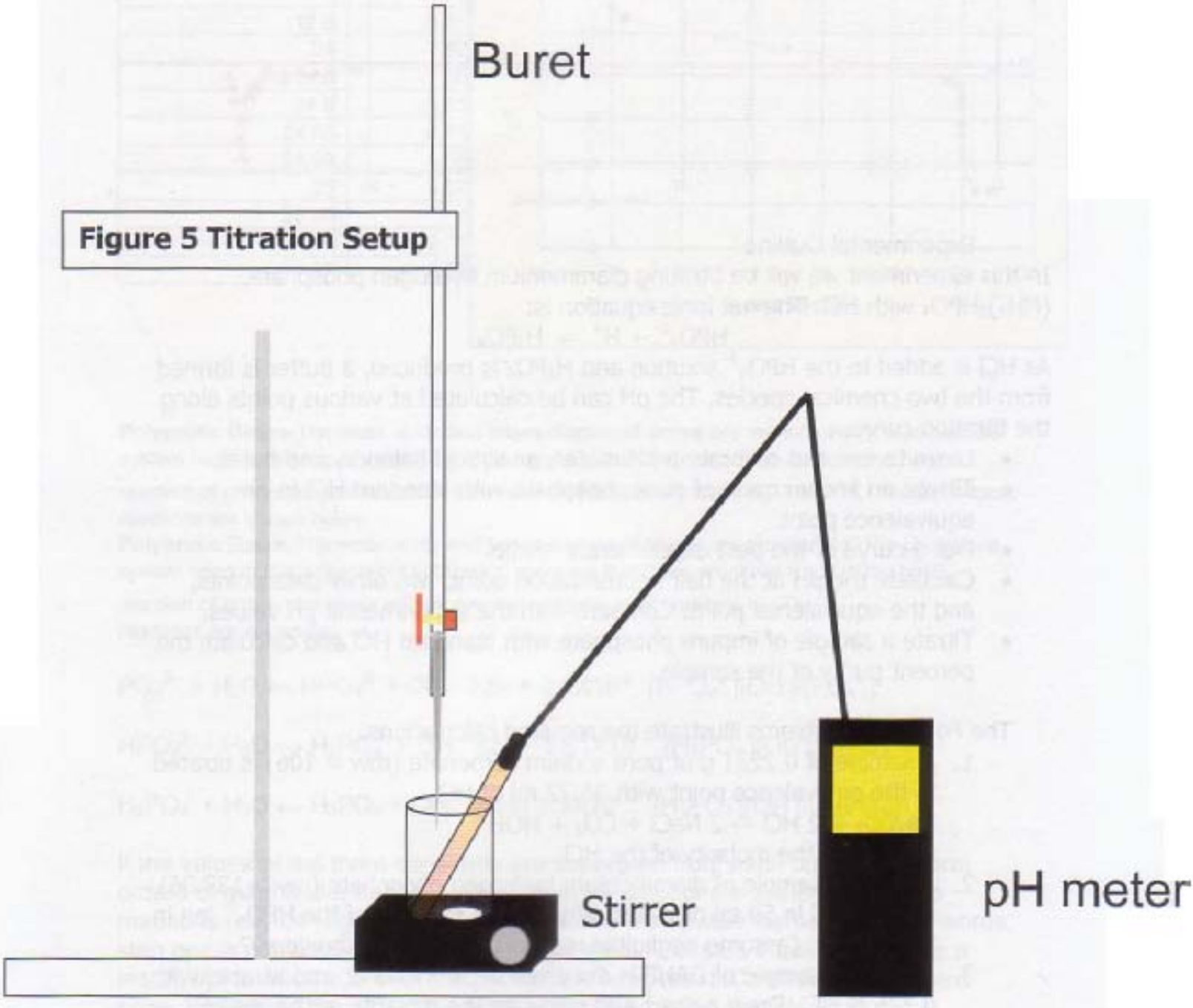


Figure 5 Titration Setup

Experimental Procedure

Prepare your meter for use as described in appendix V of the lab manual. Refer to the set up diagram found in figure 5 for the placement of your equipment.

Rinse the buret once with deionized water and then twice with the standard hydrochloric acid. Your lab instructor will demonstrate how to safely fill the buret with the acid, eliminate the air bubble, and zero the buret.

Weigh by difference two samples of pure diammonium hydrogen phosphate into separate 150 ml beakers. Each sample mass should be between 0.35-0.40 g and weighed to the nearest 0.1 mg. Record the mass on your titration work sheet.

Place a magnetic spin bar in the first sample. With a 50 ml graduated cylinder deliver exactly 50 ml of deionized water to fully dissolve the sample. Place the beaker on the stirrer box. Immerse the electrode tip in the solution as in figure 5. Adjust the stirrer to a very slow speed to assure mixing without striking the electrode. Read and record the initial pH value for o ml on your work sheet.

Strategy 1

Begin by adding 1 ml increments of the standardized HCl. Record the pH and volume on your work sheet after each addition of acid. As the equivalence point is approached, decrease the size of the acid addition until, finally, 0.1 ml portions are being added. Continue the titration until you have added 8-10 ml of HCl past the equivalence point.

Strategy 2

Record the initial pH at 0.0 ml. Add acid at a slow rate until the meter shows a reading between 6.0-6.1 and record the data. From pH 6.0 to approximately 5.25 add 0.5 ml HCl and record all results. From pH 5.2 to 4.0 add 0.1 ml portions and record all results. Stop at pH 4.

Perform as many titrations as needed to submit 2 results, which confirm the posted percentage. (End session 2)

Initially a simple subtraction will be performed on your data to find the equivalence point. The class will plot their best two results with CBL Graph. The plot will locate the equivalence point and the half neutralization value. Your lab instructor will help you to locate the equivalence point more precisely with the use of the derivative function on the program. The template for this experiment is called pH.dat.

An 8.5 X 14 inch calculation sheet will be provided for calculation of the pH at four data points. Compare the experimental and calculated results. (Session 3)

For analysis of the Unknown Sample of Phosphate.

1. Weigh by difference 4 samples of 0.4-0.5 g to the nearest 0.1mg into 150 ml beakers. Record the masses on the unknown work sheet.
2. Perform the titration as you did with the known phosphate material.
3. Determine the percent phosphate in the sample. (% Precision +/-0.25)

Report Sheet For pH Titration Experiment

Name_____Class_____ Section__

"Known" Phosphate Determination (week 2)

	Mass, g	Ml HCl needed to reach eq. pt.	Exp. pH at eq. pt.
Sample 1			
Sample 2			
Molarity HCl		**% Diammonium hydrogen Phosphate**	**1.** **2.**

Unknown Phosphate Determination

Sample vial #_____ Molarity HCl_____

Mass, g	Ml HCl	% Phosphate
1		
2		
3		
4		
Ave %		

Known Phosphate Work Sheet

Sample 1	V HCl	pH	Notes	Sample 2	V HCl	pH	Notes
Mass				Mass			

Sample 3	V HCl	pH	Notes	Sample 4	V HCl	pH	Notes
Mass				Mass			

Unknown Phosphate Work Sheet

Run 1	V HCl	pH	Run 2	V HCl	pH	Run 3	V HCl	pH	Run 4	V HCl	pH
Mass			Mass			Mass			Mass		

Analytical Group 1

Ag^+ Silver (I) or argentous ion
Pb^{2+} lead (II) or plumbous ion
Hg_2^{2+} *mercury (I) or mercurous ion*

Preparation for this group
Complete the pre-laboratory assignment for analytical group 1

Part I Preliminary tests.

The ions in this group form insoluble chlorides and are removed from solution by adding chloride ion. First we will test the individual ions a test solution of an ion consists of 3 drops of its side shelf solution plus 7 drops of water. Label three 10 X 75 mm test tubes and make test solutions of the three ions in this group.

1.The insoluble chlorides

Add 2 drops of 6M HCl to each test solution. If the precipitate does not appear within half a minute, scratch the inside of the tube vigorously with a small stirring rod. Record your observations. Important things to note about a precipitate are its color and its appearance. Your lab instructor will demonstrate the use of a centrifuge. Centrifuge the three mixtures. Remove each centrifugate with a pipette or by decanting. Discard the centrifugate and keep the precipitate.

Imagine what will happen when you add HCl to an unknown solution that might contain two or three of the group I ions. The unknown precipitate will then contain two or three chlorides mixed together.

2. Solubility of the chlorides in hot water

Add about 1 ml water to each precipitate and heat in a boiling water bath for a few minutes with frequent mixing. Centrifuge any remaining precipitates while still hot, and immediately decant each centrifugate into a separate test tube (save the precipitates). Add 1 drop of KI to each of the solutions. Record your observations which solution produced an iodide precipitate? Write its formula. Why did no precipitate appear in the other solutions?

In analyzing an unknown: If the iodide test shows Pb^{2+} to be present, treat the remaining precipitate with hot water again to remove all traces of $PbCl_2$ before continuing with further tests.

3. Effect of ammonia on the remaining chloride precipitates

Two chloride precipitates should remain after the hot water treatment. Add 6M NH_3 drop wise with constant stirring to the AgCl precipitate until it dissolves. Then add about the same amount of NH_3 to the Hg_2Cl_2 precipitate.

AgCl dissolves in ammonia to form the complex diaminesilver ion, $Ag(NH_3)_2^+$. Acid destroys the complex ion by converting the NH_3 to NH_4^+.

$$\mathbf{AgCl\ (s) + 2\ NH_3\ (aq) \rightarrow Ag(NH_3)_2^+(aq) + Cl^-(aq)}$$

$$\mathbf{Ag(NH_3)_2^+(aq) + 2\ H^+(aq) + Cl^-(aq) \rightarrow AgCl(s) + NH_4Cl\ (aq)}$$

Ammonia converts Hg_2Cl_2 to a mixture of black mercury and white mercuric amidochloride. The combined precipitate appears black.

$Hg_2Cl_2(s) + 2\ NH_3(aq) \rightarrow HgNH_2Cl(s) + Hg(s) + NH_4Cl(aq)$

Imagine what you would see if you add ammonia to a precipitate that contains both AgCl and Hg_2Cl_2. How could you tell whether AgCl is present?

Add 6 M HNO_3 to both solutions until the ammonia has been neutralized to pH paper. Record your observations.

Part II Other reactions of Group I ions

The following reactions are important in the chemistry of the group I ions even though they are not part of the standard analytical scheme.

1. Iodides
   Add 1 drop of 6M KI to a few drops of the silver and mercury ion test solutions (you have already seen the lead iodide precipitate). Record the color of each precipitate and write its chemical formula.
2. Hydroxides and oxides
   Add 1 drop of 6 M NaOH to each test solution. Observe. Add several more drops of 6 M NaOH to each mixture stir and observe.
   Lead ion forms a hydroxide, silver ion forms an oxide, and mercurous forms a mixture of Hg and HgO.
   Write the equations!

Part III Analysis of an unknown solution containing group I ions

Obtain a group I unknown and analyze it for silver, lead, and mercury ions using the flow chart which follows. The flow chart is based on the reactions, which you did in part 1. It serves as a road map for analysis, showing at each step what is present and where to go next. A horizontal line represents a separation, usually by centrifugation. A box represents a precipitation reaction. Observe that each formula in the flow chart represents the actual form of the element at that stage of the procedure.

Analytical Group I Flow Chart

Take 10 drops of group 1 unknown (do not dilute)
Add 2 drops of 6M HCl. Let Stand. Scratch the tube with a glass rod if no precipitate appears. Centrifuge for 2-3 minutes.

$AgCl$, $PbCl_2$, Hg_2Cl_2
All white ppt.

Ions of later groups

Add 1 ml water, heat for 2-3 minutes. Centrifuge Briefly.
Pipette off the liquid
Save Precipitate. Test liquid

$AgCl$, Hg_2Cl_2

Pb^{2+}
Add 1 drop of KI

Yellow PbI_2

Add 6M Ammonium hydroxide and observe if there is a color change, complete dissolution of ppt, or partial dissolution. Centrifuge for 2-3 minutes. Pipette off the colorless liquid

Hg (black)
$HgNH_2Cl$ (white)

$Ag(NH_3)_2^+$
Add 6M HNO_3 to acidify. Observe formation of ppt

AgCl (white)

Prelaboratory Assignment

Name	
Lab Section	

Fill in the following table with the correct formulas for the nitrates, chlorides, iodides, and oxides of the three ions in this group.

	Nitrate	Chloride	Iodide	Oxide
Silver (I)				
Lead (II)				
Mercury (I)				

Write formulas for the following (you will find them in the lab instructions).

diamine silver (I) ion_____ mercuric amido chloride _____

Precipitate A is white and precipitate B is black. What color would a precipitate appear if it contains

i. A only_____
ii. B only_____
iii. B plus a small amount of A, well mixed_____?

If these three precipitates were unlabeled, which one or ones could you identify by color alone? _____

Precipitate p dissolves in acid, precipitate q does not. What would you observe if each of the following precipitates is well mixed with acid?

a. p only_____
b. q only_____
c. q plus a small amount of p mixed _____

If these three precipitates were unlabeled, which one or ones could you easily identify by acid treatment alone? _____

Qualitative Analysis: Analytical Group 1 Report Sheet

Name	
Lab Section	Date

Analysis of Unknown

Summary: Ions Detected_____

Ions not present_____

Draw a flow diagram for how you achieved your results. Indicate by boxes the precipitates you found.

Electrochemistry Experiment For Qualitative and Quantitative Measurement of Silver Ion Equilibriums

Objectives

1. To learn how to construct galvanic cells and measure their electrical potential.
2. To calculate silver ion equilibrium constants and solubility constants from experimental data using the Nernst Equation.
3. To develop a quantitative model for anion concentration determination.

Preliminary Reading

1. Review chapter 20 in the Brown and Lemay Text.
2. Review the appendices in the lab manual for volume measurement and the use of a digital multimeter.

Introduction

The cell potentials of four silver ion reaction are measured in this experiment.

1. $Ag^+ + Cl^- \rightarrow AgCl\ (s)$
2. $Ag^+ + Br^- \rightarrow AgBr\ (s)$
3. $Ag^+ + I^- \rightarrow AgI\ (s)$
4. $Ag^+ + 2S_2O_3^{2-} \rightarrow Ag(S_2O_3)_2^{3-}$

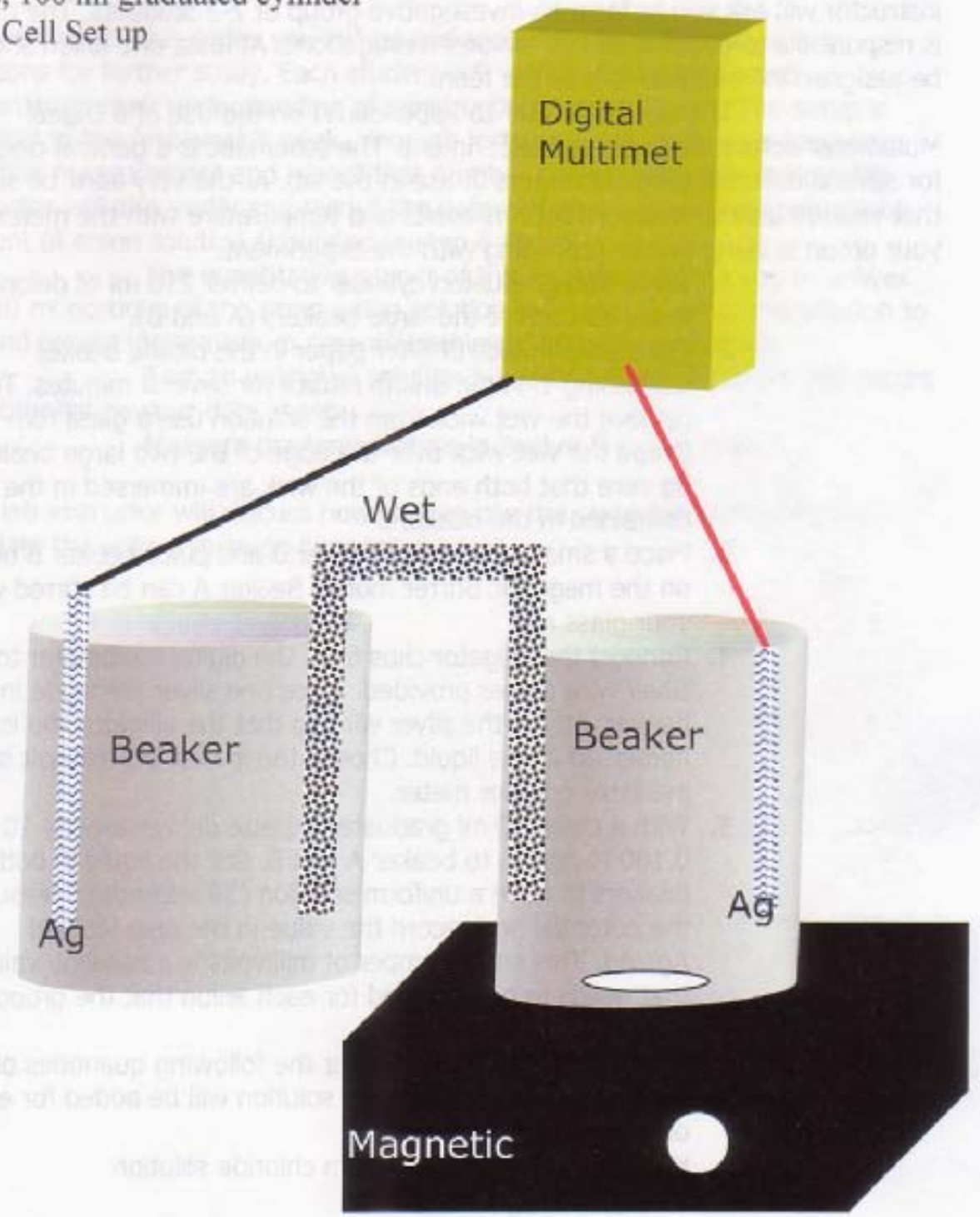
In week 1 of this experiment the cell potential, E_{cell}, will be measured with a digital multimeter at ion concentrations other than 1 mol/l. In addition, the temperature of the experimental setup will measured (beaker B). From the measured E_{cell} value, the standard potential, E^0_{cell} will be calculated. The exact directions for construction of a galvanic cell are given in the next section.

In week 2 of the experiment, each student will measure the cell potential for five different concentrations of an anion. This will assist in generating an average standard cell potential. The average cell potential will be used to find an unknown anion concentration.

Experimental Procedure

- Required Materials per student
  Two 400 ml beakers, two 150 ml beakers, 10,25 ml pipettes, plastic wash bottle, 100 ml graduated cylinder

2. Galvanic Cell Set up



This setup is the starting point for all other work done in this experiment. The lab instructor will ask you to form an investigative group of 2-3 students. The group is responsible to perform all four anion investigations. At least one anion should be assigned to each member of the team.

The class will refer to appendix VI on the Use of a Digital Multimeter before we begin the experiment. The schematic is a general diagram for several different types of meters in use in the lab. At the very least be sure that you are able to measure D.C. millivolts and temperature with the meter that your group is using before proceding with the experiment.

1. Use a 100 graduated cylinder to deliver 210 ml of deionized water to each of the large beakers (A and B).
2. Dip a single piece of filter paper in the plastic beaker containing 1M ammonium nitrate for several minutes. To remove the wet wick from the solution use a glass rod. Drape the wet wick over the edge of the two large beakers. Be sure that both ends of the wick are immersed in the liquid contained in the beakers.
3. Place a small spin bar in beaker B and place beaker B only on the magnetic Stirrer motor. Beaker A can be stirred with your glass rod.
4. Connect the alligator clips from the digital multimeter to the silver wire pieces provided. Place one silver electrode in each beaker. Adjust the silver wire so that the alligator clip is not immersed in the liquid. Choose the lowest DC millivolt setting available on your meter.
5. With a clean 10 ml graduated pipette deliver exactly 10 ml of 0.100 M $AgNO_3$ to beaker A and B. Stir the liquid in both beakers to have a uniform solution (30 seconds). Measure the potential and record the value in the area labeled Ag//Ag. This small number of millivolts is a baseline value that needs to be recorded for each anion that the group measures.
6. Use a 25 ml pipette to deliver the following quantities of anion to beaker B. Only one solution will be added for each determination.
   KCl-20 ml of 0.1 M potassium chloride solution
   KBr- 15 ml of 0.1 M solution
   KI- 15 ml of 0.1M solution
   $Na_2S_2O_3$ – 40 ml of 0.1 M solution
7. Stir the solution in beaker B and allow 30-45 seconds for mixing. The meter should reach a maximum potential for each anion. Record that potential as E_{cell} on your data sheet. Measure the temperature for Beaker B and record on your data sheet.

8. Your lab instructor will discuss the calculations for E^0 and K_{sp}.

In Week two of this series you will be assigned one of the four silver ion reactions for further study. Each student will work independently and demonstrate their understanding of constructing a galvanic cell. The setup is identical to the first week's work. Your lab instructor will verify your base line potential measurement and record that number on your data sheet. Your lab instructor will also verify and record the potential after adding the appropriate amount of anion solution stipulated in step 6 above.

The quantitative aspect of this experiment asks you to deliver five 10 ml portions of the same anion solution to beaker B. Allow the solution to stir and record the maximum potential achieved after each addition.

Test an unknown solution by adding 10 ml. Measure and record the potential on your data sheet.

Measure the temperature in beaker B at this point.

Your lab instructor will discuss how to evaluate the quantitative model and calculate the unknown anion concentration.

Data Table For Electrochemistry Experiment of Silver Ion Equilibrium

Qualitative Determination of Potentials for Silver Systems

	Cl	Br	I	S_2O_3
$Ag^+//Ag^+$				
E_{cell}				
Temperature				
E^0_{cell}				
K_{sp}				

Quantitative Determination of Potential for a Silver System

Ag//Ag						
E_{cell} Verification						
E_{cell}	V 1	V2	V3	V4	V5	Unknown
E^0_{cell}						
E^0_{cell} Average		Temperature		Notes		
Anion Conc. Net						

Student Name_____

Anion_____

Appendix I Volume Measurements

You will often need to measure the volumes of liquids in your laboratory work. Several measuring vessels are available and the choice of which to use will depend on the required accuracy of the measurement.

Beakers and conical flasks some of these have approximate volume markings that can be used when rough estimates of volume are acceptable.

Graduated Cylinders These are used if reasonable accuracy is important. A 10 ml graduated cylinder has 1 ml graduations; these are numbered. Each 1 ml area is divided into five small divisions of 0.2 ml each; these are not numbered. The position of the bottom of the liquid meniscus gives the volume reading. In figure 1 the meniscus is between the 7.6 and 7.8 ml marks; the volume is more than 7.6 but less than 7.8 ml. Mentally divide the distance into smaller divisions and estimate where the meniscus lies along this scale. Because the 0.2 ml marks are so close together you will probably find it possible to divide the distance only into two halves rather than into smaller divisions such as tenths; that is, you will probably be able to distinguish a distance that is about halfway between the marks but not a smaller distance. Volumes from about 7.65 ml to 7.75 ml would be indistinguishable and the meniscus would look like it was about halfway between 7.6 ml and 7.8 ml; your reading would therefore be 7.7 ml. Since any true volume from 7.65 ml to 7.75 ml would look the same to you, there is an uncertainty of 0.1 ml in the volume reading of 7.7 ml, a possible error that cannot be eliminated even with practice, for it arises from the limitations of your eyes and of the equipment.

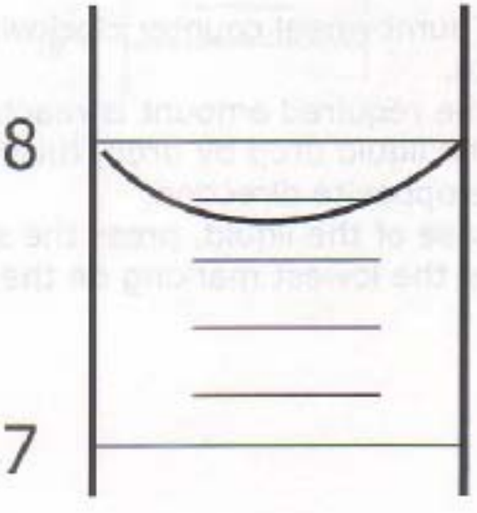
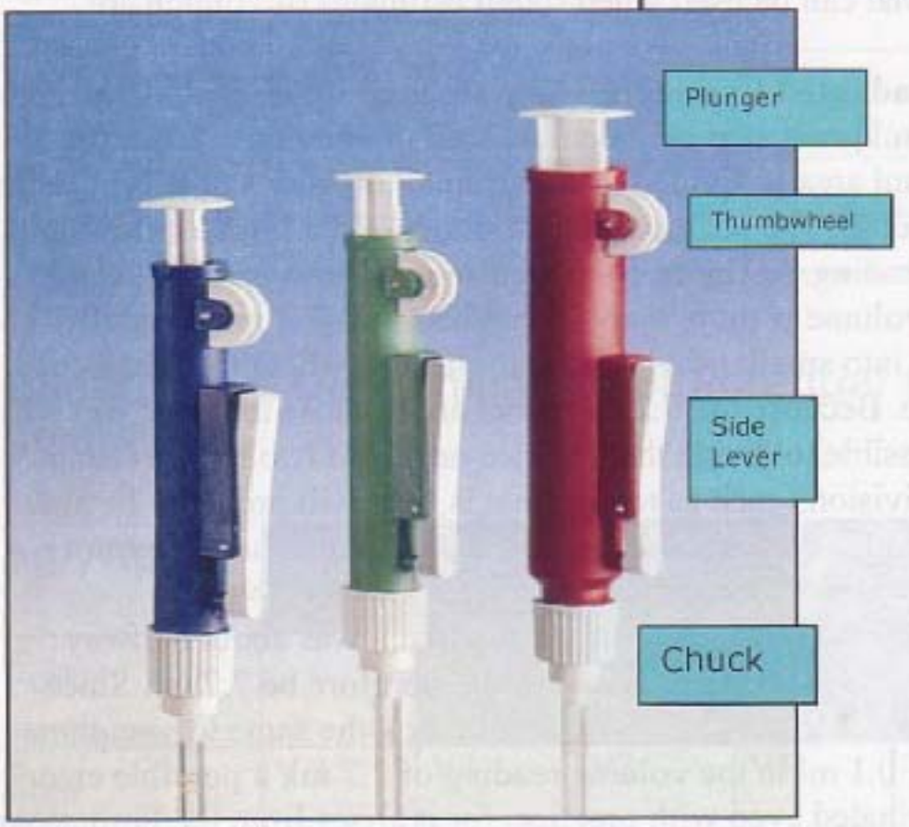


Figure 1

Volumetric Glassware

This term includes pipettes, burets, and volumetric flasks. These are constructed and calibrated to be much more accurate than graduated cylinders and are the most accurate glassware you will use to measure volumes.

Fast Release Pipette Pump II



To insert pipette:

1. Depress the plunger.
2. Insert the proper pipette into the chuck.

To pipette:

1. Rotate the Thumbwheel counter clockwise; the liquid will rise in the pipette.
2. Stop when the required amount is reached.
3. To release the liquid drop by drop, turn the thumbwheel slowly in the opposite direction.
4. For fast release of the liquid, press the side lever until the level reaches the lowest marking on the pipette.

Burets. A Teflon stopcock never needs to be greased. To Clean the buret makeup a dilute soap solution and coat the inside of the buret. From a beaker rinse out the soap with a large amount of tap water . Finally rinse the buret with deionized water from a plastic bottle Clamp the buret in place, close the stopcock, and fill the buret with solution. Open the stopcock and drain solution from the buret until the tip of the buret is filled and does not contain an air bubble. If necessary add more solution so that the buret is filled to just below the 0.00 mark.

Each graduation mark on the buret corresponds to 0.1 mL. Estimate the fractional distance between two marks to obtain a reading to the nearest 0.02 mL. The position of the meniscus in Figure 3 is 18.37 mL. In your readings it is important to avoid errors that result from viewing the meniscus from various angles. Note that the meniscus seems to change position depending on whether you look at it from above or below (again, see Figure 3). To make an accurate reading the eye must be level with the meniscus. To ensure this, look at the buret so that the front of the mL graduation mark nearest the meniscus is superimposed on the back of this same mark and your eyes see only a single line; read the meniscus level from this position.

When you begin to use a buret you might find it difficult or awkward to master the proper technique. However, it will be worthwhile to exert the effort required to use a buret properly. If you are right-handed operate the stopcock with your left hand (see Figure 4A); grasp the stopcock's handle between your thumb on the front of it and your first and second fingers on the back of it. With your right hand, continuously swirl clockwise the flask into which the solution flows. If you are left-handed, operate the stopcock with the thumb and first fingers of your right hand (see Fig. 4b); swirl the flask counterclockwise with your left hand.

Before beginning a titration, touch the buret tip against the inside of a waste beaker to remove the drop of liquid that might be clinging to it.

After running solution out of a buret, wait a minute before making a volume reading so that the liquid remaining on the upper wall has time to drain down into the bulk of the liquid.

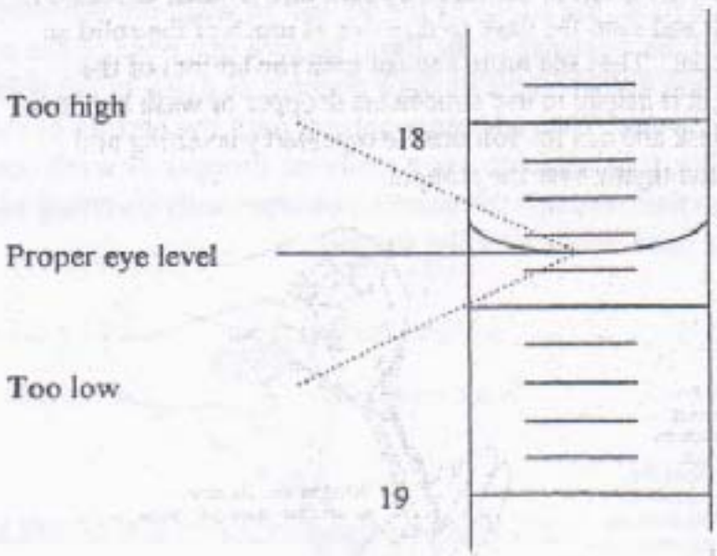


Figure 3 Reading a buret

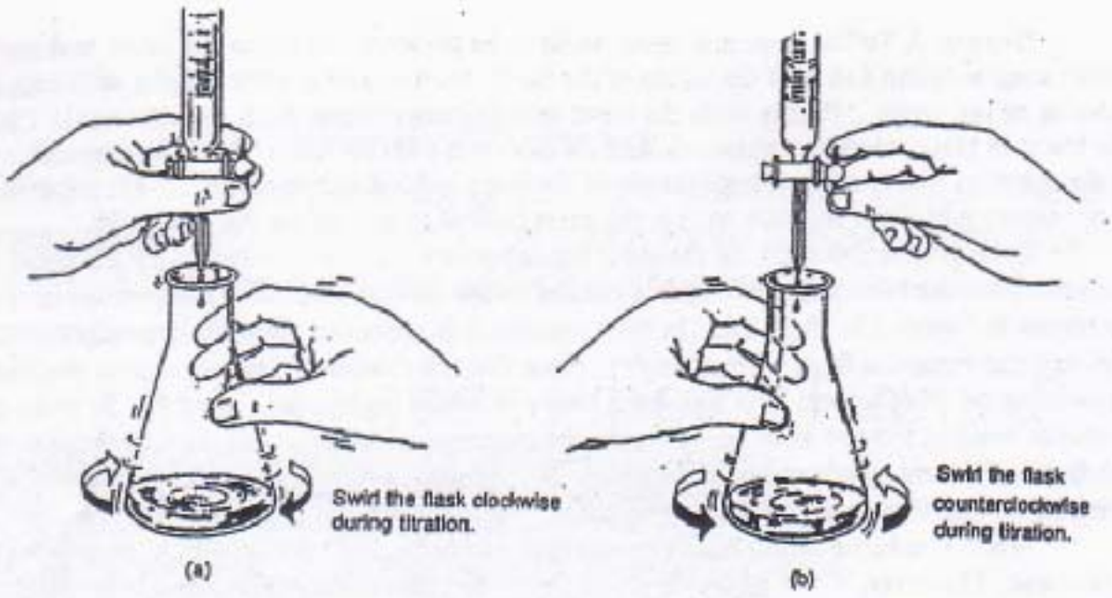


Figure 4 Proper Buret technique

Volumetric flasks. Volumetric flasks (see Figure 5) are calibrated to contain a specified volume; they are used to prepare solutions of accurately known molarity (moles of solute per liter of solution). For example, 0.100 mole of NaCl is put into a 1.00-liter volumetric flask and the flask is filled with water to the calibration mark giving 1.00 liter of solution; the concentration is 0.100M. The solid that is to be dissolved must be very carefully weighted, but it is not necessary to measure the amount of solvent that is used; instead, the final volume of solution is accurately known. After you put the solid into the flask, use a little of the solvent to wash out the container in which the solid was weighed and add the washings to the flask; be sure that none of the solid is lost. Add a little more solvent to the flask and swirl the flask to dissolve as much of the solid as possible before the flask is filled with solvent. Then add more solvent until the bottom of the meniscus just touches the calibration line; it is helpful to use a medicine dropper or wash bottle to add the last few milliliters. Stopper the flask and mix the solution be repeatedly inverting and uprighting the flask while holding your hand tightly over the stopper.

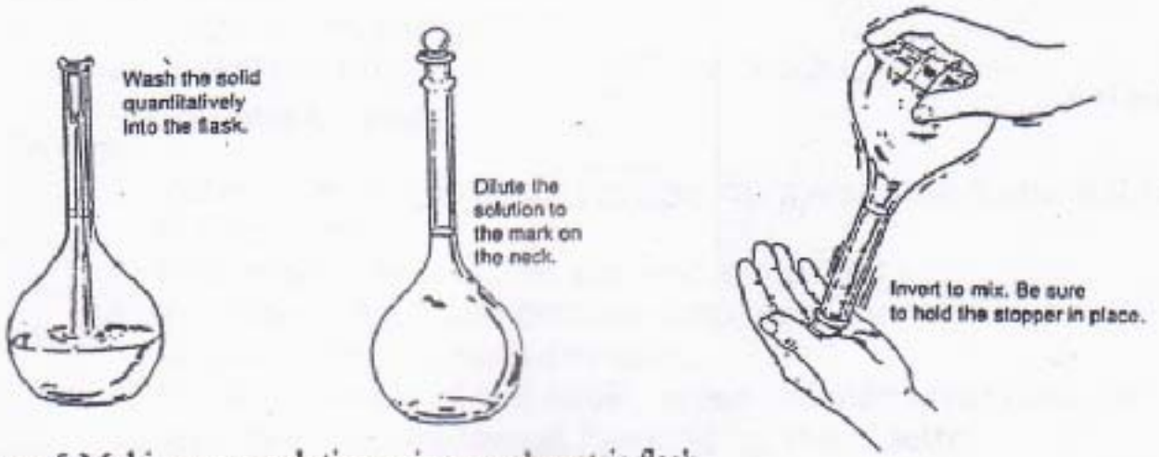


Figure 5 Making up a solution using a volumetric flask

Appendix II

PROCESSING THE DATA--CBL Graphing Made Easy

- The CBL Graphing program is designed to help you gain a basic understanding of simple graphing techniques with the use of a computer based program. This program is designed to help you with more accurate graphing and most importantly time conservation.

- Firstly, double click the CBL Graphing Icon on the monitor to get into the application, then click OK to begin. When the program starts, you will see a Data Table window on the left of the screen and a Graph window to the right of the screen. If you do not see these windows, ask for help from your workshop leader. If you do see these windows, begin.

Entering and Editing Data for a one plot graph:

A. The first step is to enter your recorded data onto the data table of the graphing program. (You will note the data table window is labeled **X** and **Y**.)

B. You will note that the top **X** box is already highlighted in bold gray. You may begin typing your first entry immediately. Don't worry about the correct number of significant figures, we will correct that later. Then press **enter**.

- You will now see that the top **Y** box is highlighted in bold gray. Type your first "**Y**" value and press **enter**.

C. Follow this routine until you have entered all your data. When you have entered the final entry for the **Y** box press return and enter your initials in the final **X** box which will be highlighted.

D. As you enter the "**X**" and "**Y**" values, the program will automatically graph the data for you.

Note: If you are entering numbers in scientific notation, use the "**E**" or "**e**" key for the exponent.

Ex>	TO ENTER:	TYPE THIS:
	3.5×10^4	3.5 E4 or 3.5 e^4
	-3.5×10^4	-3.5 E4 or 3.6 e^4

Editing the Axis labels, Units and Graph Title:

A. You now have a completed graph, but there is a problem, you forgot to label your Axis on the graph. Don't worry, you can go back and change it.

- Remember that your initial boxes are labeled "**X**" and "**Y**". To re-label your Axis, simply go back to the Data Table, containing the data you previously typed and double click the box containing the "**X**" and "**Y**", and a pop-up window appears.

B. To make these changes, click your mouse in **"New Names"**. Delete **"X"** or **"Y"** and enter your title in **"New Name"** box. Click in **"New Units"** and enter the appropriate units.

- Go to **"Rounding"** and click on **"decimal places"** box. Delete the number then enter the correct decimal places.

- Click in circle next to **"Significant Figures"**. Once the box appears, click in the box, delete the number and enter the correct number of significant figures.

- Now is a good time to look at your changes before your proceed. All of these changes can be done in the same pop-up window. (Do not press **enter/return** until absolutely all changes have been made or you will have to click **"X"** or **"Y"** cell to get the pop-up window again.)

- At this time you may also change your **"point protector"**, the symbol that represents your data to which ever symbol you want. (To actually change the color of the point protector and the symbol al changes have to be done when changing the **"Y"** Axis label.)

- Once you are satisfied with the changes, click the box that says **OK**. Your screen will return to the data table and graph with the changes you have just made.

- To change the tittle of your graph, simply click the title of the graph window. You will see the graph title highlighted. Press **"delete"** and enter the change along with your initials and press **return**. (Be sure at this point to personalize your graph with your initials to avoid confusion before printing!)

- Congratulations, you have made your first graph!

Printing your Data Tables and Graphs:

- To print the data table, click on the **Data Table Window**. The title will be highlighted in blue. Go to **File** menu and click, select **Print**. Choose **Data Table** from the small blue box and click. Click the **OK** box on the pop-up window.

- To print your graph, click on **Graph Window**. The title will be highlighted in blue. Go to **File** menu and click. Select **Print**. From the blue box choose **Selected Display**. click on the **OK** box on the pop-up window.

Appendix III Processing a graph for a "Best-Fit" linear regresssion line using the CBL Graph Program

This program option causes the "best-fit" linear regression line to be drawn through all or part of the data. The line is calculated using the method of least squares.

1. *See appendix 2 for entering and editing data. Stop at the congratulations salutation.*

2. To proceed, you may remove the connecting lines on your graph by highlighting the graph window in blue. Go to the word **Graph** at the top of the screen and highlight it. A pull down menu will appear. Drag the mouse down to " **Connecting Lines**" and click. (Notice the lines have disappeared.)

3. Highlight the Data Table Window in blue. Next click on the grey area of the Data Table window above the "X" to automatically highlight all of the X values on the Table . Repeat this operation for the Y values also.

4. Go back to the Graph Window and highlight it in blue. At the top of the screen highlight the word **Analyze** and click on it. A pull down menu will appear. Drag the mouse down to the word "**regression**" and click on it. A small Regression box will appear on the right side of your graph window. The letters in the box indicate: M= slope of the line; B= y intercept; cor= correlation coefficient.

5. Click on the blue portion of the regression box and drag the box towards the upper left of the graph window. This will provide you with an uninterrupted view of your graph and fit line. (notice two dark lines on either side of your graph window. These lines indicate that you have properly highlighted all of your data points.

6. Print your results as indicated in appendix II.

Appendix IV The Use of Analog Spectronic 20 and Digital Spectronic 20D Spectrophotometers.

Figures 1 and 2 show diagrams of the two types of instruments used in our General Chemistry Labs.

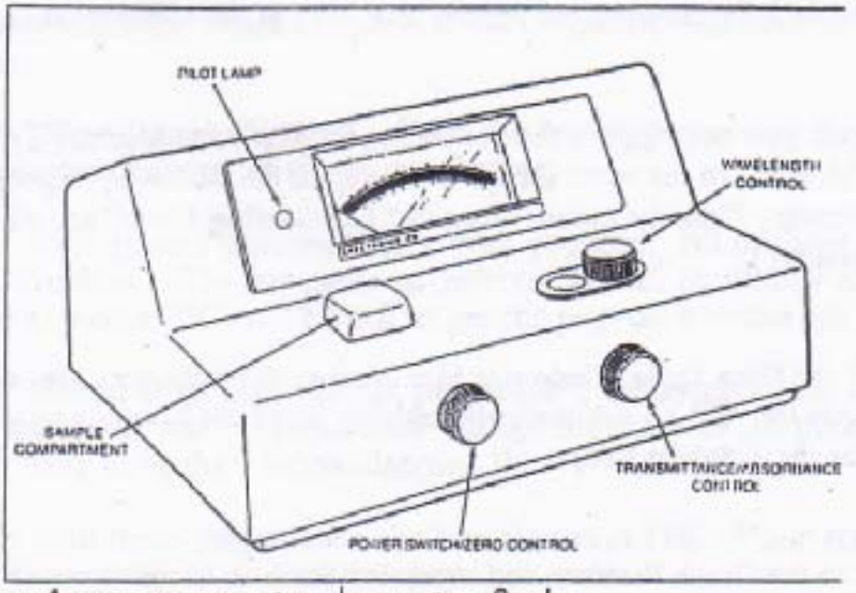


Figure 1 Key Operating Features Spectronic 20 Analog

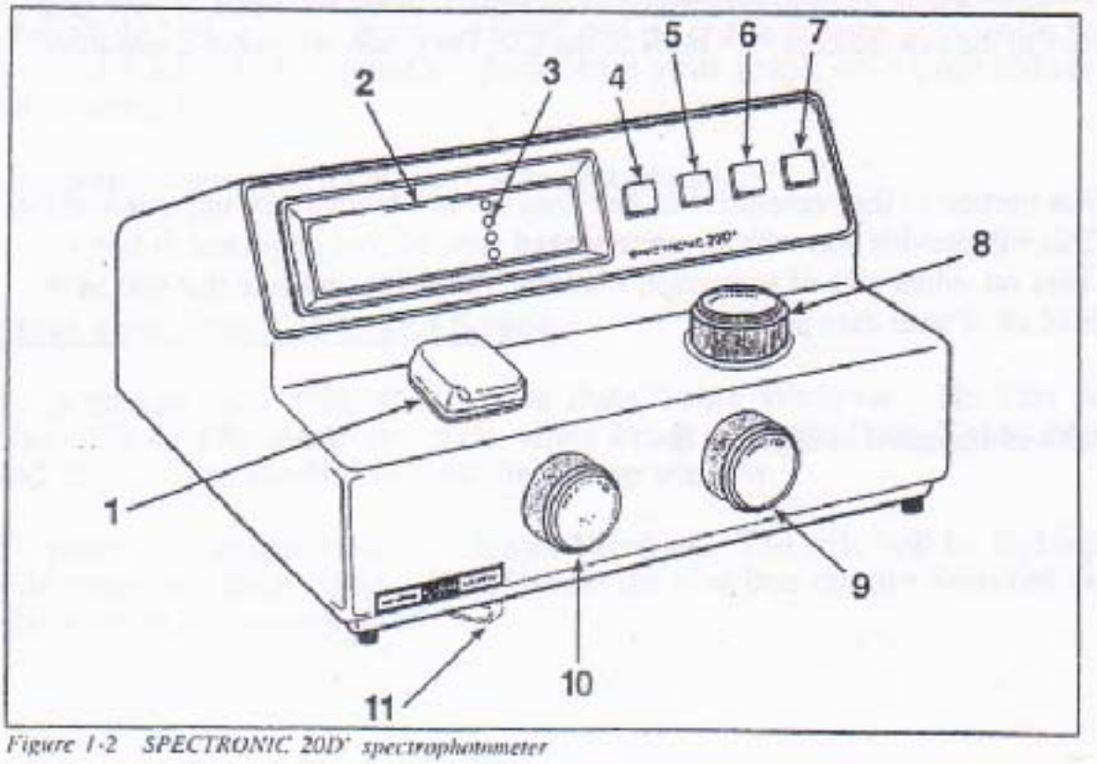


Figure 1-2 SPECTRONIC 20D' spectrophotometer

1. Sample compartment. 2.Digital Readout. 3. Mode indicators. 4. Mode selection. 5. Decrease. 6. Increase. 7. Print 8. Wavelength control. 9. Transmittance/ absorbance control (100%T/ 0A). 10. Power switch/ Zero T control. 11. Filter Lever.

Sample Measurement-Spectronic 20

a. Turn on the Spectronic 20 by turning the power switch/ zero control (knob on left side of instrument) clockwise. Allow the instrument to warm up at least 15 minutes to stabalize the source and detector.

b. After the warmup period, set to desired wavelength with the wavelength control knob.

c. Adjust the meter to 0%T with the power switch / zero control (knob on left hand side of the instrument). Make sure the sample compartment is empty and the cover is closed.

d. Fill a clean cuvet with water (or another blank solution) and wipe the cuvet with a towel to remove liquid droplets, dust, and fingerprints. Place the cuvet in the sample compartment and close the lid. Your lab instructor will demonstrate this procedure for the type of cuvet which is used for your experiment. Adjust the meter to 100%T with the transmittance/absorbance control (knob on right side of instrument). Remove the cell from the sample compartment.

e. Fill another cuvet with the solution(s) you wish to measure and insert the cuvet(s) into the sample compartment. Close the lid as before. Read the appropriate value (%T or A) from the meter

f. Remove the cuvet from the sample compartment and repeat your measurements for other solutions.

g. When all measurements are completerd, turn off the spectronic 20 by turning the power switch/ zero control counterclockwise until it clicks.

Note: To read the meter properly, align the needle with its reflection in the mirror.

Sample Measurement: Spectronic 20 D+

a. Turn on the Spectronic 20D+ by turning the power switch contol (knob on left side of instrument) clockwise. Allow the instrument to warmup for at least 15 minutes to stabalize.

b. After the warmup period, set the desired wavelength with the wavelength control knob.

c. Set the filter lever to the appropriate position for the selected wavelength

d. Adjust the display to 0%T with the zero control (knob on front left side of the instrument). Make sure that the sample compartment is empty and the cover is closed.

e. Set display mode to transmittance or absorbance by pressing the mode control key until the appropriate LED is lit.

f. Fill a clean cuvet with water (or another blank solution) and wipe the cuvet with a towel to remove liquid droplets, dust and fingerprints.

g. Place the cuvet in the cell holder and then into the compartment and close the lid. Your instructor will show you how to place the cuvet into the instrument.

h. Adjust the display to 100%T or 0.0A with the transmittance/ absorbance control (knob on the right side of the instrument).

I. Remove the cuvet from the instrument. Fill other cuvets with samples to be measured.

j. Place your samples into the instrument one at a time . Read the appropriate value (%T or A) from the display.

General Description

The Hanna Instrument 9024 is a waterproof, microprocessor-based, pH meter with the ability to accurately measure pH and temperature. All pH measurements are automatically compensated for the temperature effect.

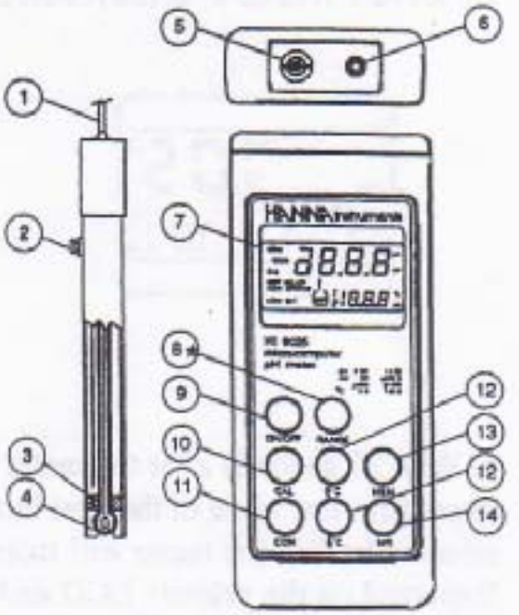
pH Calibration Procedure

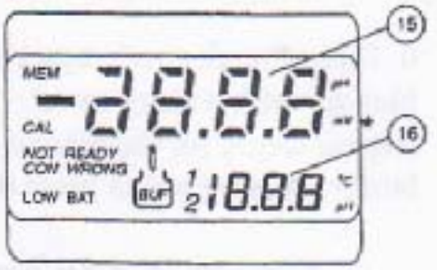
It is recommended that the instrument is calibrated each time it is used. The calibration is performed by simply submerging the electrode in 2 different standard pH buffer solutions to achieve accurate two-point calibration.

A functional description of meter is shown below. A detailed calibration routine follows.

FUNCTIONAL DESCRIPTION

HI 9024/HI 9025





1. Watertight Coaxial Cable
2. Electrolyte Fill Hole
3. Electrode Reference Junction
4. Sensing Membrane (Glass Bulb)
5. Electrode Connector (BNC)
6. Temperature Probe Connector
7. LCD Display
8. RANGE Button selects pH or mV (HI 9025 only)
9. ON/OFF Button
10. CAL Button to enter or exit calibration mode
11. CON Button to confirm calibration reading
12. ↑ °C and ↓ °C Buttons for manual temperature setting, or selecting pH buffer values
13. MEM Button stores pH in memory
14. MR Button recalls the stored value from memory
15. Primary Display
16. Secondary Display

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1. Turn on the meter with the on/off button (9).

2. Press the CAL button. The "CAL" and buffer bottle indicator will be displayed. The secondary LCD will display the fixed value of the first buffer solution - "4.01 pH". It is always good practice to calibrate the meter in pH 7 buffer first. To select this buffer, press the↑°c button. Allow the display to change until you are at 7.01 pH.
Please note that there are 5 standard buffers: 4.01, 6.86, 7.01, 9.18, and 10.01.

3. From a plastic wash bottle rinse the plastic barrel and the glass bulb of the electrode. Use a clean paper towel to blot dry the electrode.

4. Submerge the electrode into pH 7 buffer. The meter will attempt to stabilize. If the readings fluctuate for more than 10 seconds, the LCD will blink NOT READY. If the reading is stable, READY and CON will blink.

5. Wait 30 seconds after the meter has stabilized and press the "CON" button to confirm the value of the first buffer solution. If the reading is close to the selected buffer, the meter will store the reading. The buffer values is then displayed on the primary LCD and the secondary LCD will display the value of the next buffer solution together with second buffer bottle prompt.

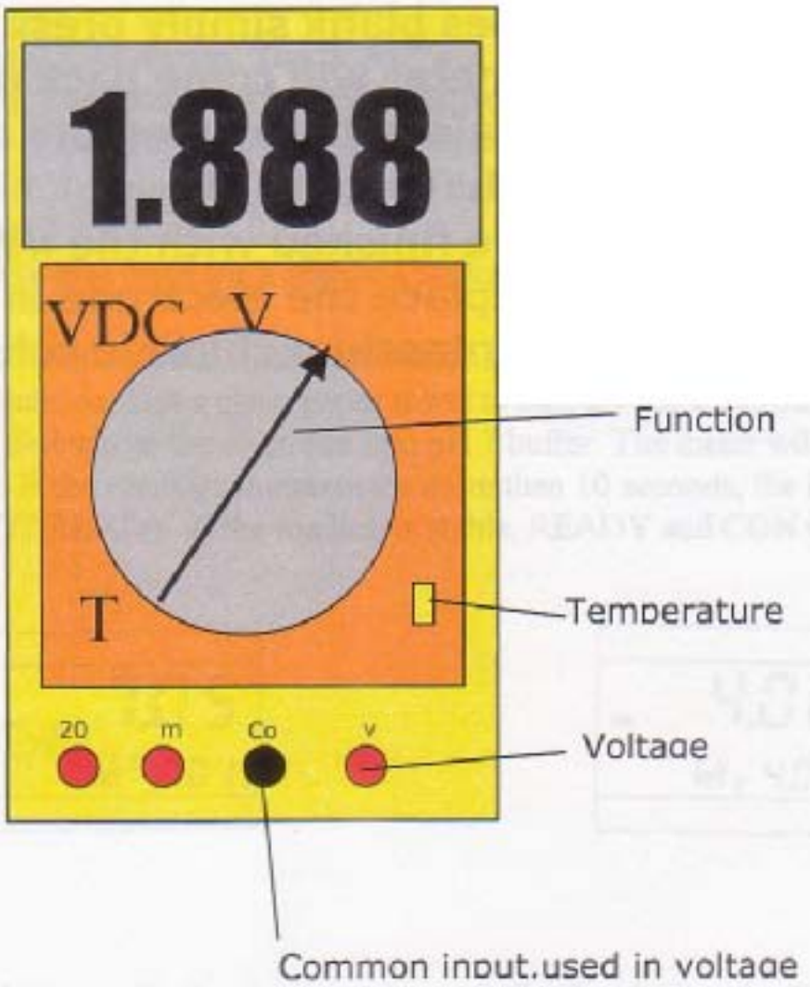
6. Rinse the electrode again with deionized water from the wash bottle and blot dry with a clean towel.
Repeat step 4 for the second buffer. Press the ↓°c to select the 4.01 pH buffer. Be sure not to press the CON button until the meter is ready.

After you have performed the 2-point calibration procedure the meter is ready for accurate pH measurements. Submerge the electrode in a beaker of solution to be measured. Do not allow the magnetic stirrer to strike the electrode.

During use the meter has a 15-minute time out feature. If the meter goes blank simply press the on/off button and the meter will come back on again. The calibration is maintained in the memory and does not need to be repeated.

When you are finished with the meter simply turn it off and replace the electrode in the plastic container with potassium chloride solution.

Appendix VI The use of a Digital



Precautions for Voltage measurements

Plug the black test lead into the COM jack.
Plug the red test lead into the V jack.
Set the function/range switch to DC volts
Begin your measurements with the 200 or 400 mv setting.
During the experiment it may be necessary to move up to the 2 or 4 volt setting.

Precautions for temperature measurements

Disconnect the red and black leads and plug in the temp. probe into the temperature input. Set the function switch to temperature and measure.