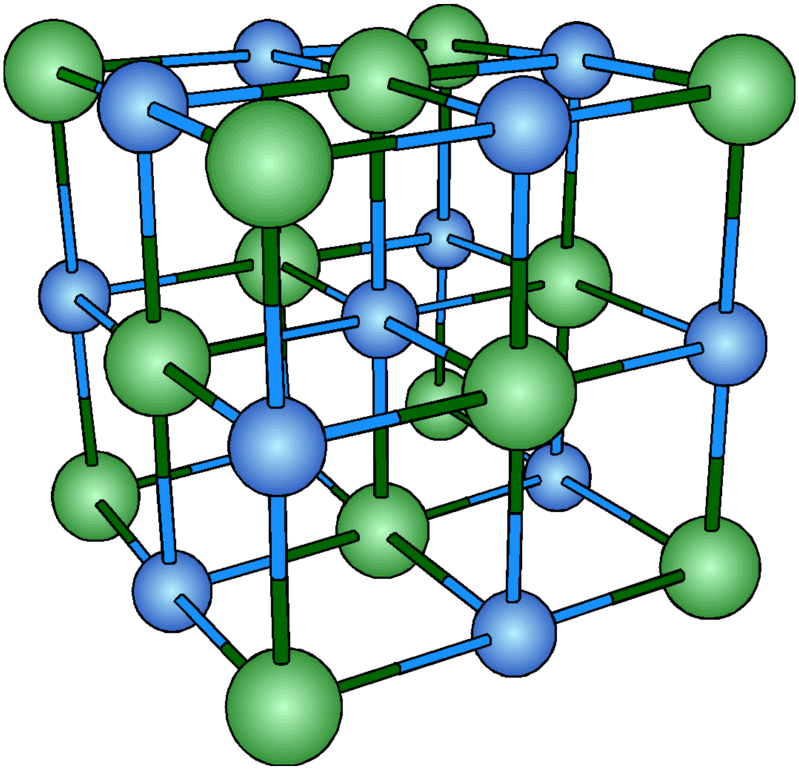
Grossmont College Chemistry 142 Laboratory Manual



Lehman, Maley, and Oakes *6th Edition*

Grossmont College
Periodic Table of the Elements

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
	1A	**2A**											**3A**	**4A**	**5A**	**6A**	**7A**	**8A**
1	**1** H 1.008																	**2** He 4.003
2	**3** Li 6.941	**4** Be 9.012											**5** B 10.811	**6** C 12.011	**7** N 14.007	**8** O 15.999	**9** F 18.998	**10** Ne 20.180
3	**11** Na 22.990	**12** Mg 24.305	**3B**	**4B**	**5B**	**6B**	**7B**	**8B**	**8B**	**8B**	**1B**	**2B**	**13** Al 26.982	**14** Si 28.086	**15** P 30.974	**16** S 32.061	**17** Cl 35.453	**18** Ar 39.948
4	**19** K 39.098	**20** Ca 40.078	**21** Sc 44.956	**22** Ti 47.867	**23** V 50.942	**24** Cr 51.996	**25** Mn 54.938	**26** Fe 55.845	**27** Co 58.933	**28** Ni 58.693	**29** Cu 63.546	**30** Zn 65.382	**31** Ga 69.723	**32** Ge 72.640	**33** As 74.922	**34** Se 78.960	**35** Br 79.904	**36** Kr 83.798
5	**37** Rb 85.468	**38** Sr 87.62	**39** Y 88.906	**40** Zr 91.224	**41** Nb 92.906	**42** Mo 95.962	**43** Tc (98)	**44** Ru 101.07	**45** Rh 102.906	**46** Pd 106.42	**47** Ag 107.868	**48** Cd 112.411	**49** In 114.818	**50** Sn 118.710	**51** Sb 121.760	**52** Te 127.60	**53** I 126.905	**54** Xe 131.293
6	**55** Cs 132.905	**56** Ba 137.327	**57** La 138.906	**72** Hf 178.49	**73** Ta 180.948	**74** W 183.84	**75** Re 186.207	**76** Os 190.23	**77** Ir 192.217	**78** Pt 195.078	**79** Au 196.967	**80** Hg 200.59	**81** Tl 204.383	**82** Pb 207.2	**83** Bi 208.980	**84** Po (209)	**85** At (210)	**86** Rn (222)
7	**87** Fr (223)	**88** Ra (226)	**89** Ac (227)	**104** Rf (261)	**105** Db (262)	**106** Sg (266)	**107** Bh (264)	**108** Hs (269)	**109** Mt (268)	**110** Ds (281)	**111** Rg (272)	**112** Cn (285)	**113** Nh (284)	**114** Fl (289)	**115** Mc (288)	**116** Lv (293)	**117** Ts (294)	**118** Og (294)

6	**58** Ce 140.116	**59** Pr 140.908	**60** Nd 144.24	**61** Pm (145)	**62** Sm 150.36	**63** Eu 151.964	**64** Gd 157.25	**65** Tb 158.925	**66** Dy 162.500	**67** Ho 164.930	**68** Er 167.259	**69** Tm 168.934	**70** Yb 173.04	**71** Lu 174.967
7	**90** Th 232.038	**91** Pa 231.036	**92** U 238.029	**93** Np (237)	**94** Pu (244)	**95** Am (243)	**96** Cm (247)	**97** Bk (247)	**98** Cf (251)	**99** Es (252)	**100** Fm (257)	**101** Md (258)	**102** No (259)	**103** Lr (262)

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Chemistry 142 Laboratory Manual

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Contents

EXPERIMENT 1

The Kinetics of the Dissociation of Hydrogen Peroxide

Background

Kinetics is the study of the rate of chemical reactions. The study of kinetics is a key aspect of chemistry because it provides a great deal of insight into the step-by-step mechanism by which chemical reactions occur.

One could generalize by stating that there are three things which affect the rate of chemical reactions. These are temperature, concentration of reactants, the presence of a catalyst.

To explain these effects, a simple model known as a reaction coordinate diagram can be used (see your text for an illustration). The reaction coordinate diagram provides a model for a chemical reaction. For example, one could study a generic bimolecular reaction such as:

$$A + B \rightarrow C + D \qquad \textbf{(EQ 1.1)}$$

In order for a reaction to occur, molecule A must collide with molecule B with sufficient kinetic energy to allow the activated complex to surpass the barrier known as the activation energy (E_a). Raising the temperature increases the rate of a chemical reaction by increasing the average kinetic energy available in any single collision. It also increases the rate of a chemical reaction by increasing the number of collisions per second.

Increasing the concentration of the reactants in a chemical reaction increases the rate of that reaction because it increases the number of collisions between reactant molecules per unit time. The greater the number of collisions per second, the greater the number of successful collisions leading to product formation, and the faster the reaction.

Adding a catalyst to a chemical reaction increases the rate of the reaction by decreasing the size of the activation energy. The catalyst changes the mechanism of the reaction in some way which provides an alternative path for the reaction such that the energy needed to produce product, the activation energy, is lowered. Therefore, at a given temperature, more molecules will have sufficient energy to get over the activation energy barrier, and the rate of the reaction is increased. In this laboratory, you will be studying all three of the things which affect the rate of a chemical reaction--temperature, concentration of reactant, and the presence of a catalyst.

The basic unit in a kinetic study is the rate law. For the generic reaction used as an example above, the generic rate law will be:

$$\text{rate} = k[\text{A}]^x[\text{B}]^y \qquad \textbf{(EQ 1.2)}$$

where k is the rate constant. The rate constant is not a true constant, as its value depends on temperature. However, for a given temperature, it will have a constant value. In the above equation, x and y are the order of the reaction with respect to A and B. The overall order of the reaction is x+ y. One of the goals of this laboratory is to determine the value of the rate constant and the order with respect to the reactants in a reaction.

If there is a catalyst affecting the rate of the reaction, it will in general enter into the rate law. For example if the substance E is a catalyst for the reaction above, then the rate law will be:

$$\text{rate} = k[\text{A}]^x[\text{B}]^y[\text{E}]^z \qquad \textbf{(EQ 1.3)}$$

for the reaction:

$$\text{A} + \text{B} \overset{\text{E}}{\rightarrow} \text{C} + \text{D} \qquad \textbf{(EQ 1.4)}$$

In this laboratory, you will be determining the order of a particular reaction with respect both to a reactant and to a catalyst. You will be using the method of initial rates to determine the order of the reaction with respect to the relevant chemical species. An example of the method is given below and will be detailed by your instructor. But in essence, the method of initial rates involves doing two or more runs of the chemical reaction to be studied. In the two runs, all the parameters are kept constant (temperature, and the concentration of any reactants and/or catalyst) except one varies the concentration of the species whose order is to be determined. For example, in the reaction above, if one wanted to determine the order of the reaction with respect to the species A, one would do two runs. In the first run, convenient values of temperature, and concentration of A, B and E would be chosen and the initial rate would be measured. In the second run, one would keep the initial concentration of B and of E, as well as the temperature constant, but double the concentration of the reactant A. If the one doing the experiment were to then measure the rate of both the runs, he or she would be able to determine from the ratio of the rate of the two runs the value of x, the order of the reaction with respect to A.

$$\frac{rate1}{rate2} = \frac{k[A]^x[B]^y[E]^z}{k[2A]^x[B]^y[E]^z} \qquad \textbf{(EQ 1.5)}$$

The initial rate of reaction, rate 1 and rate 2, will be determined from a graph of concentration (or volume in this experiment) versus time. The order of reaction x can be found for by simplifying the equation and taking the natural logarithm of both side of the equation to solve for x. Using further kinetic study x, y and z can be determine. Next, the measured rate of any of the reaction runs can be used to solve for the rate constant, k, as shown by the equation:

$$k = \frac{\text{rate}}{[\text{A}]^x[\text{B}]^y[\text{E}]^z} \qquad \textbf{(EQ 1.6)}$$

Finally, the overall rate law with orders x, y, and z, the rate constant k with standard deviation can be reported.

EXAMPLE 1.1

In an experiment similar to yours the diluted concentrations of A, B, and E and the initial rate are listed below where all reactions took place at the same temperature.Determine the overall rate law.

TABLE 1.2

Mixture	[A] (M)	[B] (M)	[E] (M)	Initial Rate (mL/s)
1	0.055	0.052	0.035	0.00429
2	0.110	0.052	0.035	0.0118
3	0.110	0.110	0.035	0.0516
4	0.055	0.052	0.025	0.00424

One way to determine x, y, and z is to use the method of initial rates. To find z compare use the ratio of rate 1 to rate 4:

$$\frac{rate1}{rate4} = \frac{4.29 \times 10^{-3}\frac{mL}{s}}{4.24 \times 10^{-3}\frac{mL}{s}} = \frac{k[0.055M]^x[0.052M]^y[0.035M]^z}{k[0.055M]^x[0.052M]^y[0.025M]^z} \quad \textbf{(EQ 1.7)}$$

Simplify by canceling like terms:

$$\frac{4.29 \times 10^{-3}\frac{mL}{s}}{4.24 \times 10^{-3}\frac{mL}{s}} = \frac{[0.035M]^z}{[0.025M]^z} \quad \textbf{(EQ 1.8)}$$

To find z take the natural log (or log, remember that ln x = 2.303 log x) of both sides and solve for z:

$$z = \frac{\ln\left(\frac{4.29 \times 10^{-3}\frac{mL}{s}}{4.24 \times 10^{-3}\frac{mL}{s}}\right)}{\ln\left(\frac{0.035M}{0.025M}\right)} = 0.034842289 \approx 0 \quad \textbf{(EQ 1.9)}$$

The order is rounded to the nearest integer or half-integer. Using similar calculations x is calculated to be 1.46 rounded to 1.5 and y is calculated to be 1.97 rounded to 2. This reaction is one and one-half order with respect to A, second order with respect to B, and zero order with respect to C. The overall order of the reaction is three and one-half order.

Using Equation 1.6 the rate constant, k, can be calculated for each mixture of the same temperature. Using data for mix 1:

$$k = \frac{4.29 \times 10^{-3}\frac{mL}{s}}{[0.055M]^{1.5}[0.052M]^2[0.035]^0} = 123.0004133\frac{mL}{M^{3.5}s} \approx 120\frac{mL}{M^{3.5}s} \quad \textbf{(EQ 1.10)}$$

An average k is calculated to be 120 mL $M^{-3.5}$ s^{-1} with a standard deviation of 2.7 mL $M^{-3.5}$ s^{-1}. This data has fair precision because all of the k values are within two standard deviations of the average value. So, the overall law is

$$\text{rate} = (120 \pm 2.7 \text{ mL M}^{-3.5}\text{ s}^{-1})\,[A]^{1.5}[B]^2[E]^0 \text{ or simplified to} \quad \textbf{(EQ 1.11)}$$

$$\text{rate} = (120 \pm 2.7 \text{ mL M}^{-3.5}\text{ s}^{-1})\,[A]^{1.5}[B]^2 \quad \textbf{(EQ 1.12)}$$

In the experiment on the decomposition of hydrogen peroxide, you will also measure the effect of temperature. You will repeat one of your earlier runs, with the identical concentrations as before, but now performing the reaction at both increased and at decreased temperatures. Of course, this will change the rate of the reaction, because it will change the value of the rate constant. In this case, you will measure the rate constant of the reaction at all four temperatures. These values will allow you to calculate the activation energy (E_a) for the reaction by using the Arrhenius method. According to the Arrhenius equation:

$$k = Ae^{-\frac{E_a}{RT}} \qquad \textbf{(EQ 1.13)}$$

or, taking the natural log:

$$\ln(k) = \ln(A) - \frac{E_a}{RT} \text{ or } \ln(k) = -\frac{E_a}{RT} + \ln(A) \qquad \textbf{(EQ 1.14)}$$

Using this second equation, it can be seen that if one can collect data for a particular reaction of the rate constant at various temperatures then a graph of the natural log of the rate constant for a reaction versus the inverse of the temperature (ln k vs. $1/T$), the graph will be a straight line with a slope of E_a/R, R being the universal gas constant. The y-intercept of the graph will equal ln A.

In summary, then, for the catalyzed decomposition of hydrogen peroxide, you will be able to determine the rate law and the rate constant at various temperatures, as well as the activation energy of the reaction.

The Experiment

The particular reaction to be studied is the decomposition of hydrogen peroxide in the presence of the catalyst iodide ion. The reaction to be studied can be represented by:

$$2\ H_2O_{2\ (aq)} \xrightarrow{I^-} 2\ H_2O_{\ (l)} + O_{2\ (g)} \qquad \textbf{(EQ 1.15)}$$

The decomposition of hydrogen peroxide is spontaneous at room temperature, but it is too slow to measure conveniently. The rate of the reaction is increased by the presence of ultraviolet light, which is why commercial hydrogen peroxide is sold in light-resistant brown bottles. The addition of iodide ion in the form of a solution of potassium iodide to the reaction will cause the reaction to occur at a rate appropriate to study on the time scale of a few minutes.

The progress of the reaction will be followed by measuring the volume of oxygen released as a function of time. For this reason, although a true rate constant will be measured, it will be in non-conventional units. The units of the rate of reaction will be in mL of O_2 per minute. The actual rate of the reaction will be determined from a graph of volume of O_2 versus time. The initial rate of the reaction will be calculated as the maximum tangent slope of the graph.

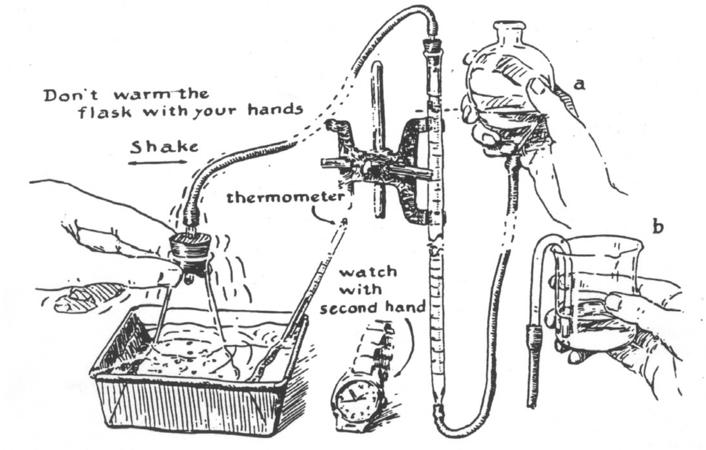
By measuring the rate of the reaction at room temperature, but with a number of different reactant concentration ratios, the “order” of the reaction with respect to both hydrogen peroxide and iodide will be determined, as well as the rate constant at room temperature. By doing one of the reaction concentration ratios at three other temperatures, and by using the Arrhenius equation, the student will be able to calculate the activation energy and frequency factor for the reaction.

Procedure

Experimental Method

The experiment must be performed by groups of two or three (three being ideal). Begin by setting up the apparatus as illustrated below:

FIGURE 1.1



Your instructor will provide specifics, as the setup may vary somewhat. The 50 mL buret or gas tube should be filled to somewhere near the top of the readable markings. The whole system should be checked carefully for leaks. This can be done by sealing up the entire system and lowering the beaker or leveling bulb. Use a rubber stopper if you are using the bulb to seal the system. If you use a beaker, then pinch the hose to seal in order to check for leaks. If the system is sealed, the water level in the buret or gas tube will go down slightly but after that hold steady. The purpose of the beaker or leveling bulb is to assure that the pressure within the reaction vessel is the same as that in the room. If there is a pressure differential between the room and the gases in the system, the recorded volume change will be effected.

The effect of concentration of reactants on the rate of decomposition of H_2O_2. You will be measuring the initial rate of reaction for three different concentration ratios. The three mixtures are described in the table below:

TABLE 1.3

Reagents	Mixture #1	Mixture #2	Mixture #3
0.10 *M* KI	15.0 mL	15.0 mL	30.0 mL
distilled H_2O	35.0 mL	25.0 mL	20.0 mL
3% hydrogen peroxide	10.0 mL	20.0 mL	10.0 mL
total volume	60.0 mL	60.0 mL	60.0 mL

The first three reactions should be performed at room temperature. The potassium iodide solution and the water can be added to the 250 mL Erlenmeyer flask and allowed to equilibrate at room temperature in the water bath. The water in the bath should be between 4 and 8 cm deep. The hydrogen peroxide should be added to a separate container and also allowed to equilibrate to the temperature of the water bath. The solutions can be measured using graduated cylinders, but **be sure to get the**

volumes as precise as possible and close to each other as possible (this will help you when you do your calculations). If measuring pipets or burets are available, that would be preferable.

Before performing the experiment, measure the temperature of the water in the bath. It should be very close to room temperature. This will be important, because for mixtures 1–3, you need to do all three runs at the same temperature. Record the temperature of the bath in your lab notebooks.

Prepare a table in you lab notebook to record the data. The table should look something like this:

TABLE 1.4

time interval (min.)	Mix #1 Temp volume reading	Mix #2 Temp volume reading	Mix #3 Temp volume reading	Mix #4 Temp volume reading	Mix #5 temp volume reaching	Mix #6 temp volume reading
0.0						
0.5						
1.0						
1.5						
2.0						
2.5						
3.0						
3.5						
4.0						
4.5						
5.0						
5.5						
6.0						
6.5						
7.0						
7.5						
8.0						
8.5						
9.0						
9.5						
10.0						

When all is ready, pour the hydrogen peroxide into the reaction mixture, raise the beaker or leveling bulb to somewhere near the top reading on the buret or gas tube and seal up the system. Once you bring the level of the beaker of leveling bulb to the same height as the liquid in the buret, take your first reading. It is not necessary to take readings in the first few seconds, so it is more important to get a good reading than to take a reading as fast as possible. Because the water level will be moving, you will only be able to measure the volume to within ± 0.1 mL. While one member of your group is recording data, another should be swirling the Erlenmeyer flask **at as constant a rate as possible**. If mixture #1 is stirred much less rapidly than mixture #3, this will affect your results. Continue reading data every thirty seconds (being sure to equalize the water level each time) for ten minutes or until at the water level in the buret has dropped at least 35 mL. Re-measure the temperature in the bath. Your temperature will be the average of that measured before and after the experiment.

Repeat the procedure for mixture #2 and #3, being sure to record the temperature before and after the run.

The effect of changing temperature on the rate of decomposition of H_2O_2. Repeat the procedure, using the same volumes of reagents as that used in mixture #1 at three other temperatures. The minimum temperature should not be below 5 degrees centigrade, and the maximum temperature should not be above 45 degrees. For example if your room temperature data was collected at 21.2 °C, you could do runs at 12 °C, 30 °C and 40 °C (remember to always record your temperature to the maximum precision the thermometer allows). In these runs it is especially important to let the solutions equilibrate at the temperature of the water baths. The solutions should be allowed to equilibrate for at least three minutes. Hopefully, the cold or hot water baths will be at a fairly constant temperature. Be sure to record the temperature both before and after each run, and take an average.

Calculations

The first step in performing the calculations is to prepare plots of volume versus time for all six runs. If your graphing routine allows, you can plot all six runs on the same graph. Another option is to plot runs 1-3 on one graph and runs 1, 4, 5, and 6 on another. Be absolutely sure you know which curve corresponds to which run, and label your graph so that it is clear which is which as well.

For each of your runs, determine the maximum slope of the graph. You may do this by hand using a ruler and getting the slope from calculating the rise over the run. Alternatively, you may use a computer program such as VernierGraph or LoggerPro to determine the maximum slope of the curve.

In any case, report the maximum slope of each run. This is the initial rate of the reaction. Be careful about the units of the reaction rate. It would be helpful to record the results in a table.

Next, use the method of initial rates and your room temperature data to determine the order of the reaction with respect to each of the reactants. Whatever mathematical method you use to extract these orders, **do not round off to an integer or to a half-integer at this point**.

Once you have the orders, report your rate law for the reaction you studied. At this point, go ahead and round the orders to the nearest integer or half-integer.

Now that you have the rate law, calculate the rate constant for each of your six runs. Again, be careful about units. Note that in order to calculate *k*, you will have to calculate the concentration of iodide ion and of hydrogen peroxide. This may be a bit trickier than it seems. For the three runs at room temperature, calculate the average rate constant and the standard deviation. Report your answer as $k =$ ### ± ### (average ± standard deviation). Remember the standard deviation equation is:

$$\sigma = \sqrt{\frac{\sum d^2}{n-1}} = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}} \qquad \textbf{(EQ 1.16)}$$

Next, prepare a graph of natural log of *k* versus the inverse of temperature. Use your average value of *k* for the room temperature data. From a linear fit to your graph and the Arrhenius equation, determine the value of the activation energy (E_a) and the frequency factor (A).

Post Lab Questions

1. What does the size of the standard deviation of k say about the precision of your measurements?

2. How linear was your Arrhenius plot? What does that say about your value of E_a?

3. What percentage of the hydrogen peroxide has been decomposed in mixture #1 when 20.0 mL of O_2 gas has been evolved? Assume your room temperature, 740 torr of pressure, and a density of 3% H_2O_2 of 1.00 g/ml. Do not forget to take into account the vapor pressure of water.

4. Propose a mechanism for the reaction consistent with the rate law you measured.

EXPERIMENT 2

A Kinetic Study of the Oxidation of an Alcohol by Dichromate Ion

Background

Kinetics

In the previous experiment, The Kinetics of the Dissociation of Hydrogen Peroxide, the initial rate of the reaction was determined using a graph of concentration vs. time. The order of reaction was found using the method of initial rates and the rate constant was solved for to determine the overall rate law. But, the order and rate constant can also be determined using an integrated rate law. Using the unimolecular reaction A → D + E a general rate expression

$$\frac{\Delta[\mathrm{A}]}{\Delta t} = -k[\mathrm{A}]^{x} \qquad \textbf{(EQ 2.1)}$$

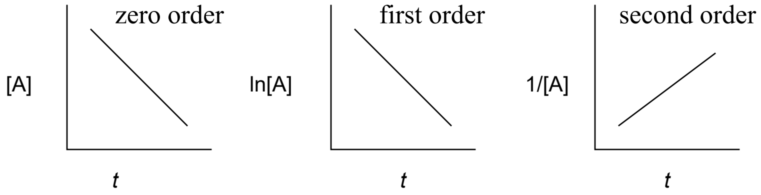
can be read as "The molar concentration of reactant A decreases with time in proportion to the instantaneous molar concentration of A to the x^{th} power. The overall reaction order be x. The letter k represents the specific rate constant for the reaction.

The value of x, hence the kinetic order in [A], may be determined by observing the change in the value of [A] as the reaction proceeds. The integrated rate expressions for zero, first and second order reactions are given in Equation 2.2:

$$\begin{array}{lll} \text{zero order} & [\mathrm{A}] = -kt + [\mathrm{A}]_0 & \\ \text{first order} & \ln\frac{[\mathrm{A}]}{[\mathrm{A}]_0} = -kt \quad \text{or} \quad \ln[\mathrm{A}] = -kt + \ln[\mathrm{A}]_0 & \textbf{(EQ 2.2)} \\ \text{second order} & \frac{1}{[\mathrm{A}]} = kt + \frac{1}{[\mathrm{A}]_0} & \end{array}$$

Each of these expressions is seen to be in the form of a linear equation, $y = \mathrm{m}x + \mathrm{b}$ where x is time and y is some function of [A]. A linear plot of [A] vs. t is observed for a zero order dependence of rate upon [A] with a slope of k. First order reactions yield a linear plot of ln[A] vs. t with a slope of $-k$. A linear plot of 1/[A] vs. t indicates a second order dependence of rate upon [A] with a slope of k. Figure 2.1 illustrates these relationships.

FIGURE 2.1



Spectrophotometry

An instrument that measures the relative intensity that is associated with the wavelength of radiation from a sample is called a spectrophotometer. Spectroscopic measurements generally use a light source, dispersive device (like a mirror), and a detector to analyze the absorption or emission spectrum of a sample. Absorption spectra are often defined by their percent transmittance, %T, defined in Equation 2.3:

$$\%\mathrm{T} = 100\left(\frac{I}{I_0}\right) \qquad \textbf{(EQ 2.3)}$$

where I = light transmitted by the solution, and I_o = light incident upon the solution. Absorbance, A, is another way to describe spectra: Rearranging Equation 2.3 for absorbance yields Equation 2.4:

$$A = \log\left(\frac{100}{\%\mathrm{T}}\right) \qquad \textbf{(EQ 2.4)}$$

The amount of visible light a sample absorbs in aqueous solution is in direct proportion to the concentration of the solute according to **Beer's Law** Equation 2.5:

$$A = -\log\left(\frac{I}{I_0}\right) = \varepsilon bc \qquad \textbf{(EQ 2.5)}$$

where A = absorbance, ε = the extinction coefficient (or molar absorptivity), b = the length of the light path in centimeters and c = the molar concentration of solute. A It is therefore possible to follow quantitatively the rate of a chemical reaction involving a light-absorbing reactant or product by observing the change in the absorbance of the reactant or product with time. Rearranging Equation 2.5 in terms of concentration yields:

$$c = \frac{A}{\varepsilon b} \qquad \textbf{(EQ 2.6)}$$

So, combining the first order reaction Equation 2.2 and Equation 2.6, where c is [A] and $[\mathrm{A}]_0$ respectively, changes the first order equation from being in terms of concentration to absorbance:

$$\ln\frac{[\mathrm{A}]}{[\mathrm{A}]_0} = -kt \text{ becomes } \ln\left(\frac{\frac{A}{\varepsilon b}}{\frac{A_0}{\varepsilon b}}\right) = -kt \qquad \textbf{(EQ 2.7)}$$

Simplifying and putting into y = mx+ b form gives:

$$\ln(A) = -kt + \ln(A_0) \qquad \textbf{(EQ 2.8)}$$

However, A_∞ is not so small that it can ignored. A correction needs to be included to account for the fact that when the reaction has reached completion at $t = \infty$, there will still be some absorbance of light. So, the absorbance at $t = \infty$, A_∞, must be subtracted from the absorbance terms in Equation 2.8:

$$\ln(A - A_\infty) = -kt + \ln(A_0 - A_\infty) \qquad \textbf{(EQ 2.9)}$$

So, if the reaction is first order a graph of ln(A-A_∞) versus time will give a linear graph where the slope of the line is k or in this experiment k_{obs}. Similar relationships can be derived for zero and second order reactions as well. In this experiment a pseduo-first order reaction will be used to determine the overall rate law.

The **activation energy** for a reaction may be determined by application of the Arrhenius equation in the form:

$$\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \qquad \textbf{(EQ 2.10)}$$

E_a is the activation energy, R = 8.314 J/K•mol and T_2 and T_1 are the kelvin temperatures for reactions having rate constants k_2 and k_1 respectively. By determining k or k_{obs} for a reaction at different temperatures maintaining constant reactant concentrations, and substituting the proper values into the expression the activation energy is obtained.

You will use either the SpectroVis or the Spec20 for your experiment, consult your instructor for more information.

Pseudo-x-th Order Reactions

Many reactions have more than one reactant. A general rate expression for the termolecular reaction $\mathrm{A + B + C \longrightarrow D + E + F}$ would be:

$$\frac{\Delta[\mathrm{A}]}{\Delta t} = -k[\mathrm{A}]^x[\mathrm{B}]^y[\mathrm{C}]^z \qquad \textbf{(EQ 2.11)}$$

read as “The molar concentration of reactant A decreases with time in proportion to the instantaneous molar concentration of A to the x^{th} power times B to the y^{th} power times C to the z^{th} power.” The values of *x, y* and *z* are respectively the orders of the reaction in A, B and C. The overall reaction order would be $x + y + z$. The letter *k* represents the specific rate constant for the reaction.

However, solving for the orders of multiple reactants can be complicated. So, pseudo-x-th order conditions are used. For example, the reaction conditions may be arranged such that the values of [B] and [C] remain essentially constant over the course of the reaction. For instance, if $[\mathrm{B}]_o = [\mathrm{C}]_o$ = 1.000 M and $[\mathrm{A}]_o = 1\times10^{-3}$ M, according to stoichiometry of the reaction at $t = \infty$, [B] = [C] =

0.999 M and [A] = 0 M. Thus, [B] and [C] and therefore $[B]^y$ and $[C]^z$ are essentially constant. The rate expression then becomes:

$$\frac{\Delta[A]}{\Delta t} = -k[A]^x[B]^y[C]^z = -k_{obs}[A]^x \quad \textbf{(EQ 2.12)}$$

wherein k_{obs} (the observed rate constant) is equal to $k\,[B]^y[C]^z$. This is then a pseudo - x^{th} order reaction, where x = the reaction order in [A] (i.e. if $x = 1$ the reaction is pseudo-first order, if $x = 2$ it is pseudo-second order). As only [A] is changing, only the effect of [A] on the rate is observed.

Having now determined the value of k_{obs} and the kinetic order of the reaction in A, the reaction order in B and C and the value of the specific rate constant k can be evaluated. Maintaining pseudo-x^{th} order conditions of relatively large concentrations of B and C, the values of [B] and [C] are varied. The effect of variation of [B] and [C] on the calculated value of k_{obs} will indicate the reaction order in B and in C. Once again using the method of initial rates to determine y and z.

Consider the example where $[A] = 1\times10^{-3}$ M and [B] = [C] = 1.000 M. Recall that $k_{obs} = k[B]^y[C]^z$. What would be the effect of doubling the concentration of B to 2.000 M, if y = 0? Using the method of initial rates:

$$\frac{k_{obs\,1}}{k_{obs\,2}} = \frac{-k[1.000\ M]^0[1.000\ M]^z}{-k[2.000\ M]^0[1.000\ M]^z} \quad \textbf{(EQ 2.13)}$$

$$\frac{k_{obs\,1}}{k_{obs\,2}} = 1 \quad \textbf{(EQ 2.14)}$$

$$k_{obs\,1} = k_{obs\,2} \quad \textbf{(EQ 2.15)}$$

Therefore, when y = 0 and the concentration is doubled the observed rate constants, $k_{obs\,1}$ and $k_{obs\,2,}$ are equal. So, for a zero order reaction changing the concentration has no effect on the observed rate constant or the rate.

What would be the effect of doubling the concentration of B to 2.000 M, if y = 1? Using the method of initial rates:

$$\frac{k_{obs\,1}}{k_{obs\,3}} = \frac{-k[1.000\ M]^1[1.000\ M]^z}{-k[2.000\ M]^1[1.000\ M]^z} \quad \textbf{(EQ 2.16)}$$

$$\frac{k_{obs\,1}}{k_{obs\,3}} = 0.5000 \quad \textbf{(EQ 2.17)}$$

$$2k_{obs\,1} = k_{obs\,3} \quad \textbf{(EQ 2.18)}$$

Therefore, when y = 1 and the concentration is doubled the observed rate constant is also doubled. So, for a first order reaction the rate changes by the same factor as the concentration.

What would be the effect of doubling the concentration of B to 2.000 M, if y = 2? Using the method of initial rates:

$$\frac{k_{obs\,1}}{k_{obs\,4}} = \frac{-k[1.000\ M]^2[1.000\ M]^z}{-k[2.000\ M]^2[1.000\ M]^z} \quad \textbf{(EQ 2.19)}$$

$$\frac{k_{\text{obs 1}}}{k_{\text{obs 4}}} = (0.5000)^2 \qquad \textbf{(EQ 2.20)}$$

$$4k_{\text{obs 1}} = k_{\text{obs 4}} \qquad \textbf{(EQ 2.21)}$$

Therefore, when y = 2 and the concentration is doubled the observed rate constant is quadrupled. So, for a second order reaction the rate changes by the square of the factor that the concentration changes. Table 2.1 gives a summary of these data:

TABLE 2.1

Reaction	*order of y*	$[\mathbf{A}]_0$ (M)	$[\mathbf{B}]_0$ (M)	$[\mathbf{C}]_0$ (M)	k_{obs}
1	y	1×10^{-3}	1.000	1.000	x
2	0	1×10^{-3}	2.000	1.000	x
3	1	1×10^{-3}	2.000	1.000	$2x$
4	2	1×10^{-3}	2.000	1.000	$4x$

A similar series of experiments will serve to evaluate z. With x determined by graphical analysis along with k_{obs}, and y and z determined by variation of [B] and [C], the overall specific rate constant k may be evaluated for each kinetic run by simply substituting the determined values of each variable into Equation 2.22:

$$k = \frac{k_{\text{obs}}}{[\mathrm{B}]^y[\mathrm{C}]^z} \qquad \textbf{(EQ 2.22)}$$

The Experiment

The specific rate constant at room temperature and the activation energy for the oxidation of isopropyl alcohol by dichromate ion in acid solution will be determined by measuring spectrophotometrically the rate of disappearance of dichromate ion in the course of the reaction under controlled conditions specifically pseudo-first order conditions will be used to simplify the math. The overall rate law for the reaction can then be determined.

Dichromate ion oxidizes isopropyl alcohol in the presence of hydrogen ion in aqueous solution to yield acetone. The unbalanced equation is:

$$C_3H_8O_{(aq)} + Cr_2O_7^{2-}{}_{(aq)} \xrightarrow{H^+} C_3H_6O_{(aq)} + Cr^{3+}{}_{(aq)} \qquad \textbf{(EQ 2.23)}$$

2-propanol	dichromate ion	2-propanone	chromium(III) ion
colorless	yellow-orange	colorless	green

In the process, the dichromate ion is reduced to chromium(III) ion. The only reactant that absorbs visible light is dichromate ion. Remember that the color of an object is the result of the absorption of light energy by its electrons. The dichromate ion appears yellow-orange, but that means that it absorbs light in the blue-purple portion of the spectrum. So the maximum absorbance should be in the range of 400 to 490 nm. The only other colored product is chromium(III) ion which does not absorb light at this wavelength because it appears green and absorbs in the red portion of the spectrum. It is therefore possible to utilize the absorbance of the solution at approximately 444 nm (or at wavelength at maximum absorbance as determined by the instrument) as a direct measure of the dichromate ion concentration in a kinetic study of the reaction.

The rate expression for the reaction is written in Equation 2.24:

$$-\frac{\Delta[\mathrm{Cr_2O_7^{2-}}]}{\Delta t} = k[\mathrm{Cr_2O_7^{2-}}]^a[\mathrm{H^+}]^b[\mathrm{alcohol}]^c \quad \textbf{(EQ 2.24)}$$

Under conditions wherein $[H^+]$ and [alcohol] » $[Cr_2O_7^{2-}]$ and therefore changes very little because dichrmoate in the limiting reagent in the reaction. The reaction may be considered pseudo - a^{th} order in dichromate ion, and the concentrations of hydrogen ion and alcohol are relatively constant (which is why the correction factor in necessary). Under these conditions k_{obs} can be expressed as in Equation 2.25:

$$k_{\mathrm{obs}} = k[\mathrm{H^+}]^b[\mathrm{alcohol}]^c \quad \textbf{(EQ 2.25)}$$

Therefore the observed rate can be expressed as:

$$-\frac{\Delta[\mathrm{Cr_2O_7^{2-}}]}{\Delta t} = k[\mathrm{Cr_2O_7^{2-}}]^a[\mathrm{H^+}]^b[\mathrm{alcohol}]^c = k_{obs}[\mathrm{Cr_2O_7^{2-}}]^a \quad \textbf{(EQ 2.26)}$$

$$rate_{obs} = k_{obs}[\mathrm{Cr_2O_7^{2-}}]^a \quad \textbf{(EQ 2.27)}$$

In this experiment a pseudo-first order will be applied, so a = 1. Therefore, a graph of ln(A-A_∞) versus time will give a linear graph where the slope of the line is k or using pseudo order conditions k_{obs}. Then using the method of initial rates the orders for b and c can be found as well as the average rate constant, k, and standard deviation. So that the overall pseudo first order rate law can be determined.

$$rate = k[\mathrm{Cr_2O_7^{2-}}]^1[\mathrm{H^+}]^b[\mathrm{alcohol}]^c \quad \textbf{(EQ 2.28)}$$

Procedure

Your instructor will tell you if you are using the SpectroVis or the Spec20 to collect your data.

Using SpectroVis

1. Starting in "Time Based" mode, calibrate the spectrometer using a cuvette filled with deionized water, a "blank", before the first use. The absorbance reading should be 0.000. Recalibrate until you get an absorbance of about 0.000. Condition the cuvette by rinsing it 2-3 times with DI water.
2. Now, change to "Full Spectrum" mode to find the maximum absorbance of potassium dichromate using the spectrometer by graphing absorbance versus wavelength. Fill a clean cuvette with 1 mL of potassium dichromate solution and dilute with deionized water and generate a graph.
3. Change back to "Time Based" mode to do the experiment. Set up the SpectroVis to record absorbance versus time at 0.5 minute intervals for 7 minutes.
4. Now your dilute dichromate solution should have an absorbance reading if you left it in the spectrophotometer when you changed modes.Check to see that your blank has an absorbance of 0.000 and recalibrate if it does not.
5. Label three clean, dry tubes and as precisely as possible measure, from the burets provided, the following quantities of reagents.

TABLE 2.2

	tube 1	tube 2	tube 3
isopropyl alcohol 0.75*M*	1.00 mL	2.00 mL	1.00 mL
H_2SO_4, 3.0 *M*	5.00 mL	2.50 mL	2.50 mL
DI H_2O	0.50 mL	2.00 mL	3.00 mL

6. Rapidly (but precisely) pipet 1.00 mL of 1.81×10^{-2} *M* potassium dichromate solution into "tube 1", stopper and invert to mix, and pour into the small cuvette (you will have more than enough solution).
7. Measure the temperature of the solution and begin reading *A* at 0.5 minute intervals. After 7 minutes have elapsed, discontinue readings, measure the temperature of the solution (the average of the two temps will be used), and set the cuvette aside. Do not dispose of the solution in this cuvette yet.
8. Repeat steps 3–4 for tubes 2 and 3.
9. After one hour has elapsed since the last reading, read the *A* for the tube exhibiting the fastest reaction rate. Use this value for your infinity reading.
10. Repeat the procedure (these are runs 4 & 5) of runs two and three at a temperature of 35 °C. Prepare a water bath at 35 °C and equilibrate the tubes containing all reagents except dichromate solution, which should be equilibrated separately. Equilibrate the dichromate solution separately. Between readings keep the tubes in the water bath. Be careful to dry tubes before each reading. Measure the temperature of the solutions before and after the kinetic runs. Use the average temperature in your calculations. Determine infinity readings after one hour.

Using Spectronic 20

1. The "Spectronic 20" spectrophotometer should be turned on (left-front knob) and allowed to warm up while solutions are prepared. Adjust the wavelength dial to 444 nm with the filter setting in the correct position. Follow the instructions on the instrument to calibrate it before your

first use. Using the left knob set the %T to 0. Set mode to %T on A. Insert the blank, a cuvette filled with water. Set %T to 100% or A to o using the right knob. Insert sample. Record measurements. When you are finished calibrating, make sure that you **set the instrument to measure in absorbance.**

2. Label three clean, dry tubes and as precisely as possible measure, from the burets provided, the following quantities of reagents.

TABLE 2.3

	tube 1	**tube 2**	**tube 3**
isopropyl alcohol 0.75*M*	1.00 mL	2.00 mL	1.00 mL
H_2SO_4, 3.0 *M*	5.00 mL	2.50 mL	2.50 mL
DI H_2O	0.50 mL	2.00 mL	3.00 mL

3. Measure the temperature of the solutions at the beginning and at the end of the kinetic runs. **Use the average temperature in your calculations**.
4. Rapidly (but precisely) pipet 1.00 mL of 1.81×10^{-2} *M* potassium dichromate solution into each of the three tubes—stopper and invert to mix—begin reading *A* in a rotating sequence at 0.5 min intervals (see Table 2.4 on page 23). Be careful to position the tubes in exactly the same way for each reading. After 22 minutes have elapsed, discontinue readings. After one hour has elapsed since the last reading, read the *A* for the tube exhibiting the fastest reaction rate. Use this value for your infinity reading.
5. Repeat the procedure (runs 4 & 5) of runs two and three at a temperature of 35 °C. Prepare a water bath at 35 °C and equilibrate the tubes containing all reagents except dichromate solution, which should be equilibrated separately. Equilibrate the dichromate solution separately. Between readings keep the tubes in the water bath. Be careful to dry tubes before each reading. Measure the temperature of the solutions before and after the kinetic runs. Use the average temperature in your calculations. Determine infinity readings after one hour.

Sample Notebook Page

TABLE 2.4 ***A*** **Readings at maximum wavelength (nm) (Sample Table for Spectronic 20)**

	run 1		**run 2**		**run 3**	
0.75 *M* alcohol	1.00 mL	M	2.00 mL	M	1.00 mL	M
3.0 *M* H_2SO_4	5.00 mL	M	2.50 mL	M	2.50 mL	M
DI H_2O	0.50 mL	M	2.00 mL	M	3.00 mL	M
1.8×10^{-2} *M* $Cr_2O_7^{2-}$	1.00 mL	M	1.00 mL	M	1.00 mL	M
	t **(min)**	**A**	***t*** **(min)**	**A**	***t*** **(min)**	**A**
	0					
	0.5					
	1.0					
	1.5					
	2.0					
	2.5					
	3.0					
	3.5					
	4.0					
	4.5					
	5.0					
	5.5					
	6.0					
	6.5					
	7.0					
	∞		∞		∞	
initial temperature			final temperature			

TABLE 2.5 **Sample Activation Energy Data Table**

Run #	**T°C**	**[ROH]**	$[H^+]$	$[Cr_2O_7^{2-}]$	k_{obs}	k

Calculations

1. Make a plot of ln($A–A_\infty$) vs. time for each of the five kinetic runs. From the slopes of the plots determine the observed rate constant for the reaction.
2. From the relationship $k_{obs} = k[H^+]^b[\text{alcohol}]^c$ calculate the overall rate constant for each of the first three runs and report these values and the average value.
3. Use the values of k_{obs} and the temperatures for paired runs two and four and three and five to determine the activation energy for the reaction. Report the individual and average values for the activation energy.

Post Laboratory Questions

1. The formula for isopropyl alcohol is C_3H_8O. The product of the oxidation of isopropyl alcohol is C_3H_6O. Write a balanced equation for the oxidation of isopropyl alcohol by dichromate ion in acidic solution.

2. If the observed rate constant for the oxidation reaction at 35.0 °C is 6.75×10^{-2} min^{-1} and at 25.0 °C is 3.25×10^{-2} min^{-1}, what is the activation energy for the reaction?

3. What is the rate constant for the reaction in Question 2 at 45.0 °C?

4. If the initial concentration of dichromate ion in Question 2 at 25.0 °C is 1.50×10^{-4} *M*, what will be the concentration of dichromate at 30.0 min?

EXPERIMENT 3

Determination of K_a, K_b, and % Ionization from pH

Background

Like many substances acids and bases were first defined phenomenologically. That is, chemists defined them according to their chemical behavior. For instance, acids were those substances that tasted sour, reacted with certain metals to produce hydrogen gas, and caused a color change in certain indicator solutions. Bases, were those substances that tasted bitter, turned certain indicator solutions a certain color, and felt slippery. As time has progressed chemists have devised more fundamental definitions of acids and bases.

There are a number of different definitions of acids and bases which are useful to chemists. One example is the **Arrhenius** definition. In this definition acids are those substances that increase the concentration hydrogen ion in solution and bases are those substances that increase the concentration of hydroxide ion in solution.

A broader definition was developed by the Danish chemist Johannes Brønsted and the English chemist Thomas Lowry. Their definitions follow:

Brønsted-Lowry Acid: A substance that can donate a proton.

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons A^-_{(aq)} + H_3O^+_{(aq)} \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]} \tag{EQ 3.1}$$

Brønsted-Lowry Base: A substance that can accept a proton.

$$B_{(aq)} + H_2O_{(l)} \rightleftharpoons BH^+_{(aq)} + OH^-_{(aq)} \qquad K_b = \frac{[BH^+][OH^-]}{[B]} \tag{EQ 3.2}$$

Acid and base molecules and ions that differ only by the addition or removal of a proton are called **conjugate pairs**. For example HA/A^- and B/BH^+ both represent conjugate acid-base pairs. It may be shown that the K_a of an acid times the K_b of its conjugate base are equal to K_w (*Make sure that you can derive this.*). Therefore for the acid HA, the K_b of its conjugate base, A^-, is K_w/K_a where $K_w = 1.0 \times 10^{-14} = [H_3O^+][OH^-]$ at 25 °C and pH = $-\log[H_3O^+]$.

Strong Acids and Bases

Acids and bases which are essentially 100% dissociated in water are said to be strong. The common strong acids and bases are listed in Table 3.1

TABLE 3.1 **Common Strong Acids and Bases**

Strong Acids	Strong Bases
hydrochloric acid (HCl)	lithium hydroxide (LiOH)
hydrobromic acid (HBr)	sodium hydroxide (NaOH)
hydroiodic acid (HI)	potassium hydroxide (KOH)
nitric acid (HNO_3)	calcium hydroxide ($Ca(OH)_2$)
sulfuric acid (H_2SO_4)	strontium hydroxide ($Sr(OH)_2$)
perchloric acid ($HClO_4$)	barium hydroxide ($Ba(OH)_2$) *slightly soluble*
chloric acid ($HClO_3$)	

The dissociation constants for the strong acids and bases are undefined because the concentration of the undissociated form is essentially zero, which would result in a value of infinity.

Calculating K_a and K_b

Consider the reaction of an acid HA in water to produce A^- and the hydronium ion. Each conjugate pair can be identified. Numerical values of the dissociation constants for weak acids and bases may be determined by measuring the pH of the solution. If the pH is observed to be 3.20 then:

$$[H_3O^+] = 10^{-3.20}M = 6.31\times10^{-4}M = x \tag{EQ 3.3}$$

For a weak acid, the hydronium ion concentration, $[H_3O^+]$, is approximately equal to the concentration of the conjugate base $[A^-]$ as shown below:

	acid		base		conjugate base		conjugate acid
	$HA_{(aq)}$	+	$H_2O_{(l)}$	$\rightleftharpoons$	$A^-_{(aq)}$	+	$H_3O^+_{(aq)}$
I	$0.10\ M$		$55\ M$		0 M		$10^{-7}\ M$
Δ	$-x$		$-x$		$+x$		$+x$
	$0.10\text{ M} - x \approx$		$55\text{ M} - x \approx$		$x = 6.31\times 10^{-4}\text{ M}$		$10^{-7}\text{ M} + x \approx$
	$0.10\text{ M} - 6.31\times 10^{-4}\text{ M} \approx$		$55\text{ M} - 6.31\times 10^{-4}\text{ M} \approx$				$x \approx 6.31\times 10^{-4}\text{ M}$
E	0.10 M		55 M				

Substituting the equilibrium values from above into the K_a expression yields a numerical value for the experimental K_a:

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{[x][x]}{(0.10 - x)} = \frac{(6.31\times10^{-4})^2}{(0.10 - 6.31\times10^{-4})} = 4.0\times10^{-6} \tag{EQ 3.4}$$

We can also use the expression given above for the relationship of K_b to K_a:

$$K_b \text{ for } A^- = \frac{K_w}{K_a} = \frac{1.0\times10^{-14}}{4.0\times10^{-6}} = 2.5\times10^{-9} \tag{EQ 3.5}$$

If the pH reading is greater than 7 the solution is basic and the $[OH^-]$ will be used to calculate K_b.

If the pH is observed to be 11.45 then the $[OH^-] = 10^{-pOH} = 10^{-2.55} = 0.0028$ M = x and,

	base		acid		conjugate acid		conjugate base
	$B_{(aq)}$	+	$H_2O_{(l)}$	$\rightleftharpoons$	$BH^+_{(aq)}$	+	$OH^-_{(aq)}$
I	$0.10\ M$		$55\ M$		0		10^{-7}
Δ	$-x$		$-x$		$+x$		$+x$
	$0.10\ \mathrm{M} - x \approx$		$55\ \mathrm{M} - x \approx$		$x = 0.0028\ \mathrm{M}$		$10^{-7}\ \mathrm{M} + x \approx$
	$0.10\ \mathrm{M} - 0.0028\ \mathrm{M} \approx$		$55\ \mathrm{M} - 0.0028\ \mathrm{M} \approx$				$x \approx 0.0028\ \mathrm{M}$
E	0.10 M		55 M				

Notice that water is amphoteric and can act as either as acid or a base. The experimental K_b is

$$K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{(10^{-2.55})^2}{(0.10 - 0.0028)} = 8.2\times10^{-5} \qquad \textbf{(EQ 3.6)}$$

Within what pH range can you prudently neglect the molarities of the ions in deionized water when added to dissociation products?

A more precise way of measuring K_a for a weak acid is to prepare a solution containing *equal molarities* of the weak acid and a salt of its conjugate base. Under this maximum buffer capacity condition the pH = pK_a, or $[H_3O^+] = K_a$. **Make certain that you know why this is so**.

Percent Dissociation

The percentage dissociation is a measure of the molarity of one conjugate species in the equilibrium mixture compared to the initial molarity of the other conjugate species. It is a measurement of the extent of ionization. The greater the % dissociation the more ionized the acid or base.

For a weak base the percent dissociation can be calculate in the following manner. The data are from the example above.

$$\%\text{ dissociation} = \frac{[BH^+]}{[B]_{\text{initial}}} \times 100\% = \frac{[OH^-]}{[B]_{\text{initial}}} \times 100\% = \frac{10^{-2.55}}{0.10} \times 100\% = 2.82\% \qquad \textbf{(EQ 3.7)}$$

Procedure

Part 1

1. Measure the pH of each of the following:
    a. tap water
    b. deionized water
    c. “Outgassed” deionized water

d. The outgassed water after you have bubbled your breath through this water for 20-30 seconds.

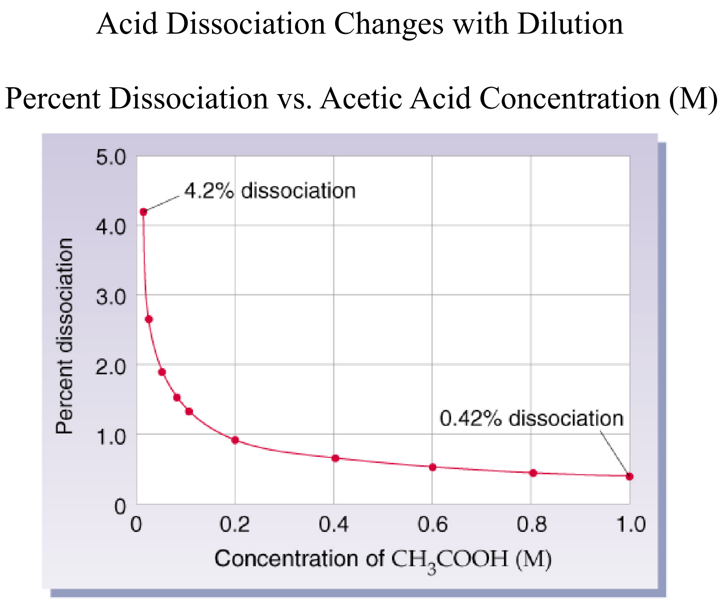
To outgas a sample of deionized water, gently boil it in an Erlenmeyer flask for at least 10 minutes. Cool and stopper the flask to prevent contact with the lab's atmosphere.

Answer the procedure questions to questions to explain your observations for a-d.

Part 2

1. Obtain about 10 mL of 6 M acetic acid. Dilute exactly 5 mL of the 6 *M* solution to 25 mL in a graduated cylinder. Repeat the dilution by diluting 5 mL of the second solution to 25 mL. Repeat this procedure until $[HC_2H_3O_2] \approx 7\times10^{-5}$ M.
2. Measure the pH of each solution starting with the most dilute, $[HC_2H_3O_2] \approx 7\times10^{-5}$ M, to the most concentrated, 6 M.
3. Calculate the % dissociation for each solution. Prepare a graph of %D vs. $[HC_2H_3O_2]$ and compare it to the Figure 3.1 on page 30. Explain the trend observed. Generate a linear graph by choosing an appropriate function. Calculate K_a from the graph. Find the percent error.
4. Manually calculate the K_a for acetic acid. Determine an average K_a, standard deviation, and percent error. Analyze both K_a values, which is the more accurate way of determining K_a?

FIGURE 3.1



Calculations

Be sure to look up the theoretical pK_a values for acetic acid, and the acids and bases in the post lab questions in the CRC Handbook.

Procedure Questions

Part 1

1. What is the pH of the tap water? Was this value what you expected? Why or why not? What ions contribute to the pH?

2. What is the pH of the deionized water? Was this value what you expected why or why not?

3. What is the pH of the outgassed water? Why did the pH change?

4. What is the pH of the outgassed water that you bubbled into for 20-30 seconds? Why did the pH change? Write a balanced chemical equation to support your answer.

Post Lab Questions

1. The experimental pH of a 0.25 M solution of acetic acid, $HC_2H_3O_2$, is 2.65.
   - a. Is the solution acidic, basic, or neutral? ________________.
   - b. Write the balanced net ionic equilibrium reaction. Identify the acid, base, conjugate acid, and conjugate base. Write the equilibrium expression K_a for the reaction.
   - c. The theoretical pK_a of acetic acid from the CRC Handbook is 4.756. Calculate the theoretical K_a.
   - d. What is the theoretical pK_b?

2. The experimental pH of a 0.25 M $NaC_2H_3O_2$ solution is 9.14.
   - a. Is the solution acidic, basic, or neutral? ________________.
   - b. Write the balanced net ionic equilibrium reaction. Identify the acid, base, conjugate acid, and conjugate base. Write the equilibrium expression K_b for the reaction.
   - c. Why don't you include the sodium ion in the net ionic equation?
   - d. The theoretical pK_b of sodium acetate is 9.244. Calculate the theoretical K_b.
   - e. What is the theoretical pK_a?

3. What do you notice about the theoretical pK_a and pK_b for acetic acid and sodium acetate?

4. Write the overall reaction if the net ionic equilibrium reactions 1b and 2b are combined. What is the numerical value of new equilibrium constant for the overall reaction?

5. The experimental pH of a 0.25 M solution of ammonia, NH_3, is 11.33.

- **a.** Is the solution acidic, basic, or neutral? ________________
- **b.** Write the balanced net ionic equilibrium reaction. Identify the acid, base, conjugate acid, and conjugate base. Write the equilibrium expression K_b for the reaction.
- **c.** Look up the theoretical pK_a from the CRC Handbook ____________.
- **d.** Calculate the theoretical pK_b and K_b.

6. The experimental pH of a 0.25 M solution of ammonium chloride, NH_4Cl, is 4.89.

- **a.** Is the solution acidic, basic, or neutral? ________________.
- **b.** Write the balanced net ionic equilibrium reaction. Identify the acid, base, conjugate acid, and conjugate base. Write the equilibrium expression K_a for the reaction.
- **c.** Why don't you include the chloride ion in the net ionic equation?
- **d.** Look up the theoretical pK_a from the CRC Handbook ____________.
- **e.** Calculate the theoretical K_a.

7. The experimental pH of a 0.25 M solution of phosphoric acid, H_3PO_4, is 1.48.

a. Is the solution acidic, basic, or neutral? ________________

b. Write the balanced net ionic equilibrium reaction. Identify the acid, base, conjugate acid, and conjugate base. Write the equilibrium expression K_a for the reaction.

c. Look up the theoretical pK_a from the CRC Handbook ____________

8. The experimental pH of a 0.25 M solution of potassium dihydrogen phosphate, KH_2PO_4, is 3.99.

a. Is the solution acidic, basic, or neutral? ________________.

b. Write the balanced net ionic equilibrium reaction. Identify the acid, base, conjugate acid, and conjugate base. Write the equilibrium expression K_a for the reaction.

c. Look up the theoretical pK_a from the CRC Handbook ____________.

9. The experimental pH of a 0.25 M solution of potassium hydorgen phosphate, K_2HPO_4, is 10.25.

a. Is the solution acidic, basic, or neutral? ________________.

b. Write the balanced net ionic equilibrium reaction. Identify the acid, base, conjugate acid, and conjugate base. Write the equilibrium expression K_b for the reaction.

c. Look up the theoretical pK_a from the CRC Handbook ____________

10. The experimental pH of a 0.25 M solution of potassium phosphate, K_3PO_4, is 12.86.

a. Is the solution acidic, basic, or neutral? ________________.

b. Write the balanced net ionic equilibrium reaction. Identify the acid, base, conjugate acid, and conjugate base. Write the equilibrium expression K_b for the reaction.

c. Look up the theoretical pK_a from the CRC Handbook ____________.

11. Why does pH become more (very) basic as each hydrogen ion is removed?

12. The experimental pH of a 0.25 M solution of boric acid, H_3BO_3, is 4.98.

a. Is the solution acidic, basic, or neutral? ________________.

b. Write the balanced net ionic equilibrium reaction. Identify the acid, base, conjugate acid, and conjugate base.

c. Calculate the $[H_3O^+]$.

d. Calculate the pOH.

e. Calculate the $[OH^-]$.

f. Using the net ionic equilibrium reaction complete an ICE table to show the concentrations of all species at equilibrium.

g. Calculate the experimental K_a and pK_a.

h. Calculate the percent dissociation.

i. From CRC Handbook theoretical pK_a ____________ calculate K_a ________________.

j. What is the percent error of K_a?

13. The experimental pH of a 0.25 M solution of methylamine, CH_3NH_2, solution is 11.95.

a. Is the solution acidic, basic, or neutral? ________________.

b. Write the balanced net ionic equilibrium reaction. Identify the acid, base, conjugate acid, and conjugate base.

c. Calculate the $[H_3O^+]$.

d. Calculate the pOH.

e. Calculate the $[OH^-]$.

f. Using the net ionic equilibrium reaction complete an ICE table to show the concentrations of all species at equilibrium.

g. Calculate the experimental K_b and pK_b.

h. Calculate the percent dissociation.

i. From CRC Handbook theoretical pK_a ____________.

j. Calculate the theoretical pK_b ____________ and K_b _______________.

k. What is the percent error of K_b?

14. The experimental pH of a 0.25 M solution of methylammonium chloride, CH_3NH_3Cl, is 5.58.

a. Is the solution acidic, basic, or neutral? ________________.

b. Write the balanced net ionic equilibrium reaction. Identify the acid, base, conjugate acid, and conjugate base.

c. Calculate the $[H_3O^+]$.

d. Calculate the pOH.

e. Calculate the $[OH^-]$.

f. Using the net ionic equilibrium reaction complete an ICE table to show the concentrations of all species at equilibrium.

g. Calculate the experimental K_a and pK_a.

h. Calculate the percent dissociation.

i. From CRC Handbook theoretical pK_a ____________ calculate K_a ________________

j. What is the percent error of K_a?

EXPERIMENT 4

pH Indicators

Background

Acid-base indicators are weak organic acids and bases whose colors change with the pH of their environment. The general equation for their dissociation is illustrated below:

$$\mathrm{HIn}_{(aq)} \rightleftharpoons \mathrm{H}^+_{(aq)} + \mathrm{In}^-_{(aq)} \qquad \textbf{(EQ 4.1)}$$

$$K_{\mathrm{HIn}} = \frac{[\mathrm{H}^+][\mathrm{In}^-]}{[\mathrm{HIn}]} \qquad \textbf{(EQ 4.2)}$$

The acid form, HIn, and the conjugate base, In^-, each have distinctive color characteristics and light absorption properties. The human eye averages the color of transmitted light and observes the acid color when the $[HIn]/[In^-]$ ratio is ten or greater and the color of the basic form when the $[In^-]/[HIn]$ is greater than or equal to ten. The intermediate color is observed when $[HIn]/[In^-]$ is close to one. Your eye can be used to approximate these ratios. A more objective method would use a spectrophotometer.

Beer's Law

A spectrophotometer is an instrument that measures the absorbance of light (usually visible and ultraviolet) when passed through an aqueous solution. This absorbance is proportional to the concentration of the absorbing species.

The relationship between the concentration of a species and the absorbance is given by **Beer's Law**:

$$A = \varepsilon bc \qquad \textbf{(EQ 4.3)}$$

In this equation A is the absorbance, ε is the molar absorptivity constant, b is the path length, and c is the molar concentration of absorbing species. Often % transmittance is measured rather than absorbance. The following is the relationship between A and % T.

$$A = \log\left(\frac{100}{\%T}\right) \qquad \textbf{(EQ 4.4)}$$

In the Beer relationship ε and b are constants, making absorbance and concentration directly proportional. Exploiting this relationship allows us to determine the K_a for an indicator knowing the pH and the ratio, [HIn]/[In$^-$].

For phenolphthalein the only absorbing species is In$^-$. At pH 11 essentially all of the indicator is in the form of In$^-$. At pH 11:

$$A_{11} = \varepsilon b[\mathrm{In}^-]_{11} \qquad \textbf{(EQ 4.5)}$$

where $[\mathrm{In}^-]_0$ equals the total concentration of the indicator. In the pH 9 buffer, some of the indicator is in the form HIn and some is in the form In$^-$. If the concentration of In$^-$ in the buffer is called $[\mathrm{In}^-]_9$, then in the pH 9 buffer:

$$A_9 = \varepsilon b[\mathrm{In}^-]_9 \qquad \textbf{(EQ 4.6)}$$

Now let us consider the ratio, [In$^-$]/[HIn] at pH 9. We know that the [In$^-$] is proportional to the absorbance, A_9. [HIn] at this pH will take a bit more reasoning. At pH 11 we can assume that all the HIn has been converted to In$^-$. This means that the [In$^-$] at pH 11 is equal to the initial $[\mathrm{HIn}]_o$. Therefore, the difference in the absorbance at pH 11 and the absorbance at pH 9 represents the [HIn] at pH 9. This gives the following relationship.

$$[\mathrm{In}^-]_9 = \frac{A_9}{A_{11}}[\mathrm{In}^-]_{11}$$

$$[\mathrm{HIn}]_9 = [\mathrm{In}^-]_{11} - [\mathrm{In}^-]_9 \qquad \textbf{(EQ 4.7)}$$

$$\frac{[\mathrm{In}^-]_9}{[\mathrm{HIn}]_9} = \frac{[\mathrm{In}^-]_9}{([\mathrm{In}^-]_{11} - [\mathrm{In}^-]_9)} = \frac{A_9}{A_{11} - A_9} \qquad \textbf{(EQ 4.8)}$$

Procedure: Determination of the K_a of an Indicator

Observation of the Ka of an Indicator Based on Color Change of Buffered Solutions:

Colors of Indicators. In the first part of this experiment you will observe the color of 5 indicator solutions. Four of the indicators will be prepared for you, the fifth, a universal indicator, you will prepare from cabbage leaves.The following are the four prepared indicator solutions.

TABLE 4.1

Indicator	pH Range
congo red	2–6
methyl orange	2–6
methyl red	3–7
cresol red	5–9

You will observe the colors of each of these to determine the K_a of the indicator and calculate a percent error.

Preparation of Cabbage Juice Indicator.

1. Break a leaf of red cabbage into small pieces and place them in a 250 mL beaker.
2. Add enough distilled water to cover the cabbage leaf, and heat the mixture to boiling. The indicator will be extracted from the leaves.
3. Set up a series of pH buffers of 2, 4, 6, 8, 10, and 12 by adding 3 to 4 mL of buffer solutions to separate test tubes. Add 1 mL of the extract to the 6 test tubes, and record the color of each.

Determine the K_a of the cabbage juice indicator in the same manner as the other prepared indicator solutions. That is, by inspection of their color relative to the pH of the solution.

Determination of the K_a of an Indicator using Spectrometry

The method of K_a determination in the first part of this experiment is capable of yielding data that is no better than 1 significant figure in precision. In order to obtain more precise data, a spectrophotometer will be used to determine the K_a of phenolphthalein. A spectrophotometer is necessary for phenolphthalein, as there is no discernible intermediate color. This is due to the fact that the only absorbing species (in the visible spectrum) is the In^- in phenolphthalein.

Phenolphthalein Solution Preparation.

1. Obtain approximately 1mL of phenolphthalein solution in a clean, dry test tube.
2. Transfer 1 drop of the indicator into each of four clean, dry test tubes. Label each container with the pH of the buffer to be added (9, 9.5, 10, and 11).
3. Using a 10.0 mL graduated cylinder, measure 3 mL of pH 9 buffer. Add the pH 9 buffer to the appropriately labeled test tube. Mix well.
4. Repeat with each buffer.
5. Each container should contain approximately a 1:50 ratio of phenolphthalein to a single buffer.
6. Rinse and fill an empty cuvette with each of the indicator solutions.

> ⚠ Make sure that you make up the pH 11 phenolphthalein indicator solution fresh.

Finding the λ of Max Absorbance. Refer to the instructions with your instrument to make sure that it is properly calibrated before performing the next steps. Ask your instructor if you are using the SpectroVis or Spec20.

SpectroVis

1. Calibrate the SpectroVis in “Time Based Mode”. Set the machine to record wavelengths from 380 nm to 660 nm.
2. Place your sample in the cuvette and have the machine scan absorbance as a function of the wavelength in “Full Spectrum”. Determine the wavelength of the maximum absorbance.

Absorbance for the Indicator Solutions. Once the wavelength of maximum absorbance is obtained measure the A for each of the indicator solutions at this wavelength. When you are finished you should have measured the absorbance of the pH 9, 9.5, 10, and 11 solutions at the wavelength that you determined to have the highest absorbance.

Spec20

1. For calibration instructions “Procedure using SpectroVis” on page 18
2. Set the wavelength to 380 nm and place the pH 10 solution of the indicator sample into the spectrophotometer.
3. Record the absorbance of the sample from 380 nm to 660 nm in 15 nm increments. Take three to four extra reading near the maximum absorbance to better define the peak.
4. Plot the absorbance measurements vs. the wavelength. Determine the wavelength range in which the colored species is most sensitive from the maximum absorbance peak.

Absorbance for the Indicator Solutions. Once the wavelength of maximum absorbance is obtained measure the A for each of the indicator solutions at this wavelength. When you are finished you should have measured the absorbance of the pH 9, 9.5, 10, and 11 solutions at the wavelength that you determined to have the highest absorbance.

Calculations and Results

1. Estimate the pK_{HIn} of the visual indicators by comparing the color change of the indicator in its acid form to its base form. Calculate the K_{HIn} and the percent error.
2. Estimate the pK_{HIn} value(s) of the red cabbage buffer solutions.
3. Calculate the value of K_{HIn}, pK_{HIn} and percent error of K_{HIn} for phenolphthalein.
4. Buffering capacity of phenolphthalein. Calculate the pH of phenolphthalein when the ratio of In^-/HIn in solution is:
    a. 10 to 1
    b. 1 to 10
    c. 1 to 1

EXPERIMENT 5

Titration Curves

Background

In this experiment we will investigate three titration curves of known acids and bases as well as that of an unknown. This analysis will yield two pieces of information about each acid. First, you will determine the molarity of each acid. Keep in mind that the molarities provided on the container of each known acid are approximate. Second, you will determine the K_a of each weak acid.

The molarity of each acid can be experimentally determined by titration with a base of known concentration. The number of moles of base added, the stoichiometric ratio of base to acid, and the *original* volume of acid are all needed in order to determine the molarity of the acid. This is something that you did in both Chemistry 120 and Chemistry 141.

The K_a of an acid can be determined by titrating the acid and determining the pH at a point halfway to the equivalence point. If the equivalence point occurs at a volume of 31.10 mL, then the so-called half equivalence point would be at a volume that is one half of this value (15.55 mL). Why is knowing the pH at this point helpful in determining the K_a of an acid? How are the concentrations of the protonated acid, HA, and conjugate base, A^-, related at this point in the titration?

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons A^-_{(aq)} + H_3O^+_{(aq)} \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]} \qquad \textbf{(EQ 5.1)}$$

Procedure

You will need to work in pairs to complete this experiment. You will use the Vernier computer interface to collect your data. It is important that each student be familiar with Vernier function as well as the data analysis tools available in the package. Each student will be required to perform the necessary calculations.

Each student pair is to titrate the acids listed below with 50 mL of approximately 0.1 *M* NaOH solution. *Make sure that you record the actual molarity of the NaOH*. It will be close to 0.1000 *M*, but it most-likely won't be exactly 0.1000 *M*.

1. 25.00 mL of approximately 0.1 *M* HCl
2. 25.00 mL of approximately 0.1 *M* $HC_2H_3O_2$
3. 25.00 mL of approximately 0.05 *M* H_3PO_4

You will measure the pH of the solution as a function of the total mL of NaOH added.

After the first three titrations, *each* student will titrate 25.00 mL of an unknown acid, obtained from the stockroom, with 0.1000 *M* NaOH.

Using the Vernier Interface

You will be measuring the volume of NaOH added to the acid solution with a drop counter. Since we need actual volume in mL it is necessary to calibrate the drop counter.

Calibrating the Drop Counter

Ask your instructor if you will calibrate the drop counter using the calibration directions below or using the calibration function on the data acquisition device.

1. Place a clean, dry, *weighed* beaker underneath the drop counter and start measuring drops.
2. Open the stopcock on the buret to begin dropping the NaOH into the clean, dry, *weighed* beaker.
3. The computer will then begin recording the number of drops added to the beaker. After approximately 25 mL of NaOH has been added to the beaker, close the stopcock on the buret and stop the measuring of drops. Record the number of drops placed into the beaker.
4. Weigh your beaker again and determine the mass of NaOH in the beaker. Use a density value of 1.00 g/mL for the NaOH solution to calculate the actual volume of NaOH per drop.

$$\frac{\text{Mass of NaOH}}{\text{\# of Drops}} \times \frac{1\text{ mL NaOH}}{1.00\text{ g NaOH}} = \text{mL NaOH/drop NaOH} \qquad \textbf{(EQ 5.2)}$$

You will use this value for mL/drop to determine the total volume of NaOH added to your flask.

Collecting Titration Data

Once your drop counter is calibrated you are ready to calibrate your pH meter and collect your titration data.

1. Calibrate your pH electrode using two buffer solutions of known pH. Once the reading stabilizes, follow the directions on the screen.
2. You are now ready to collect pH as a function of number of drops added. Make sure that you prepare your solutions to be titrated, and begin measuring the pH as you add the NaOH dropwise. Collect data until you have reached 1.5 times the volume at the equivalence point.

Data Analysis

Plot four separate, full-page graphs. Each plot should include the following.

1. The equivalence point. You may locate this by performing the appropriate calculus (where the second derivative is 0). You may also locate it graphically. Make sure that you plot the volume of the NaOH on the *x*-axis, and not # of drops.
2. On the graph indicate the predominant species present in the titration beaker:
   - **a.** At the half equivalence point.
   - **b.** At the equivalence point.
   - **c.** At a point one and one half times beyond the equivalence point. You do not need to include water in this list.
3. Calculate the molarity of the titrated acid calculated from the location of the equivalence point and the concentration of the base used for the titration. Do this with as great a precision as your plot allows.

> Keep in mind that this is a Chemistry 120 type calculation. You have done one or two acid-base titrations prior to this; it is the same calculation as you have done in the past.
>
> Make sure that your calculated molarities of the acids make sense! ~0.1 M HCl, $HC_2H_3O_2$, and unknown. ~0.05 M H_3PO_4.

4. The pH of the system can be calculated from the appropriate equilibrium constant before, at, and past the equivalence point.

   For acetic and phosphoric acids, write out the equilibrium constant expression (along with its numerical value) that *could* be used to calculate the pH of the system before, at, and past the equivalence point.

   If, at any one of these points, the pH is determined primarily by the presence of a strong acid or base, then state this fact and do not try to give an equilibrium expression.
5. Report the experimentally determined K_a for the dissociation of the acid **using the pH at the half equivalence point of the titration**. Do this for the acetic acid, for K_{a1} and K_{a2} of the phosphoric acid *and for your unknown acid*. Calculate the percent error for the K_as of acetic acid and phosphoric acid.
6. In your "Data and Calculations" section of your lab report be sure to report your unknown number, the molarity of your unknown acid and its K_a value.

EXPERIMENT 6

The Solubility Product of Calcium Iodate

Background

The **solubility product constant** is simply the equilibrium constant for the solution of a slightly soluble salt in water. When the generic salt M_xA_y dissolves in water there are produced x moles of M^{y+} and y moles of A^{x-} for every mole of M_xA_y that dissolves according to:

$$M_xA_{y\,(s)} \rightleftharpoons x\,M^{y+}{}_{(aq)} + y\,A^{x-}{}_{(aq)} \qquad \textbf{(EQ 6.1)}$$

and the equilibrium constant for the reaction (omitting M_xA_y because it is a solid) would be:

$$K_{sp} = [M^{y+}]^x[A^{x-}]^y \qquad \textbf{(EQ 6.2)}$$

EXAMPLE 6.1The solubility of a salt can be found using titration.

To determine the solubility constant, K_{sp}, at 50.0 °C of nickel(II) iodate, a chemist prepares a saturated solution of the salt at this temperature. They obtain a 10.00 mL aliquot of this solution and add 50.0 mL of deionized water, 2.0 g of potassium iodide, and 10.00 mL of 3 M hydrochloric acid to the flask. Thiosulfate solution is added to the flask and a 2% starch solution after which the solution turns purple-blue. The chemist adds more thiosulfate from the buret until the solution in the flask is colorless. It takes 52.19 mL of 0.0515 M sodium thiosulfate to reach the endpoint of the titration.

a. How many moles of thiosulfate are needed to reach the end point of the titration?

$$0.05219\ L\ S_2O_3^{2-} \times \frac{0.0515\ mol\ S_2O_3^{2-}}{1\ L\ S_2O_3^{2-}} = 2.69 \times 10^{-3}\ mol\ S_2O_3^{2-} \qquad \textbf{(EQ 6.3)}$$

In the presence of an excess of iodide and acid the iodate is converted quantitatively to iodine:

$$IO_3^-{}_{(aq)} + 5\,I^-{}_{(aq)} + 6\,H^+{}_{(aq)} \rightarrow 3\,I_{2\,(aq)} + 3\,H_2O_{(l)} \qquad \textbf{(EQ 6.4)}$$

Three moles of iodine are produced per mole of iodate:

The iodine is then reduced to iodide by thiosulfate ion, according to reaction 6.5:

$$I_{2\,(aq)} + 2\,S_2O_3^{2-}{}_{(aq)} \rightarrow 2\,I^-{}_{(aq)} + S_4O_6^{2-}{}_{(aq)} \qquad \textbf{(EQ 6.5)}$$

Two moles of thiosulfate reduce one mole of iodine.

It is seen that the moles of iodate in the initial solution will be one sixth the number of moles of thiosulfate used to titrate the iodine.The balanced oxidation-reduction reaction is:

$$IO_3^{-}{}_{(aq)} + 6\,H^{+}{}_{(aq)} + 6\,S_2O_3^{2-}{}_{(aq)} \rightarrow I^{-}{}_{(aq)} + 3\,S_4O_6^{2-}{}_{(aq)} + 3\,H_2O_{(l)} \qquad \textbf{(EQ 6.6)}$$

b. How many moles of iodate ions are present at the endpoint of the titration?

$$2.69 \times 10^{-3}\ mol\ S_2O_3^{2-} \times \frac{1\ mol\ IO_3^{-}}{6\ mol\ S_2O_3^{2-}} = 4.48 \times 10^{-4}\ mol\ IO_3^{-} \qquad \textbf{(EQ 6.7)}$$

c. If 10.00 mL of the saturated $Ni(IO_3)_2$ solution was used, what is the concentration of iodate at the end point?

$$\frac{4.48 \times 10^{-4}\ mol\ IO_3^{-}}{0.01000\ L} = 4.48 \times 10^{-2} M\ IO_3^{-} \qquad \textbf{(EQ 6.8)}$$

d. Write the balanced equation, K_{sp} expression, and start the ICE table for nickel(II) iodate.

$$Ni(IO_3)_{2\,(s)} \rightleftharpoons Ni^{2+}{}_{(aq)} + 2\,IO_3^{-}{}_{(aq)} \qquad K_{sp} = [Ni^{2+}][IO_3^{-}]^2 \qquad \textbf{(EQ 6.9)}$$

	$Ni(IO_3)_{2\,(s)}$	$\rightleftharpoons$	$Ni^{2+}{}_{(aq)}$	+	$2\,IO_3^{-}{}_{(aq)}$
I	n/a		0 M		0 M
Δ	n/a		+S		$+2S$
E	n/a		S		$2S = 4.48 \times 10^{-2}$ M

e. Based on your results from part c and d, what is the concentration of Ni^{2+} ions at the end points? What is the numerical value for the solubility?

$$\frac{4.48 \times 10^{-2}\ mol\ IO_3^{-}}{1\ L} \times \frac{1\ mol\ Ni^{2+}}{2mol\ IO_3^{-}} = 2.24 \times 10^{-2} M\ Ni^{2+} = S \qquad \textbf{(EQ 6.10)}$$

A saturated solution of $Ni(IO_3)_2$ is 2.90×10^{-2} molar in Ni^{2+} and 5.80×10^{-2} molar in IO_3^{-}. So, the solubility, S, of $Ni(IO_3)_2$ was found to be 2.90×10^{-2} M at 50.0 °C. Now complete the ICE table:

	$Ni(IO_3)_{2\,(s)}$	$\rightleftharpoons$	$Ni^{2+}{}_{(aq)}$	+	$2\,IO_3^{-}{}_{(aq)}$
I	n/a		0 M		0 M
Δ	n/a		+S		$+2S$
E	n/a		$S = 2.24 \times 10^{-2}$ M		$2S = 4.48 \times 10^{-2}$ M

f. Determine the K_{sp} of $Ni(IO_3)_2$ at 50.0 °C.

You can plug your molarity values directly into the K_{sp} expression to get the answer:

$$K_{sp} = [Ni^{2+}][IO_3^{-}]^2 = (2.24 \times 10^{-2} M)(4.48 \times 10^{-2} M)^2 = 4.50 \times 10^{-5} M^3 \qquad \textbf{(EQ 6.11)}$$

Or you can plug in the solubility value, S, of 2.90×10^{-2} M into the K_{sp} expression:

$$K_{sp} = [Ni^{2+}][IO_3^{-}]^2 = (S)(2S)^2 = 4S^3 = 4(2.24 \times 10^{-2} M)^3 = 4.50 \times 10^{-5} M^3 \qquad \textbf{(EQ 6.12)}$$

Remember that the units for equilibrium values are often left off because they depend on the equilibrium expression, so, $K_{sp} = 4.50 \times 10^{-5}$ for a saturated solution of nickel(II) iodate.

EXAMPLE 6.2 **According to Le Châtelier's principle, addition of either Ni^{2+} or IO_3^- should depress the solubility of $Ni(IO_3)_2$.**

A second titration is preformed in the presence of a solution of 0.10 M $NaIO_3$. The solubility, S, of the solution was calculated to be 3.99×10^{-3} M. Notice that the solubility decreased with the addition of iodate ions.

g. What is the measured K_{sp} value in the presence of 0.10 M $NaIO_3$?

Setting up an ICE table notice that the initial value of IO_3^- *is 0.10 M:*

	$Ni(IO_3)_{2\,(s)}$	$\rightleftharpoons$	$Ni^{2+}_{(aq)}$	+	$2\ IO^-_{3\,(aq)}$
I	n/a		0 M		0.10 M
Δ	n/a		+S		*+2S*
E	n/a		S		*0.10 M + 2S =*

Using the titration data the solubility, S, was found to be 3.99×10^{-3} M. Plug this value into the ICE table:

	$Ni(IO_3)_{2\,(s)}$	$\rightleftharpoons$	$Ni^{2+}_{(aq)}$	+	$2\ IO^-_{3\,(aq)}$
I	n/a		0 M		0.10 M
Δ	n/a		+S		+2S
	n/a		$S = 3.99 \times 10^{-3}$ M		$0.10\ M + 2S =$ $0.10\ M + 2(3.99 \times 10^{-3}\ M) \approx$ $0.10\ M + 7.98 \times 10^{-3}\ M \approx$
E					0.10 M

You can now *solve the* K_{sp} *expression:*

$$K_{sp} = [Ni^{2+}][IO_3^-]^2 \quad \text{(EQ 6.13)}$$

$$K_{sp} = (S)(0.10M + 2S)^2 \quad \text{(EQ 6.14)}$$

$$K_{sp} = (3.99 \times 10^{-3} M)(0.10M + 2(3.99 \times 10^{-3} M))^2 = 4.65 \times 10^{-5} M^3 \quad \text{(EQ 6.15)}$$

The K_{sp} *value in the presence of the common ion of* 4.65×10^{-5} *and the* K_{sp} *value in the presence of water of* 4.50×10^{-5} *are a bit different probably due to experimental errors. The actual* K_{sp} *of nickel(II) iodate,* $Ni(IO_3)_2$*, at 25 °C is* 4.71×10^{-5}*. Also notice that the solubility in the presence of a common ion of* 3.99×10^{-3} *M is less than the solubility in water* 2.24×10^{-2} *M, therefore the solubility does decrease in the presence of additional iodate ions.*

K_{sp} of $Ca(IO_3)_2$

In this experiment you will determine the K_{sp} of $Ca(IO_3)_2$ and observe the common ion effect of added $Ca(NO_3)_2$ on the solubility of $Ca(IO_3)_2$. The concentration of iodate ion in solution will be determined by reducing the iodate to iodine with excess iodide solution, and subsequently titrating the iodine with thiosulfate. Iodine binds to starch to form a very dark blue-purple complex, so starch is used as an indicator in the titration.

Procedure

Saturated solutions of calcium iodate in water and in 0.10 *M* calcium nitrate have been prepared, as well as standardized 0.05 *M* sodium thiosulfate solution. *Make sure that you record the actual molarity of these solutions.* This is found on the container label.

Solubility Product of $Ca(IO_3)_2$

1. To a 250 mL Erlenmeyer flask, add approximately 2.0 g of KI and 50 mL of water.
2. Then pipet 10.00 mL of the saturated calcium iodate solution into the flask and add 50 mL of 1.0 *M* HCl.
3. Titrate the brown solution with standardized 0.05 *M* sodium thiosulfate to a light amber color.
4. To the light amber solution add 5 mL of prepared starch solution. Titrate the purple solution until it turns colorless.
5. Record the temperature of the solution.
6. Repeat the procedure two more times for a total of three trials.

TABLE 6.3 Titration of $Ca(IO_3)_2$

	Trial #1	Trial #2	Trial #3
Mass of KI			
Volume $Ca(IO_3)_2$ (mL)			
Molarity of $Na_2S_2O_3$ (M)			
Initial buret reading $Na_2S_2O_3$ (mL)			
Final buret reading $Na_2S_2O_3$ (mL)			
Temperature of solution (°C)			

Common Ion Effect

Duplicate the procedure in "Solubility Product of $Ca(IO_3)_2$" (above) with 10.00 mL samples of the saturated solution of calcium iodate prepared in 0.100 *M* calcium nitrate solution.

Calculations

Solubility Product of $Ca(IO_3)_2$

1. Calculate the solubility of $Ca(IO_3)_2$ in water.
2. Calculate the value of K_{sp} for $Ca(IO_3)_2$ in water including an average value and standard deviation.
3. Using the average value of K_{sp} for $Ca(IO_3)_2$ in water determine the % error from the value in the CRC.
4. The following table may be a good way to organize and present your data:

TABLE 6.4 **Analysis of Titration of $Ca(IO_3)_2$ in Water**

	Trial #1	Trial #2	Trial #3
Temperature of solution (°C)			
Volume of $Na_2S_2O_3$ used (mL)			
Molarity of $Na_2S_2O_3$ (M)			
Volume $Ca(IO_3)_2$ (mL)			
Equilibrium molarity of IO_3^- (M)			
Equilibrium molarity of Ca^{2+} (M)			
Molar Solubility of $Ca(IO_3)_2$ (M)			
Ksp of $Ca(IO_3)_2$ at 25 °C			
Average Ksp of $Ca(IO_3)_2$			
Standard deviation of Ksp of $Ca(IO_3)_2$			
Actual Ksp of $Ca(IO_3)_2$			
Percent error of Ksp of $Ca(IO_3)_2$			

Common Ion Effect

5. Calculate the solubility of $Ca(IO_3)_2$ in 0.10 *M* $Ca(NO_3)_2$ solution.
6. Calculate the value of K_{sp} for $Ca(IO_3)_2$ in0.10 *M* $Ca(NO_3)_2$ solution including an average value, standard deviation, and percent error.
7. Create a table to organize and present your data for this part of the experiment.

Pre-Laboratory Questions

1. If 2.65 g of barium hydroxide is dissolved in 70.0 mL of water to produce a saturated solution at 20 °C, calculate the solubility in
   - a. g/100 mL
   - b. g/L
   - c. M

2. Write the dissociation reaction and K_{sp} expressions for the following salts:
   - a. Iron(II) carbonate
   - b. Aluminum sulfate

3. Consider the following equilibrium system: $PbCl_{2\,(s)} \rightleftharpoons Pb^{2+}{}_{(aq)} + 2\ Cl^{-}{}_{(aq)}$ and describe what happens to the solubility of lead(II) chloride under the following conditions:

- **a.** lead(II) chloride solid is added.
- **b.** lead(II) nitrate is added.
- **c.** sodium chloride is added.
- **d.** water is added.
- **e.** silver nitrate is added.
- **f.** sodium bromide is added.

Post Lab Questions

1. A saturated solution of the slightly soluble salt MA_3 is 1.4×10^{-3} *M* in MA_3. What is its K_{sp} value?

2. A 20.0 mL sample of $NaIO_3$ was treated with an excess of KI and HCl and the iodine produced titrated with 0.05125 *M* $Na_2S_2O_3$. If 19.35 mL, of $Na_2S_2O_3$ solution were required to reach a starch-iodine endpoint, what was the concentration of the $NaIO_3$?

3. K_{sp} for Ag_2SO_4 is 1.2×10^{-5} at 25 °C. Calculate the expected molar solubility of Ag_2SO_4 at 25°C

   a. in water

   b. in 0.20 *M* $AgNO_3$

   c. in 0.20 *M* Na_2SO_4

   d. in 0.20 *M* $NaNO_3$

EXPERIMENT 7

Solubility Product and Potentiometric Titrations

Background

Ion Selective Electrodes

One of the most common things done by chemists is to measure the concentration of species in a sample. Nothing is more basic to analytical chemistry than such quantitative measurements. One of the most common, accurate, inexpensive and rapid means to do so is the use of a calibrated ion selective electrode (ISE). Such, electrodes, when immersed in an aqueous solution, produce a voltage which is related to the concentration of a single species, usually an ion, in solution.

Using the Nernst equation, the following relationship between voltage produced by an ion selective electrode and the confrontation of the ion in an aqueous solution:

$$E = E^{\circ} - \frac{RT}{nF}\ln Q \qquad \textbf{(EQ 7.1)}$$

where E, is the measured voltage, E° is the standard voltage of the cell, which is the voltage of the reference cell in the electrode, R is 8.314 J mol^{-1} K^{-1}, n is the number of electrons in the relevant half-reaction involving the ion being measured, F is the Faraday constant 9.6485 x 10^4 C mol^{-1}, and Q represents the concentration of the ion in question. Since R and F are constants; at T = 25 °C and $\frac{RT}{nF}\ln Q = \frac{0.0592}{n}\log Q$ then Equation 7.1 becomes:

$$E = E^{\circ} - \frac{0.0592}{n}\log Q \qquad \textbf{(EQ 7.2)}$$

In real ISEs the slope of the voltage versus the log of concentration is only approximately 0.0592 V. It is an experimental parameter. The most common ISE is the pH electrode. Such an electrode has a semi-permeable membrane and internal chemistry which allows it to measure a voltage which is linear with respect to the log of the hydrogen ion concentration. In other words, it gives a voltage which is linearly related to pH. This, with a two-point calibration using standard, known buffers, allows the pH of any solution to be measured quickly and easily.

In this laboratory, a chloride-selective electrode will be used. Again, the electrode has a special kind of semi-permeable membrane and a chemical system which produces a voltage which is proportional to the log of the chloride ion concentration. Such electrodes are not perfect and small corrections need to be made for interfering ions such as bromide, Br^-. This will not be taken into account in this laboratory as the solutions will not have a significant amount of interfering ions. For this laboratory, then, the equation relating voltage is:

$$E = E° - k \log[Cl^-] \qquad \textbf{(EQ 7.3)}$$

In this equation, 0.0592/n is substituted by the slope of the graph, which is represented by k, which will have units of volts. If the voltage of several standardized chloride solution is measured, then a graph of voltage versus the log of the chloride ion concentration should be linear. The graph should have a negative slope. From a linear fit of the voltage versus the log of the concentration of the graph, an equation in the form y = mx + b can be obtained. In this case, by inspection of the equation, the y-intercept is E°, and -k is the slope. Using the calibration equation from the graph, it is a simple matter to turn the voltage produced using the electrode into the chloride ion concentration for any solution.

Measuring K_{sp} for a chloride ion using a calibrated chloride ISE

The **solubility product constant** is simply the equilibrium constant for the solution of a slightly soluble salt in water. One application of an ion selective electrode is to measure the K_{sp} of a compound which contains the ion whose concentration the electrode measures. For example, if a saturated solution of an unknown chloride of the formula XCl_2 was made:

$$XCl_{2\,(s)} \rightleftharpoons X^{2+}{}_{(aq)} + 2\ Cl^-{}_{(aq)} \qquad \textbf{(EQ 7.4)}$$

and the equilibrium constant for the reaction (omitting XCl_2 because it is a solid) would be:

$$K_{sp} = [X^{2+}][Cl^-]^2 \qquad \textbf{(EQ 7.5)}$$

given that $[Cl^-] = 2\,[X^{2+}]$:

$$K_{sp} = \frac{1}{2}[Cl^-]^3 \qquad \textbf{(EQ 7.6)}$$

Of course, not all chlorides have a formula XCl_2, but a similar calculation can be done to calculate K_{sp} for any chloride ion given the voltage from a calibrated chloride ISE.

Potentiometric Titrations

You have already done a **potentiometric titration**. The titration curve lab involved doing a potentiometric titration to create a titration curve. In such an experiment, an ISE is used to measure the concentration (actually the log of the concentration) of an ion versus volume added from a buret. In an effective titration, the concentration of an ion, which can be detected by an ISE changes quite dramatically at the equivalence point. The point of greatest slope of voltage versus volume of titrant will be the endpoint of the titration. The reaction being used to measure the chloride ion in this experiment is as follows:

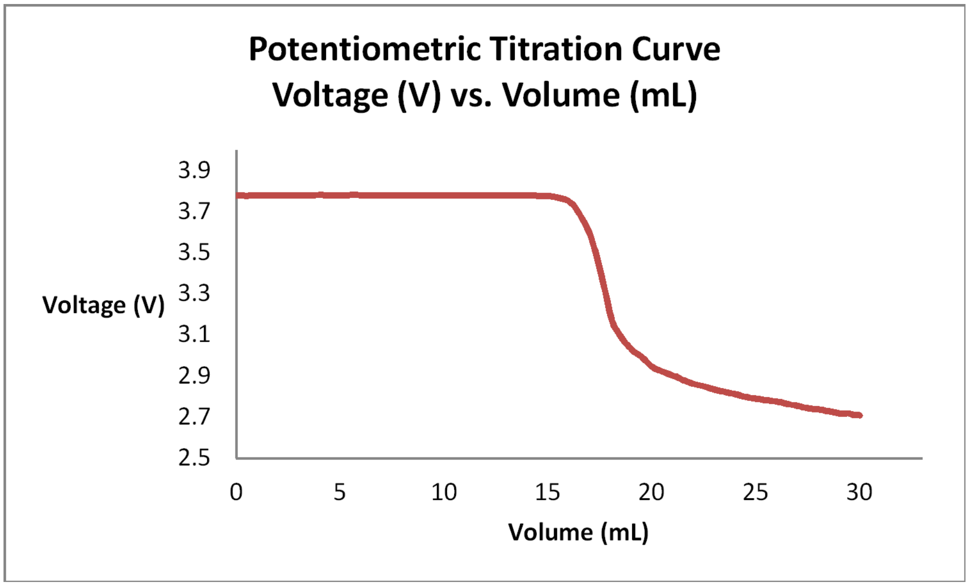
$$Ag^+{}_{(aq)} + Cl^-{}_{(aq)} \rightarrow AgCl_{(s)} \qquad \textbf{(EQ 7.7)}$$

This is a precipitation titration. If the silver ion is in the reaction vessel and the chloride ion is being delivered from the buret, then the chloride ion concentration will remain very low until near the stoichiometric point. This is because the reaction with the silver ion will keep the chloride ion concentration very low until the silver ion is nearly used up. This can be seen from the K_{sp} relationship for sliver chloride:

$$K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10} \quad \textbf{(EQ 7.8)}$$

The concept here is nearly identical to a strong acid-strong base titration. Even if 99% of the silver ion has been reacted with the chloride ion coming from the buret, the chloride ion concentration in the reaction vessel will remain quite low. At the endpoint, the chloride ion concentration increases very rapidly, producing an endpoint, which is the point of greatest slope in the voltage versus volume of unknown chloride ion concentration from the buret. A sample titration curve is provided below:

FIGURE 7.1



Using the endpoint and a simple titration equation, the concentration of the unknown chloride solution can be calculated using stoichiometry.

Procedure

Part A: Standardizing the Chloride ISE

1. Obtain about 20 mL of a standard solution of sodium chloride in a small, clean, dry beaker. If the beaker is wet, condition it with some of the solution first. The standardized sodium chloride solution should be approximately 1.00 M.
2. Carefully pipet 10.00 mL of the sodium chloride solution into a 100.00 mL volumetric flask. Be sure to follow good pipeting procedure. Add DI water to nearly the mark, mix the contents, then add DI water "to the mark" and thoroughly mix the solution.
3. Repeat this procedure with each successive solution a total of four times, each time using 10.00 mL of the new solution to make another solution.
4. At the end of the procedure there should be a total of five solutions (including the original), each of which is exactly 1/10th the concentration of the former solution.
5. Next, set the probe to measure "raw" voltage.

> **NOTE:** In order to "condition" the electrode, you may want to rinse it with a bit of the solution to be measured before immersing it in the solution. The probe must be immersed deep enough to cover the little holes on the sides of the ISE (about 1.5 cm).

6. Then, immerse the chloride-selective electrode in each of the five solutions, being sure to carefully rinse the electrode between each measurement. Wait long enough to be assured that the voltage reading is stable.

> Make sure that measure your voltage starting with your most dilute solution and ending with your most concentrated solution. This helps to avoid contaminating more dilute solutions.

7. To obtain really good data you may want to:
   - a. measure the voltage for each solution two or three times and take an average;
   - b. measure the voltage for each solution three times, then measure the voltage of your chloride salts from part B, and then remeasure the voltages of your diluted solutions two or three more times taking the average of the measurements before and after;
   - c. or some other method logical method.

   Be sure to clearly write down the method that you used in your running log.
8. When you analyze your data, you will use the voltages and concentrations of these five solutions as your calibration in order to measure the chloride ion concentration of unknown solutions.

Part B: Measuring the K_{sp} of Chloride Salts

1. Now obtain samples of saturated solutions of both thallium(I) chloride and lead(II) chloride.

> **NOTE:** Be very careful not to disturb the solutions, which could cause small particles of undissolved compound to become suspended in the solution, making your value of K_{sp} suspect.
>
> Your instructor may decant the solutions from the reagent bottle into beakers for the class to use.

2. Measure the voltage (and therefore the chloride ion concentration) of both solutions following steps 5 and 7 above.
3. As before, you should measure the voltage of each solution three times and take an average, both to get a feeling for the size of your random error, and to increase your confidence with the result.
4. Measure the temperature of both solutions. Since you want the K_{sp} of the compounds in the saturated solutions, it is best to measure the temperature of the solutions, not of your sample when you are measuring the voltage. You will be using this data, plus your calibration graph from the known solutions to calculate the K_{sp} for the two compounds.
5. In addition, measure the voltage produced by the chloride selective electrode for you unknown solution. You will use this measurement to calculate the concentration of the chloride ion in your unknown solution and compare this to the result from the titration. Ideally, you will make this measurement on the same day as the electrode is calibrated as this will make the result much more reliable.

Part C: Measuring the Concentration of an Unknown Chloride Ion Solution by Potentiometric Titration

Now you will do a potentiometric titration of a silver nitrate solution of known concentration with your unknown chloride ion solution in order to determine the concentration of chloride ions in your unknown. You are more familiar with putting the unknown solution into an Erlenmeyer flask and the known solution in the buret, but this time you will do the reverse. This will give you a better endpoint than titrating the chloride ion with the silver ion.

1. Set up a buret and condition it with your unknown chloride ion solution. Fill it to near the top with the solution.
2. To a 250 mL beaker, pipet 10.00 mL of the standardized silver nitrate solution. Be sure to write down the concentration of this solution!
3. Add a magnetic stirrer and insert the chloride selective electrode.
4. Before titrating, add sufficient DI water to the silver nitrate to raise the solution level to the holes on the side of the probe. This will NOT affect your ability to observe an endpoint.

> **NOTE:** Be sure to plug in your CSE (chloride selective electrode) before your drop counter!

5. Set up a drop counter using the identical method used in the titration curve lab. Also, set up the Vernier probe so as to measure the number of drops and the voltage.
6. Perform a titration. The voltage of the solution should hold fairly steady, but at the endpoint should change fairly dramatically. Continue the titration for a few dozen more drops. It may be advisable, in order to have a check on your data, to record the initial volume on the buret and the

volume at which you see a definite deflection in the voltage of the CSE (chloride selective electrode). The difference will give you a second means to obtain the volume at the end point in addition to that obtained from your drop counter and your titration curve.

7. Perform a second titration of your unknown as a check on the reproducibility of your data and so that you can get an average of the concentration of your unknown.

Calculations

Part A: Standardizing the Chloride ISE

1. First, create a graph of voltage from the chloride selective electrode versus log of the concentration of the standardized and diluted standardized solutions. The graph should be a straight line or nearly so.
2. If it is sufficiently linear, then perform a linear regression to obtain the value of the slope, m, and the y-intercept, b. The linear equation should allow you to calculate the chloride concentration of any unknown solution simply by measuring the voltage of the solution. At this point, you have successfully calibrated your electrode.
3. If you feel the graph is not sufficiently linear, you can free-hand the best curve you can to the data and interpolate the chloride ion concentration directly from the curve you have drawn.

Part B: Measuring the K_{sp} of Chloride Salts

1. Next, calculate the concentration for the thallium(I) and lead(II) chloride solutions using your calibration.
2. Calculate K_{sp} for these two compounds from your data.
3. Using the “known” values for these two solubility products, calculate the percent error for your measurement.

Part C: Measuring the Concentration of an Unknown Chloride Ion Solution by Potentiometric Titration

1. Calculate the concentration of your unknown solution from the voltage measurement you made on the first day. You will be comparing this to the result from the titration.
2. Create a graph of voltage versus volume of chloride ion solution added from the titration of the standardized silver nitration solution with your unknown chloride ion solution. You will need to use the drop counter calibration from the previous lab.
3. Print out titration curves for both titrations you performed. If the endpoint does not show a sufficiently sharp deflection, you may have to obtain the endpoint from drawing lines through the part of the curve before the endpoint and after the endpoint and obtain the endpoint from the intersection of the lines. The endpoint will be the steepest point on the curve of voltage versus volume. You may want to use a first derivative of voltage versus volume to get the best endpoint.
4. Now, bearing in mind the stoichiometry of the precipitation reaction between the ions, calculate the chloride ion concentration of your sample from the titrations. Calculate an average and report your result.

Post Lab Questions

1. Which measurement of the chloride ion concentration do you believe is more reliable? That from the simple measurement of voltage or that from the titrations of the sample? Why?

2. Often low concentration solutions, such as your unknown, are measured and reported in parts per thousand (ppt). Assuming that your solution has a density of 1.00 g/mL, calculate the ppt concentration of sodium chloride in your solution. Do a little research. If this were tap water coming to your home, would this be considered a high sodium-high chloride content water?

EXPERIMENT 8

Analysis of a Cation Mixture

Objective

This experiment illustrates the procedures used in developing a scheme for separating and identifying a selected group of cations.

Introduction

A chemist uses inorganic qualitative analysis to detect the various elements that are present in a sample of material. For ionic substances this is usually done by putting the substance in aqueous solution and testing for various cations and anions.

In this experiment, you will look at part of the chemistry of six cations: Ag^+, Ni^{2+}, Ba^{2+}, Zn^{2+}, Fe^{3+}, and Cr^{3+}. You will initially compare the reactions of each of these with various reagents to see which form precipitates, which are amphoteric, and which form ammonia complex ions. You will use these results to develop a scheme for separating these cations when they are present in a mixture. You will also look at some specific reactions for each of these cations that allow you to identify each cation when you know that other cations are absent.

Predicting reaction products:

You are asked to complete and balance the equations for each of the reactions occurring. The reactants are given in each case.

With the exception of one reaction which is oxidation-reduction, all the reactions in this experiment are of three types:

1. formation of an insoluble salt (precipitation reaction);
2. formation of ammine complex ions;
3. formation of hydroxide complex ions (amphoteric cations).

To predict the formula of an insoluble precipitate, use the cation under study and the anion from the reagent added. For example, if you mix Pb^{2+} solution with 3 *M* HCl, you observe a white precipitate. The net ionic equation is:

$$Pb^{2+}{}_{(aq)} + 2\ Cl^{-}{}_{(aq)} \rightarrow PbCl_{2\ (s)} \qquad \textbf{(EQ 8.1)}$$

When adding either NaOH or NH_3 solution and a precipitate forms, it is the metal hydroxide as both these solutions are bases.

Hydroxides such as $Zn(OH)_2$ and $Al(OH)_3$, which dissolve in either strong base or strong acid, are referred to as being **amphoteric**. You will test for amphoteric behavior of a cation by first adding just enough NaOH to make a solution basic (in which case most metal hydroxides precipitate) and then adding excess NaOH to see if the metal hydroxide dissolves. For example, if you add 1 drop NaOH to Pb^{2+} solution, you see a white precipitate which dissolves when an excess of 8 - 10 drops of NaOH is added.

The net ionic equations are:

$$Pb^{2+}{}_{(aq)} + 2\ OH^{-}{}_{(aq)} \rightarrow Pb(OH)_{2\ (s)} \qquad \textbf{(EQ 8.2)}$$

$$Pb(OH)_{2\ (s)} + 2\ OH^{-}{}_{(aq)} \rightarrow Pb(OH)_4{}^{2-}{}_{(aq)} \qquad \textbf{(EQ 8.3)}$$

The tetrahydroxoplumbate(II) ion, $Pb(OH)_4{}^{2-}$, is called a **complex ion**. Of the ions you are studying in this experiment, *those that are amphoteric complex with four OH^- in each case*.

You will test for the formation of ammine complex ions by first adding just enough NH_3 solution to make the cation solution basic (in which case most metal hydroxides precipitate), then by adding excess NH_3 to see if the metal hydroxide dissolves. For example, if you added 1 drop of NH_3 solution to a Cd^{2+} solution, you would see a white precipitate which dissolves on adding 8 - 10 drops excess NH_3. The net ionic equations are:

$$Cd^{2+}{}_{(aq)} + 2\ NH_{3\ (aq)} + 2\ H_2O_{\ (l)} \rightarrow Cd(OH)_{2\ (s)} + 2\ NH_4{}^{+}{}_{(aq)} \qquad \textbf{(EQ 8.4)}$$

$$Cd(OH)_{2\ (s)} + 4\ NH_{3\ (aq)} \rightarrow Cd(NH_3)_4{}^{2+}{}_{(aq)} + 2\ OH^{-}{}_{(aq)} \qquad \textbf{(EQ 8.5)}$$

The tetraamminecadmium(II) ion, $Cd(NH_3)_4{}^{2+}$, is an ammine complex. Many of the transition metal cations form ammine complexes as well as complex ions with other groups besides NH_3 or OH^- (called ligands). The number of ligands attached to a metal is called the **coordination number**. The cations in this study have the following coordination numbers when they form complex ions. **Ag^+(2), Ni^{2+}(6), Fe^{3+}(6), Cr^{3+}(4), Zn^{2+}(4)**. Use these coordination numbers to determine the number of NH_3 groups bonded to the metal for any of the cations you observe forming ammine complexes.

Frequently, in qualitative analysis, we need to bring a precipitate back into solution. There are many different ways to dissolve a precipitate. Most of these involve chemical reactions which compete with precipitate formation. Common methods involve forming a complex ion with the cation (as in the above examples) or adding H^+ if the insoluble salt contains the anion of a weak acid. An example of this is:

$$NiS_{\ (s)} + 2\ H^{+}{}_{(aq)} \rightarrow Ni^{2+}{}_{(aq)} + H_2S_{\ (g)} \qquad \textbf{(EQ 8.6)}$$

The only oxidation-reduction reaction you will observe is that of tetrahydroxochromate(III) ion, $Cr(OH)_4^-$, with H_2O_2 in basic solution. The products are chromate, CrO_4^{2-}, from the $Cr(OH)_4^-$ and hydroxide, OH^- from the H_2O_2. Using this information, you can balance the redox equation.

General Techniques

Centrifuge. A centrifuge is an instrument used to rapidly separate a solid from a liquid. A mixture of solid and liquid in a test tube is placed in a slot in the centrifuge and spun at high speed. This concentrates the solid in the bottom of the test tube in 30 - 50 seconds of spinning. After centrifuging, one can easily pour off the clear supernatant above the solid.

> **Caution:** A centrifuge must be balanced to spin properly. To balance a centrifuge, use a second test tube filled with water to the same depth as your sample tube. These two test tubes should be placed on opposite sides of the centrifuge. Most centrifuges have sufficient slots to allow 2 or 3 samples to be spun simultaneously.

Mixing of reagents. A dropper should be used to add small quantities of one reagent to another. For qualitative analysis, the general rule of thumb is that 1 mL = 20 drops, using a standard size dropper (**not a Pasteur Pipet**). On mixing 2 or more reagents, always stir the mixture before drawing any conclusions about the reaction.

Precipitation. To detect the formation of a precipitate, it is essential that the reagents being mixed together are clear. A clear solution is transparent but may be colored. Several of the cation solutions you will study are colored.

Heating of solutions in test tubes. The safest, simplest way to heat a small amount of solution in a small test tube is in a boiling water bath. For the 4" test tubes, use a 250 mL beaker with 1½ inches boiling water. Put the test tube in the boiling water for about 5 minutes, stir a couple of times during the 5 minutes.

Testing acidity. To test a solution for acidity, stir it with a stirring rod and touch the wet rod to a piece of litmus paper. Litmus is red in acid and blue in base. Never immerse the litmus paper in the solution in the test tube.

Experimental Procedure

Part I. You will study the reactions of the six cations Ag^+, Fe^{3+}, Ni^{2+}, Cr^{3+}, Zn^{2+}, and Ba^{2+} with various reagents. Record all observations such as initial colors, precipitate formations, color changes, etc. Table 8.2 on page 70 of the write-up is for a summary of all reactions observed. It will be used to develop a scheme for separating these cations, using the reagents studied. Copy this table into your lab notebook.

1. Reaction with dilute HCl. To 10 drops of each cation solution, add 1 mL (20 drops) of 3 *M* HCl. Any precipitates formed are metal chlorides.
2. Reaction with $NH_3 + H_2O$.

  - **a.** To 10 drops of each cation solution, add 1 drop of 1 *M* NH_3 solution and mix. Test each solution for acidity. To any mixture which is not basic, add additional 1 *M* NH_3 dropwise until just basic. Any precipitates formed are metal hydroxides.
  - **b.** To the above basic mixtures, add 10 drops of 15 *M* NH_3. Note any color changes or precipitates that dissolve to detect the formation of ammine complex ions.

3. Reaction with NaOH and Oxidation with H_2O_2.
   - **a.** To 10 drops of each cation solution, add 1 drop of 6 M NaOH and mix. Test each solution for acidity. To any mixture which is not basic, add additional 6 M NaOH dropwise until just basic. Any precipitates formed are metal hydroxides.
   - **b.** To the above mixtures, add 20 drops of 6 *M* NaOH and mix. Note any color changes and any precipitates that dissolve to detect the formation of any hydroxide complex ions.
   - **c.** To the above test tubes, add 10 drops of 3% H_2O_2 and heat for 5 minutes in a boiling water bath. Stir a couple of times while heating. Note any changes which occur. Immediately test for Cr^{3+}as in "7" below.
4. Reaction with H_2SO_4.
   - **a.** To 10 drops of each cation solution, add 5 drops of 3 *M* H_2SO_4 and mix. Any precipitates that form are metal sulfates.

The following are tests which can be used to confirm the presence of each of these cations when you have only one cation present. Note all color changes and precipitates.

5. Ag^+ test. The formation of white AgCl on addition of HCl as in (1) above is sufficient to confirm Ag^+.
6. Fe^{3+} test. To an Fe^{3+} solution (10 drops), add 5 drops of 0.2 *M* KSCN. This will form the complex ion thiocyanatoiron(II), $FeSCN^{2+}$, a deep red complex ion.
7. Cr^{3+} test. To a CrO_4^{2-} solution (10 drops), add 6 *M* $HC_2H_3O_2$ until acidic; then add 2 - 3 drops 0.1 *M* $Pb(C_2H_3O_2)_2$ solution. A yellow ppt of $PbCrO_4$ forms.
8. Ni^{2+} test. Take 10 drops of Ni^{2+} solution; make it just basic with 6 *M* NH_3. To this mixture, add 10 drops of dimethylglyoxime. The formation of red precipitate confirms Ni^{2+}.
9. Zn^{2+} test. To 10 drops of Zn^{2+} solution, add 6 *M* HNO_3 until just acidic; then add 10 drops of potassium hexacyanoferrate(II), $K_4Fe(CN)_6$. Formation of a pale yellow precipitate of $K_2ZnFe(CN)_6$ confirms Zn^{2+}.
10. Ba^{2+} test. The formation of white $BaSO_4$ precipitate, noted in part (4) above on addition of 3 *M* H_2SO_4, is sufficient to confirm Ba^{2+}.

Part II. Before your lab meets next session you must develop a scheme in flow chart form for separating and identifying these six cations in a mixture. **You must get your flow chart approved by your instructor before lab starts**. You will not be issued an unknown until your flow chart is approved. You will use it to analyze your unknown.

To develop your scheme for separating the ions, use the reagents and results from parts (1) - (4) above. Ideally, you would add a reagent that will precipitate out only one cation which can then be separated by centrifugation. That isn't entirely possible with these reagents. You will at some point have to separate the group of ions into two smaller groups with some cations in the precipitate you form and others left in solution. These mixtures can then be further treated to completely separate the cations. It is helpful to run the known mixture of cations at the same time that you are analyzing your unknown solution, so that you can compare results.

You can add 6 *M* HNO_3 dropwise to neutralize excess base. To dissolve metal hydroxide precipitates, add 10 drops of water, then 6 *M* HNO_3 with stirring until dissolved. Once you have separated one cation from the others, you need to run a confirmatory test to prove its presence, use the tests in parts (5) - (10) above.

Flow charts

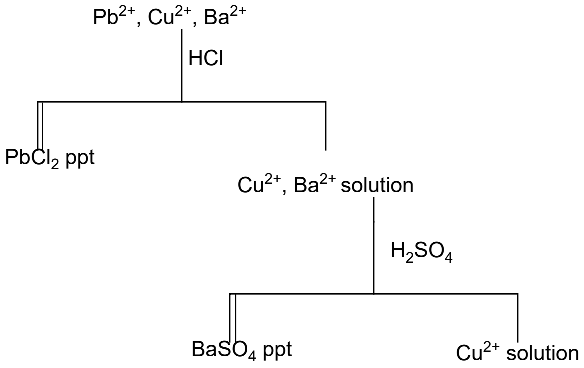
The simplest method of showing a separation scheme is in flow chart form. Table 8.1 gives you an example of three cations with various reagents and a flow chart (see Figure 8.1) developed from the table for separating these three ions from each other.

You should include formulas of all reagents added, colors of all solutions and ppts, and conclusions made from these observations.

TABLE 8.1

Reagent	Pb^{2+}	Cu^{2+}	Ba^{2+}
HCl	white ppt	no reaction	no reaction
Na_2CO_3	white ppt	pale blue ppt	white ppt
H_2SO_4	white ppt	no reaction	white ppt

FIGURE 8.1 **Sample Flow Chart**



You will be issued an unknown solution containing one or more of these six cations. You will analyze the unknown, using your approved flow chart.

Observations and Data

1. Record your observations on all reactions in your notebook using Table 8.2 as an example.

TABLE 8.2 Sample Matrix

Reagents	**A g^{+}**	**Fe^{3+}**	**Cr^{3+}**	**Ni^{2+}**	**Zn^{2+}**	**Ba^{2+}**
3 *M* HCl						
1 *M* NH_3 until basic						
15 *M* NH_3 excess						
6 *M* NaOH until basic						
6 *M* NaOH excess						
6 *M* NaOH in excess, H_2O_2 and heat						
3 *M* H_2SO_4						

2. Record the observed results for each of the individual cation tests in your notebook.
   - a. Ag^{+} test:
   - b. Fe^{3+} test:
   - c. Cr^{3+} test:
   - d. Ni^{2+} test:
   - e. Zn^{2+} test:
   - f. Ba^{2+} test:
3. Construct a flow chart and get it approved by your instructor.

Reaction Equations

Complete and balance the following equations (reactants given) in net ionic form. **Be sure to indicate the phase**.

1. $Ag^{+}{}_{(aq)} + \ Cl^{-}{}_{(aq)} \rightarrow$

2. $Ag^{+}{}_{(aq)} + \ NH_{3\ (aq)} + \ H_2O_{\ (l)}$ (until basic) →

3. $Ag(OH)_{(s)} + \ NH_{3\ (aq)}$ (excess) →

4. $Ag^{+}{}_{(aq)} + \ NH_{3\ (aq)}$ (excess) →

5. $Ag^{+}{}_{(aq)} + \ OH^{-}{}_{(aq)} \rightarrow$

6. $Fe^{3+}{}_{(aq)} + \ NH_{3\ (aq)} + \ H_2O_{\ (l)} \rightarrow$

7. $Fe^{3+}{}_{(aq)} + \ OH^{-}{}_{(aq)} \rightarrow$

8. $Fe(OH)_{3\ (s)} + \ H^{+}{}_{(aq)} \rightarrow$

9. $Fe^{3+}{}_{(aq)} + \ SCN^{-}{}_{(aq)} \rightarrow$

10. $Cr^{3+}{}_{(aq)} + \ NH_{3\ (aq)} + \ H_2O_{\ (l)} \rightarrow$

11. $Cr^{3+}{}_{(aq)} + \ OH^{-}{}_{(aq)}$ (until basic) →

12. $Cr^{3+}{}_{(aq)} + \ OH^{-}{}_{(aq)}$ (excess) →

13. $Cr(OH)_{3\ (s)} + \ OH^{-}{}_{(aq)} \rightarrow$

14. $Cr(OH)_{3\ (s)} + \ H^{+}{}_{(aq)} \rightarrow$

15. $Cr(OH)_4^-{}_{(aq)} + H_2O_{2\,(aq)} + OH^-{}_{(aq)} \rightarrow$

16. $CrO_4^{2-}{}_{(aq)} + Pb^{2+}{}_{(aq)} \rightarrow$

17. $Zn^{2+}{}_{(aq)} + NH_{3\,(aq)} + H_2O_{(l)}$ (until basic) $\rightarrow$

18. $Zn(OH)_{2\,(s)} + NH_{3\,(aq)}$ (excess) $\rightarrow$

19. $Zn^{2+}{}_{(aq)} + NH_{3\,(aq)}$ (excess) $\rightarrow$

20. $Zn^{2+}{}_{(aq)} + OH^-{}_{(aq)}$ (until basic) $\rightarrow$

21. $Zn(OH)_2(s) + OH^-{}_{(aq)}$ (excess) $\rightarrow$

22. $Zn^{2+}{}_{(aq)} + OH^-{}_{(aq)}$ (excess) $\rightarrow$

23. $Zn(OH)_{2\,(s)} + H^+{}_{(aq)} \rightarrow$

24. $Zn^{2+}{}_{(aq)} + K^+{}_{(aq)} + Fe(CN)_6^{4-}{}_{(aq)} \rightarrow$

25. $Ni^{2+}{}_{(aq)} + NH_{3\,(aq)} + H_2O_{(l)}$ (until basic) $\rightarrow$

26. $Ni(OH)_{2\,(s)} + NH_{3\,(aq)}$ (excess) $\rightarrow$

27. $Ni^{2+}{}_{(aq)} + NH_3$ (excess) $\rightarrow$

28. $Ni^{2+}{}_{(aq)} + OH^-{}_{(aq)} \rightarrow$

29. $Ni(OH)_{2\,(s)} + H^+{}_{(aq)} \rightarrow$

30. $Ba^{2+}{}_{(aq)} + SO_4^{2-}{}_{(aq)} \rightarrow$

Post Lab Questions

1. Answer the following questions about metal hydroxides of Ni^{2+} and Ba^{2+}.

$$K_{sp}\ Ni(OH)_2 = 1.6\times10^{-16} \text{ and } Ba(OH)_2 = 2.2\times10^{-2}$$

   a. What hydroxide concentration must be exceeded in order to precipitate the corresponding metal hydroxides of 0.050 *M* Ni^{2+} and 0.050 *M* Ba^{2+}?

   b. You used 10 drops of 0.050 *M* Ni^{2+} and 10 drops of 0.050 *M* Ba^{2+} and added 6 *M* NaOH until basic (assume it took 2 drops in each case to become basic). What was the concentration of each of these ions in the respective mixtures you observed?

   c. Are the results from parts a and b above consistent with your observations? Be specific.

2. What concentration of NH_3 is needed to convert all the cation in 0.050 *M* $Ni(NO_3)_2$ into the ammonia complex, hexaamminenickel(II), $Ni(NH_3)_6^{2+}$? (Assume the Ni^{2+} drops from 0.050 *M* to 1.0×10^{-6} *M*.)

$$K_d \text{ of } Ni(NH_3)_6^{2+} = 1.8\times10^{-9} \quad \text{or} \quad K_f = 5.6\times10^{8}$$

EXPERIMENT 9

Group I Cations: The Silver Group

Introduction

The Group I cations, Ag^+, Pb^{2+}, and Hg_2^{2+} are the only common cations that form insoluble chlorides in dilute hydrochloric acid. This allows the Group I cations to be separated from other cations in solution by addition of HCl. The net-ionic equations for the precipitation are:

$$Ag^+_{(aq)} + Cl^-_{(aq)} \rightarrow AgCl_{(s)} \qquad \textbf{(EQ 9.1)}$$

$$Hg_2^{2+}{}_{(aq)} + 2\,Cl^-_{(aq)} \rightarrow Hg_2Cl_{2\,(s)} \qquad \textbf{(EQ 9.2)}$$

$$Pb^{2+}_{(aq)} + 2\,Cl^-_{(aq)} \rightarrow PbCl_{2\,(s)} \qquad \textbf{(EQ 9.3)}$$

Table 9.1 gives the solubility product and molar solubility values for these chloride salts. Note that the $PbCl_2$ is significantly more soluble. The solubility of $PbCl_2$ increases significantly with increase in temperature. This increase in solubility on heating is the basis of separating $PbCl_2$ from the AgCl and Hg_2Cl_2.

$$PbCl_{2\,(s)} + H_2O_{(l)} + \text{heat} \rightarrow Pb^{2+}_{(aq)} + Cl^-_{(aq)} \qquad \textbf{(EQ 9.4)}$$

TABLE 9.1 Solubilities of Group I Chlorides at 25°C

Salt	K_{sp}	Molar Solubility, M
Hg_2Cl_2	1.1×10^{-18}	6.5×10^{-7}
AgCl	1.8×10^{-10}	1.3×10^{-5}
$PbCl_2$	1.7×10^{-5}	1.6×10^{-2}

Lead ion is confirmed by adding K_2CrO_4 to the test solution which precipitates yellow lead chromate.

$$Pb^{2+}_{(aq)} + CrO_4^{2-}{}_{(aq)} \rightarrow PbCrO_{4\,(s)} \qquad \textbf{(EQ 9.5)}$$

Aqueous ammonia is used to separate AgCl and Hg_2Cl_2 solids. Silver chloride dissolves in aqueous ammonia, forming a complex ion.

$$AgCl_{(s)} + 2\ NH_{3\,(aq)} \rightarrow Ag(NH_3)_2{}^{+}{}_{(aq)} + Cl^{-}{}_{(aq)} \qquad \textbf{(EQ 9.6)}$$

By contrast, Hg_2Cl_2 undergoes auto-oxidation-reduction in aqueous ammonia, forming metallic mercury, a black precipitate, and $HgNH_2Cl$, an insoluble white salt.

$$Hg_2Cl_{2\,(s)} + 2\ NH_{3\,(aq)} \rightarrow Hg_{(l)} + HgNH_2Cl_{(s)} + NH_4{}^{+}{}_{(aq)} + Cl^{-}{}_{(aq)} \qquad \textbf{(EQ 9.7)}$$

The formation of a black precipitate on addition of aqueous ammonia confirms mercury.

Silver ion is confirmed by acidifying the aqueous ammonia extract with nitric acid. The acid destroys the silver ammine complex, causing the silver chloride to re-precipitate.

$$Ag(NH_3)_2{}^{+}{}_{(aq)} + 2\ H^{+}{}_{(aq)} + Cl^{-}{}_{(aq)} \rightarrow AgCl_{(s)} + 2\ NH_4{}^{+}{}_{(aq)} \qquad \textbf{(EQ 9.8)}$$

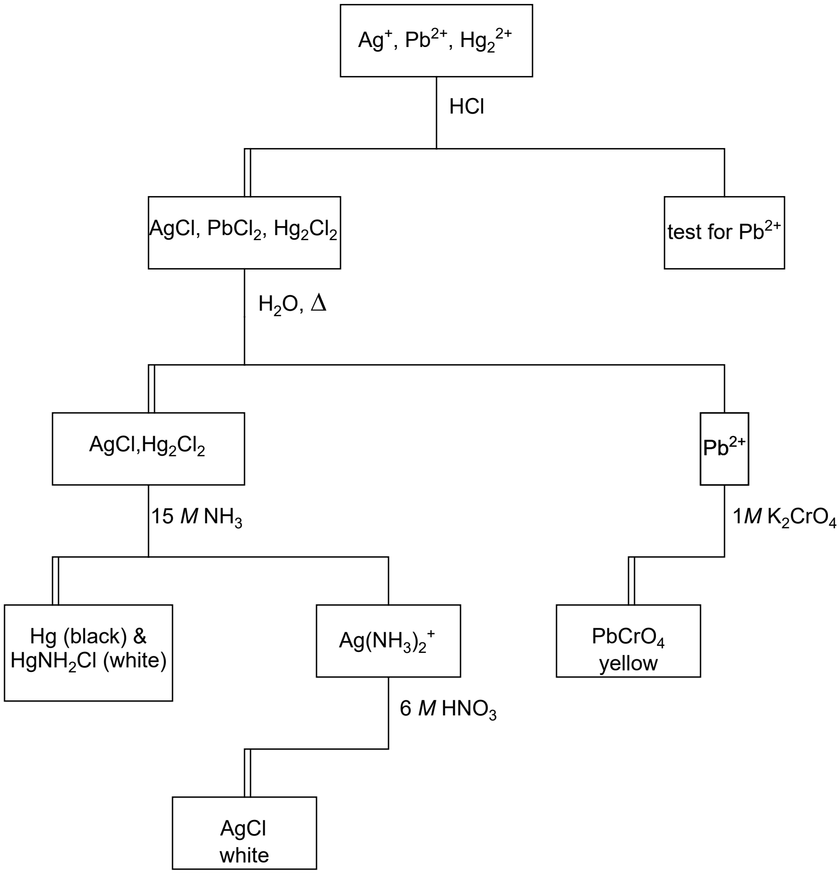
The formation of a whitish precipitate on addition of aqueous ammonia occurs when $PbCl_2$ is not completely removed by the hot water extraction. Any $PbCl_2$ remaining with the Hg_2Cl_2 and AgCl reacts with NH_3 according to the equation.

$$2\ PbCl_{2\,(s)} + 3\ NH_{3\,(aq)} + 3\ H_2O_{(l)} \rightarrow Pb(OH)Cl_{(s)} + Pb(OH)_{2\,(s)} + 3\ NH_4{}^{+}{}_{(aq)} + 3\ Cl^{-}{}_{(aq)} \qquad \textbf{(EQ 9.9)}$$

The equation is written this way because varying amounts of white insoluble products are formed.

Experimental Procedure: Analytical Group I

FIGURE 9.1 **Flow Chart for Group I: The Silver Group**



Test a known solution simultaneously with your unknown.

Step 1: Precipitation of Group 1. To 10 drops of the solution to be analyzed add 2 drops 6 *M* HCl. Stir well. Cfg and decant the solution (S1) from the ppt (P1). Treat the ppt P1 according to Step 2.

STEP 2: Dissolving Lead Chloride. Boil about 10 mL of DI water in a small beaker. Add 10 drops of the hot DI H_2O to P1 and heat in a water bath for 2-3 minutes Stir. Immediately cfg. and decant the solution (S2) while still hot. Repeat this extraction on any remaining ppt (P2). Test S2 according to Step 3. Treat the P2 as in Step 4.

STEP 3: Test for Lead. To solution S1 or S2 add 2 drops 1 *M* K_2CrO_4. Formation of a yellow ppt of $PbCrO_4$ confirms lead.

STEP 4: Separation of Silver and Test for Mercury. To ppt P2 add 4 drops 15 *M* NH_3. Stir, Cfg, and decant solution (S3). Repeat with another 4 drops 15 *M* NH_3, combining both solutions. A black ppt formed on the addition of the NH_3 confirms mercury. Test solution S3 as in Step 5.

STEP 5: Test for Silver. To solution S3 add 6 *M* HNO_3 until acidic to litmus; add 1 more drop. Formation of a white ppt of AgCl confirms silver.

Data and Calculations

1. Write a flow chart for your unknown analysis in your lab notebook. You should include formulas of all reagents added, colors of all solutions and ppts, and conclusions made from these observations.

   For example, your original solution is colorless, you add HCl forming a white ppt and a colorless solution. At this point you do not know what the formula of the white ppt is, so do not write one.

2. What cation(s) is present in your unknown?

Post Lab Questions

1. Write net-ionic equations for all the reactions occurring in the Group I analysis for each cation in the group.
    - a. Lead
    - b. Mercury
    - c. Silver
2. Calculate the [Ag^+] that would remain in solution under the conditions of the group precipitation, i.e., 1.0 *M* HCl and 0.10 M Ag^+ at time of mixing.

3. Using a single reagent, how could you distinguish between the following pairs of substances contained in separate test tubes? Give the net-ionic equation for each test.

a. $AgCl$ and $ZnCl_2$ (solids)

b. $PbCl_2$ and Hg_2Cl_2 (solids)

c. $Cd(NO_3)_2$ and $AgNO_3$ (solutions)

d. HCl and HNO_3 (solutions)

e. $Hg_2(NO_3)_2$ and $Hg(NO_3)_2$ (solutions)

EXPERIMENT 10

Cation Group II: The Acid-Insoluble Sulfides

Introduction

The ions of analytical cation Group II are called the acid-insoluble sulfide group because they can be precipitated as sulfides from a saturated solution of H_2S that is also 0.30 *M* HCl. H_2S undergoes stepwise dissociation:

$$H_2S_{(aq)} \rightleftharpoons H^+_{(aq)} + HS^-_{(aq)} \quad K_{a_1} = 1.1 \times 10^{-7} M = \frac{[H^+][HS^-]}{[H_2S]} \qquad \textbf{(EQ 10.1)}$$

$$HS^-_{(aq)} \rightleftharpoons H^+_{(aq)} + S^{2-}_{(aq)} \quad K_{a_2} = 1.3 \times 10^{-13} M = \frac{[H^+][S^{2-}]}{[HS^-\ ]} \qquad \textbf{(EQ 10.2)}$$

$$\text{overall: } H_2S_{(aq)} \rightleftharpoons 2\,H^+_{(aq)} + S^{2-}_{(aq)} \quad K_a = K_{a_1}K_{a_2} = \frac{[H^+]^2[S^{2-}]}{[H_2S]} \qquad \textbf{(EQ 10.3)}$$

Let $K_i = K_a[H_2S]$, in a saturated H_2S solution with $[H^+]$ being controlled, so:

$$\begin{gathered} K_i = [H^+]^2[S^{2-}] = K_{a_1}K_{a_2}[H_2S] = (1.1\times10^{-7}M)(1.3\times10^{-13}M)(0.10M) \\ K_i = [H^+]^2[S^{2-}] = 1.4\times10^{-21}M^3 \end{gathered} \qquad \textbf{(EQ 10.4)}$$

So when $[H^+]$ is kept at 0.1 *M* to 0.3 *M*, the $[S^{2-}]$ is high enough to precipitate the metal sulfides that are in Group II, but is too low to precipitate the cations that are in Group III. Table 10.1 gives K_{sp} values.

The common cations in this acid-insoluble sulfide group are Pb^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}, Hg(II) as tetrachloromercurate(II), $HgCl_4^{2-}$, As(III) as H_3AsO_3, As(V) as H_3AsO_4, Sb(III) as tetrachlorostibate(III), $SbCl_4^-$, Sb(V) as hexachlorostibate(V), $SbCl_6^-$, Sn(II) as $SnCl_4^{2-}$, and Sn(IV) as $SnCl_6^{2-}$.

We will do an abbreviated analysis of Group II, looking at copper(II), bismuth(III), cadmium(II), mercury(II), and tin(IV).

TABLE 10.1 **Solubility Products of Group II & Group III Sulfides**

Acid-Insoluble Sulfides		Basic-Insoluble Sulfides	
Salt	**K_{sp}**	**Salt**	**K_{sp}**
CuS	8.5×10^{-36}	ZnS	1.1×10^{-21}
Bi_2S_3	2.9×10^{-70}	CoS	5.9×10^{-21}
CdS	3.6×10^{-29}	NiS	2.0×10^{-21}
HgS	1.6×10^{-54}	FeS	4.9×10^{-18}
SnS_2	1×10^{-70}	MnS	7×10^{-16}
PbS	7×10^{-27}		
Sb_2S_3	1.6×10^{-93}		

Precipitation of the Group

We will use thioacetamide as a source of H_2S, a poisonous gas. Thioacetamide hydrolyzes in hot solutions to produce H_2S and ammonium acetate. By generating the H_2S in the solution containing the cations it reacts with, we minimize the amount of H_2S released into the laboratory. The reaction is:

$$CH_3CSNH_{2\,(s)} + 2\ H_2O_{\,(l)} \rightarrow NH_4^+{}_{(aq)} + CH_3CO_2^-{}_{(aq)} + H_2S_{\,(g)} \qquad \textbf{(EQ 10.5)}$$

Whenever directions call for adding thioacetamide and heating, you are adding H_2S to your reaction mixture.

The following equation shows the reaction of simple cations with H_2S:

$$Cu^{2+}{}_{(aq)} + H_2S_{\,(g)} \rightarrow CuS_{\,(s)} + 2\ H^+{}_{(aq)} \qquad \textbf{(EQ 10.6)}$$

Molecular substances or complex ions are converted to insoluble sulfides:

$$2\ H_3AsO_{3\,(aq)} + 5\ H_2S_{\,(g)} \rightarrow As_2S_{5\,(s)} + 8\ H_2O_{\,(l)} \qquad \textbf{(EQ 10.7)}$$

$$SnCl_6^-{}_{(aq)} + 2\ H_2S_{\,(g)} \rightarrow SnS_{2\,(s)} + 4\ H^+{}_{(aq)} + 6\ Cl^-{}_{(aq)} \qquad \textbf{(EQ 10.8)}$$

Subdivision of the Group

The basis for the separation of Group IIA, copper, bismuth, and cadmium from Group IIB, mercury and tin is the ability of Group IIB cations to form sulfide complexes. Formation of sulfide complexes requires a high sulfide ion concentration in solution. This is achieved by adding NaHS and NaOH resulting in the reaction:

$$HS^-{}_{(aq)} + OH^-{}_{(aq)} \rightarrow S^{2-}{}_{(aq)} + H_2O_{\,(l)} \qquad \textbf{(EQ 10.9)}$$

The dissolution of the metal sulfides occurs as the net reactions:

$$HgS_{\,(s)} + HS^-{}_{(aq)} + OH^-{}_{(aq)} \rightarrow HgS_2^{2-}{}_{(aq)} + H_2O_{\,(l)} \qquad \textbf{(EQ 10.10)}$$

$$SnS_{2\,(s)} + HS^{-}{}_{(aq)} + OH^{-}{}_{(aq)} \rightarrow SnS_3{}^{2-}{}_{(aq)} + H_2O_{\,(l)} \tag{EQ 10.11}$$

Analysis of Group IIA

Dissolving the Metal Sulfides. The Group IIA sulfides are dissolved by reaction with hot dilute nitric acid which oxidizes the sulfide ions to elemental sulfur. This decreases the sulfide concentration in solution, causing the metal sulfides to dissolve to replace it.

The two reactions involved for copper are:

$$CuS_{\,(s)} \rightarrow Cu^{2+}{}_{(aq)} + S^{2-}{}_{(aq)} \tag{EQ 10.12}$$

$$3\ S^{2-}{}_{(aq)} + 8\ H^{+}{}_{(aq)} + 2\ NO_3{}^{-}{}_{(aq)} \rightarrow 3\ S_{\,(s)} + 2\ NO_{\,(g)} + 4\ H_2O_{\,(l)} \tag{EQ 10.13}$$

The net reaction is the sum of these two are:

$$3\ CuS_{\,(s)} + 8\ H^{+}{}_{(aq)} + 2\ NO_3{}^{-}{}_{(aq)} \rightarrow 3\ Cu^{2+}{}_{(aq)} + 3\ S_{\,(s)} + 2\ NO_{\,(g)} + 4\ H_2O_{\,(l)} \tag{EQ 10.14}$$

Similar reactions occur for CdS and Bi_2S_3.

Separation and Identification of Bismuth.

The basis of the separation of Bi^{3+} from Cu^{2+} and Cd^{2+} is the formation of insoluble $Bi(OH)_3$ in excess NH_3. Copper and cadmium form NH_3 complexes:

$$Bi^{3+}{}_{(aq)} + 3\ NH_{3\,(aq)} + 3\ H_2O_{\,(l)} \rightarrow Bi(OH)_{3\,(s)} + 3\ NH_4{}^{+}{}_{(aq)} \tag{EQ 10.15}$$

$$Cu^{2+}{}_{(aq)} + 4\ NH_{3\,(aq)} \rightarrow Cu(NH_3)_4{}^{2+}{}_{(aq)} \tag{EQ 10.16}$$

$$Cd^{2+}{}_{(aq)} + 4\ NH_{3\,(aq)} \rightarrow Cd(NH_3)_4{}^{2+}{}_{(aq)} \tag{EQ 10.17}$$

Identification of bismuth is achieved by addition of stannite solution which reduces the $Bi(OH)_3$ to black metallic bismuth:

$$2\ Bi(OH)_{3\,(s)} + 3\ Sn(OH)_3{}^{-}{}_{(aq)} + 3\ OH^{-}{}_{(aq)} \rightarrow 2\ Bi_{\,(s)} + 3\ Sn(OH)_6{}^{-}{}_{(aq)} \tag{EQ 10.18}$$

> **NOTE**: Stannite solution is a strong reducing agent that reacts with O_2 in the air. It must therefore be made just prior to use by treating a solution of $SnC1_2$ in HCl with NaOH. The net reaction is:
>
> $$SnCl_4{}^{2-}{}_{(aq)} + 3\ OH^{-}{}_{(aq)} \rightarrow Sn(OH)_3{}^{-}{}_{(aq)} + 4\ Cl^{-}{}_{(aq)} \tag{EQ 10.19}$$

Identification of Copper. The intense blue color of tetraamminecopper(II), $Cu(NH_3)_4{}^{2+}$ is a confirmation of copper.

Identification of Cadmium. Cadmium is identified by precipitation of cadmium with H_2S to form yellow CdS:

$$Cd(NH_3)_4{}^{2+}{}_{(aq)} + H_2S_{\,(g)} + 2\ OH^{-}{}_{(aq)} \rightarrow CdS_{\,(s)} + 4\ NH_{3\,(aq)} + 2\ H_2O_{\,(l)} \tag{EQ 10.20}$$

However, if the copper ions are present, they precipitate as CuS which is black and prevent the yellow CdS from being seen. Thus, copper must be removed before running the final cadmium test. This is done by addition of sodium dithionite, $Na_2S_2O_4$, which reduces the copper(II) to metallic copper but does not react with the cadmium in solution:

$$Cu(NH_3)_4{}^{2+}{}_{(aq)} + S_2O_4{}^{2-}{}_{(aq)} + 2\ H_2O_{(l)} \rightarrow Cu_{(s)} + 2\ SO_3{}^{2-}{}_{(aq)} + 4NH_4{}^{+}{}_{(aq)} \qquad \textbf{(EQ 10.21)}$$

Analysis of Group II B

Reprecipitation of the Metal Sulfides. Acidification of the basic solution of the sulfide complexes causes the metal sulfides to reprecipitate:

$$SnS_3{}^{2-}{}_{(aq)} + 2\ H^+{}_{(aq)} \rightarrow SnS_{2\ (s)} + H_2S_{(g)} \qquad \textbf{(EQ 10.22)}$$

$$HgS_2{}^{2-}{}_{(aq)} + 2\ H^+{}_{(aq)} \rightarrow HgS_{(s)} + H_2S_{(g)} \qquad \textbf{(EQ 10.23)}$$

Separation of Mercury From Tin. SnS_2 is soluble in concentrated HCl while HgS is not:

$$SnS_{2\ (s)} + 4\ H^+{}_{(aq)} + 6\ Cl^-{}_{(aq)} \rightarrow SnCl_6{}^{2-}{}_{(aq)} + 2\ H_2S_{(g)} \qquad \textbf{(EQ 10.24)}$$

Identification of Tin. The tin(IV) is first reduced to the tin(II) state using metallic Mg in HCl solution:

$$SnCl_6{}^{2-}{}_{(aq)} + Mg_{(s)} \rightarrow SnCl_4{}^{2-}{}_{(aq)} + Mg^{2+}{}_{(aq)} + 2\ Cl^-{}_{(aq)} \qquad \textbf{(EQ 10.25)}$$

Addition of $HgC1_2$ in HCl solution to tin(II) results in a reduction of the mercury(II) to elemental Hg (black) and insoluble Hg_2Cl_2 (white) for an observed grey precipitate.

$$2\ SnCl_4{}^{2-}{}_{(aq)} + 3\ HgCl_4{}^{2-}{}_{(aq)} \rightarrow Hg_2Cl_{2\ (s)} + 2\ SnCl_6{}^{2-}{}_{(aq)} + Hg_{(s)} + 6\ Cl^-{}_{(aq)} \qquad \textbf{(EQ 10.26)}$$

Identification of Mercury. HgS is one of the most insoluble inorganic compounds and requires addition of HCl + NaOCl which oxidizes the sulfide ion to sulfur and complexes the mercury(II) ion.

$$HgS_{(s)} + 2\ H^+{}_{(aq)} + 3\ Cl^-{}_{(aq)} + ClO^-{}_{(aq)} \rightarrow HgCl_4{}^{2-}{}_{(aq)} + S_{(s)} + H_2O_{(l)} \qquad \textbf{(EQ 10.27)}$$

This solution must be heated for several minutes to destroy any excess hypochlorite ions, i.e.:

$$ClO^-{}_{(aq)} + Cl^-{}_{(aq)} + 2\ H^+{}_{(aq)} \rightarrow H_2O_{(l)} + Cl_{2\ (g)} \qquad \textbf{(EQ 10.28)}$$

Mercury is confirmed by adding $SnC1_2$ in HCl solution which reduces the Hg(II) to Hg and Hg_2Cl_2 as in the tin test above, producing a grey precipitate:

$$3\ HgCl_4{}^{2-}{}_{(aq)} + 2\ SnCl_4{}^{2-}{}_{(aq)} \rightarrow Hg_{(s)} + Hg_2Cl_{2\ (s)} + 2\ SnCl_6{}^{2-}{}_{(aq)} + 6\ Cl^-{}_{(aq)} \qquad \textbf{(EQ 10.29)}$$

Procedure

Test a known solution **simultaneously with your unknown**. Note the known solution does not contain Sn^{4+} ions, be sure to add it when you get to the appropriate step with your known solutions. Do Steps 2, 3, 4, 8 and 9 on hot plate in the hood. The flow chart is Figure 10.1 on page 86.

STEP 1: pH Adjustment. To 10 drops of solution to be analyzed add 6 *M* NH_3 until just basic to litmus (count the drops of NH_3 added). Add sufficient H_2O to make 1 mL of solution; then add exactly 2 drops 6 *M* HCl. (This results in a pH of about 0.5.)

STEP 2: Precipitation with H_2S. Add 8 - 10 drops of thioacetamide (TA) solution, stir, and heat in a boiling water bath for 5 minutes. Stir several times while heating. Add 6-8 drops TA; heat another 5 minutes. Cfg. (If the resulting solution is not clear, add 2 drops 1 *M* NH_4Cl and heat for 3 - 5 min. Cfg.) Treat the ppt (P3) as in step 3. Discard the supernatant.

STEP 3: Separation of Subgroups. Wash ppt P3 with 10 drops H_2O. Cfg. Discard the washings. To the ppt add 5 drops 6 *M* NaOH and 3 drops 2 *M* NaHS. Heat for 3-5 min., stirring occasionally. Cfg. Decant the solution (S4) from the ppt (P4). Repeat the extraction with NaOH and NaHS on the ppt and combine the two extraction solutions (S4). Treat P4 as in Step 4. Treat S4 as in Step 8.

STEP 4: Dissolving Cu Subgroups (CuS, Bi_2S_3, CdS). Wash ppt P4 with 10 drops H_2O. Discard the washings. To ppt P4 add 5 drops 6 *M* HNO_3 and 5 drops H_2O. Heat for 5 minutes to dissolve the ppt. Cfg and discard any sulfur formed. (If considerable black ppt remains, treat it with a second HNO_3 + H_2O portion and combine both solutions.) Treat the solution (S5) as in Step 5.

STEP 5: Precipitation of Bismuth. Cu Test: To solution S5 add 15 *M* NH_3 until it is distinctly basic plus 1 drop. The development of a deep blue solution of tetraamminecopper(II), $Cu(NH_3)_4^{2+}$, confirms copper. Cfg. Formation of a white gelatinous ppt (P5) indicates $Bi(OH)_3$. Test P5 as in Step 6. Test the solution (S6) as in Step 7.

STEP 6: Bismuth Test. Make a fresh solution of sodium stannite, $NaSn(OH)_3$, by putting 3 drops of 0.1 *M* $SnCl_2$ in a test tube and adding 6 *M* NaOH dropwise until the white ppt that initially forms redissolves. Add this solution to ppt P5. Formation of black elemental Bi confirms bismuth.

STEP 7: Cadmium Test. If tetraamminecopper(II), $Cu(NH_3)_4^{2+}$, is present in S6 (blue solution) add a small amount of solid $Na_2S_2O_4$ (sodium dithionite) about the size of half a pea. Stir well and heat for 3 - 5 min. The solution should become colorless and copper metal should precipitate. Cfg while warm and decant the colorless solution (S7) into another test tube. (If the solution is not colorless or if copper metal has not precipitated, treat again with $Na_2S_2O_4$). To the colorless solution S7 (or colorless S6 if Cu was absent), add 5 drops thioacetamide and heat 3 - 5 min. Formation of a yellow ppt of CdS confirms cadmium.

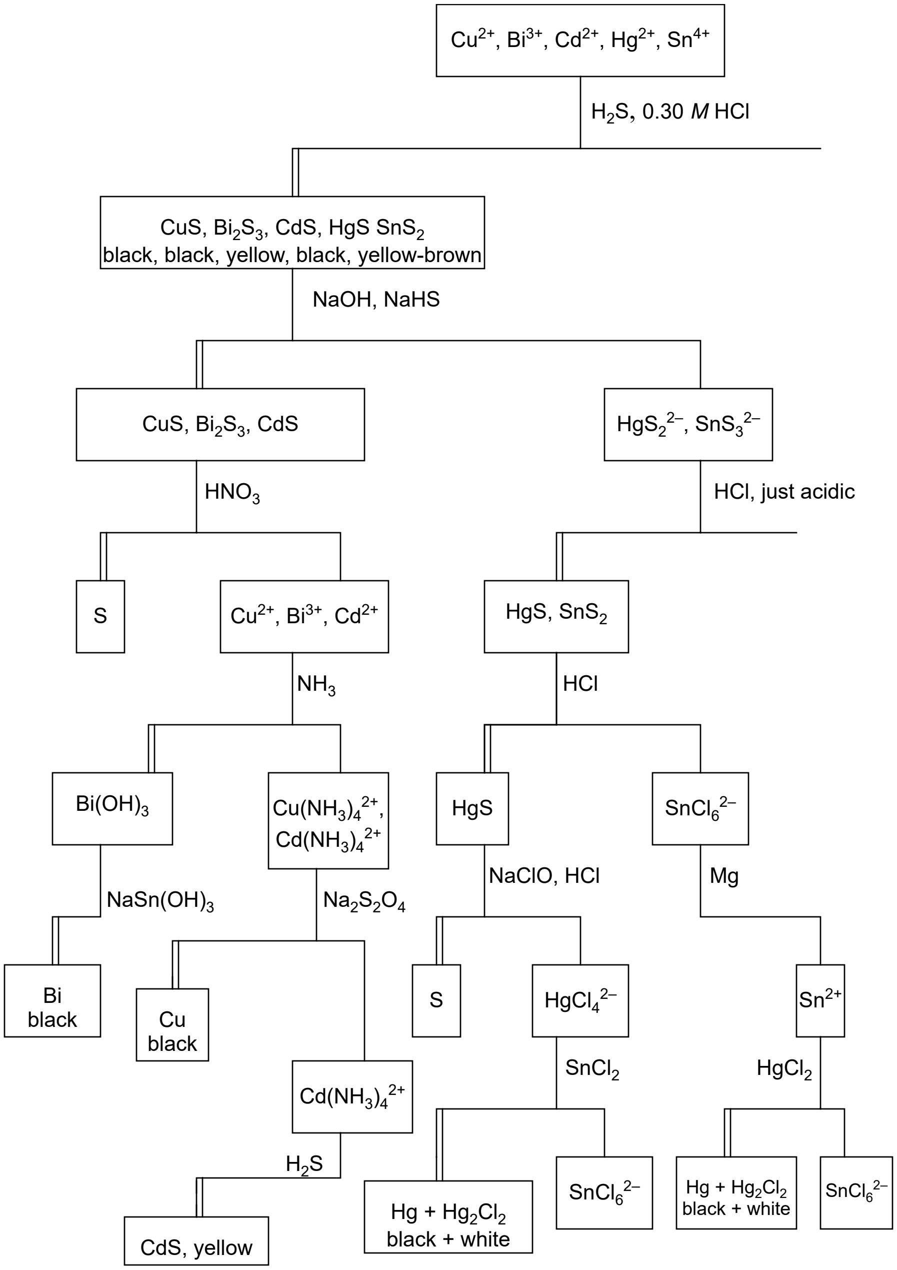
STEP 8: Precipitation of Hg Subgroup (HgS_2^{2-}, SnS_3^{2-}). To S4 from Step 3, add 6 *M* HCl with stirring until just acidic to litmus. Heat for 3 - 5 min. Cfg and discard the liquid. Treat the ppt (P6) as in step 9. (If you obtain only small amounts of a nearly white ppt, you have only elemental sulfur.)

STEP 9: Separation of HgS from SnS_2. To ppt P6 add 1 mL 6 *M* HCl, stir and heat for 3 min. Cfg. Separate the solution (S8) from the ppt (P7). Treat the remaining ppt P7 with another 10 drops HCl, heat, Cfg, and combine the solutions. Test P7 as in Step 11 and S8 as in Step 10.

STEP 10: Test for Tin. Remember that the known solution does not contain tin(IV) ions; be sure to add them to the known before continuing with this step otherwise you will get a false negative here. To solution S8 add a 1 cm piece of Mg ribbon and heat to reduce the $SnCl_6^{2-}$ to Sn^{2+}. Cfg to remove any solid formed. To the clear solution add 5 drops of 0.1 *M* $HgCl_2$. Formation of a silky grey-white ppt of Hg_2Cl_2 + Hg confirms tin.

STEP 11: Dissolving HgS. To ppt P7 add 6 drops 5% NaClO and 2 drops 6 *M* HCl. Stir to dissolve the black HgS. Heat 3 - 5 min to decompose any remaining NaClO. Cfg and decant the clear solution into a clean test tube. To the clear solution add 3 - 4 drops 0.1 *M* $SnCl_2$. Formation of a silky grey-white ppt of Hg_2Cl_2 + Hg confirms mercury.

FIGURE 10.1 Analytical Group II The H_2S Acid Group



Post Lab Questions

1. Write net-ionic equations for the reactions occurring for each cation in the group.
   a. copper

   b. bismuth

   c. cadmium

   d. mercury

   e. tin

2. Give the formula for a reagent which will:

- **a.** dissolve SnS_2 but not HgS
- **b.** dissolve $Cu(OH)_2$ but not $Bi(OH)_3$
- **c.** form a precipitate with Cu^{2+} but not with Cd^{2+}
- **d.** form a precipitate with Bi^{3+} but not with Cd^{2+}
- **e.** form a precipitate with $HgCl_2$ but not with $SnCl_2$

3. Give the formula of a site reagent (or combination of reagents if a single reagent is insufficient) which would enable you to distinguish between the following pairs of compounds contained in separate test tubes. Tell what would happen in each case to let you make the distinction.

- **a.** $Cu(OH)_2$ and $Bi(OH)_3$ (solids)
- **b.** Hg^{2+} and Cd^{2+} (solutions)
- **c.** Ag^{+} and Cu^{2+} (solutions)

4. CuS ($K_{sp} = 8.7\times10^{-36}$) is the least soluble of the Group II sulfides while PbS ($K_{sp} = 8.4\times10^{-28}$) is much more soluble. Consider a solution saturated in H_2S (0.l0 *M*) and 0.30 *M* HCl (the conditions for ppt of Group II cations).

- **a.** Calculate the $[S^{2-}]$ present. (Hint:Equation 10.4 may be useful here.)
- **b.** Calculate the concentrations of Cu^{2+} and Pb^{2+} ions that remain in solution (unprecipitated) at these conditions.

EXPERIMENT 11

Cation Group III: The Basic Insoluble Sulfides

Introduction

The cations of this analytical group are those that form insoluble sulfides or hydroxides in a buffered ammonia solution saturated with H_2S. The common cations we will look at from this group are nickel(II), iron(III), cobalt(II), chromium(III), and zinc ions.

A combination of NH_3, NH_4Cl, and thioacetamide is used to precipitate this group. The sulfides of this group have large enough solubilities that they do not precipitate under the 0.3 *M* HCl plus thioacetamide used to precipitate Cation Group II. Under these conditions, the Fe(III) and Cr(III) precipitate as hydroxides and the Co(II), Ni(II), and Zn ions precipitate as sulfides. Table 11.1 on page 89 gives solubility product values for these salts:

TABLE 11.1 **K_{sp} Values for Group III Precipitates**

Salt	K_{sp}
CoS	5.9×10^{-21}
NiS	3.0×10^{-21}
ZnS	1.1×10^{-21}
$Cr(OH)_3$	6.7×10^{-31}
$Fe(OH)_3$	6.3×10^{-38}

Metal sulfides are not very soluble, when the separation is done under acidic conditions the following equilibrium is reached:

$$MS_{(s)} + 2\ H_3O^+_{(aq)} \rightleftharpoons M^{2+}_{(aq)} + H_2S_{(aq)} + 2\ H_2O_{(l)} \qquad \textbf{(EQ 11.1)}$$

The **solubility product in acid**, K_{spa}, is used instead of K_{sp} because many ion separations are done under acidic conditions:

$$K_{spa} = \frac{[M^{2+}][H_2S]}{[H_3O^+]^2} \qquad \textbf{(EQ 11.2)}$$

The principal sulfide containing species in aqueous solutions is H_2S in acidic solutions and HS^- in basic solutions. Recall that H_2S undergoes stepwise dissociation as shown in “Cation Group II: The Acid-Insoluble Sulfides” on page 81. So:

$$K_{spa} = \frac{K_{sp}}{K_{a_1}K_{a_2}} \qquad \textbf{(EQ 11.3)}$$

Precipitation of the Group

Under the basic condition that H_2S is being generated, it rapidly converts to sulfide ion by reacting with the ammonia present:

$$2\ NH_{3\ (aq)} + H_2S_{\ (g)} \rightarrow 2\ NH_4{}^+{}_{(aq)} + S^{2-}{}_{(aq)} \qquad \textbf{(EQ 11.4)}$$

It is sulfide ion that is the precipitating agent for the insoluble sulfides. For example:

$$Co^{2+}{}_{(aq)} + S^{2-}{}_{(aq)} \rightarrow CoS_{\ (s)} \qquad \textbf{(EQ 11.5)}$$

The Fe(III) and Cr(III) react with the aqueous ammonia and precipitate as hydroxides. For example:

$$Fe^{3+}{}_{(aq)} + 3\ NH_{3\ (aq)} + 3\ H_2O_{\ (l)} \rightarrow Fe(OH)_{3\ (s)} + 3\ NH_4{}^+{}_{(aq)} \qquad \textbf{(EQ 11.6)}$$

Separation of the Nickel and Iron Subgroups

Separation of Ni and Co from Fe, Cr, and Zn is based on the fact that NiS and CoS are very slowly soluble in dilute HCl, whereas the ZnS, $Cr(OH)_3$, and $Fe(OH)_3$ dissolve rapidly. In doing this step, it is important that the NiS and CoS not remain in contact with the HCl very long. Typical reactions for dissolving the iron-subgroup are:

$$ZnS_{\ (s)} + 2\ H^+{}_{(aq)} \rightarrow Zn^{2+}{}_{(aq)} + H_2S_{\ (g)} \qquad \textbf{(EQ 11.7)}$$

$$Fe(OH)_{3\ (s)} + 3\ H^+{}_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + 3\ H_2O_{\ (l)} \qquad \textbf{(EQ 11.8)}$$

Analysis of the Nickel Subgroup

CoS and NiS readily dissolve in **aqua regia**, a mixture of HCl and HNO_3 that is a strong oxidizing agent. It readily oxidizes sulfide ion to elemental sulfur, causing the metal sulfides to dissolve:

$$CoS_{\ (s)} + 4\ H^+{}_{(aq)} + Cl^-{}_{(aq)} + NO_3{}^-{}_{(aq)} \rightarrow Co^{2+}{}_{(aq)} + S_{\ (s)} + NOCl_{\ (aq)} + 2\ H_2O_{\ (l)} \qquad \textbf{(EQ 11.9)}$$

The tests for Co and Ni can be made in the presence of each other so further separation is unnecessary. Simply divide the solution in half. To test for Ni, the solution is made basic with NH_3, forming the ammine complex:

$$Ni^{2+}{}_{(aq)} + 6\ NH_{3\ (aq)} \rightarrow Ni(NH_3)_6{}^{2+}{}_{(aq)} \qquad \textbf{(EQ 11.10)}$$

Dimethylglyoxime ($dmgH_2$) is an organic compound that forms a bright red insoluble complex with Ni(II):

$$Ni(NH_3)_6{}^{2+}{}_{(aq)} + 2\ H_2C_4H_6N_2O_{2\ (l)} \rightarrow Ni(HC_4H_6N_2O_2)_{2\ (s)} + 2\ NH_4{}^{+}{}_{(aq)} + 4\ NH_{3\ (aq)} \quad \textbf{(EQ 11.11)}$$

Cobalt(II) also forms a complex with dimethylglyoxime but it is brown in color and is soluble, so it does not interfere with the formation of the red precipitate with Ni:

The test for Co involves its reaction with thiocyanate, SCN^{-}, to form a soluble complex-ion which is a distinctive blue-green in 1:1 H_2O:acetone solution:

$$Co^{2+}{}_{(aq)} + 4\ SCN^{-}{}_{(aq)} \rightarrow Co(SCN)_4{}^{2-}{}_{(aq)} \quad \textbf{(EQ 11.12)}$$

If the separation of the Ni-subgroup from the Fe-subgroup is incomplete, any Fe(III) ions present will interfere with this test. Iron(III) reacts with thiocyanate to form a deep-red soluble complex:

$$Fe^{3+}{}_{(aq)} + SCN^{-}{}_{(aq)} \rightarrow Fe(SCN)^{2+}{}_{(aq)} \quad \textbf{(EQ 11.13)}$$

This interference can be removed by addition of fluoride ions which form a more stable and colorless complex-ion with iron:

$$Fe(SCN)^{2+}{}_{(aq)} + 6\ F^{-}{}_{(aq)} \rightarrow FeF_6{}^{3-}{}_{(aq)} + SCN^{-}{}_{(aq)} \quad \textbf{(EQ 11.14)}$$

Separation and Identification of Iron

The separation of Fe(III) from the solution containing Fe(III), Cr(III), and Zn(II) is based on the amphoteric nature of the Cr(III) and Zn(II). Addition of excess NaOH results in precipitation of $Fe(OH)_{3(s)}$ and formation of hydroxo-complex ions with Cr(III) and Zn(II).

$$Fe^{3+}{}_{(aq)} + 3\ OH^{-}{}_{(aq)} \rightarrow Fe(OH)_{3\ (s)} \quad \textbf{(EQ 11.15)}$$

$$Cr^{3+}{}_{(aq)} + 4\ OH^{-}{}_{(aq)} \rightarrow Cr(OH)_4{}^{-}{}_{(aq)} \quad \textbf{(EQ 11.16)}$$

$$Zn^{2+}{}_{(aq)} + 4\ OH^{-}{}_{(aq)} \rightarrow Zn(OH)_4{}^{2-}{}_{(aq)} \quad \textbf{(EQ 11.17)}$$

Hydrogen peroxide is also added at this step to oxidize the chromium complex to the yellow chromate ion, $CrO_4{}^{2-}$:

$$2\ Cr(OH)_4{}^{-}{}_{(aq)} + 3\ H_2O_{2\ (aq)} + 2\ OH^{-}{}_{(aq)} \rightarrow 2\ CrO_4{}^{2-}{}_{(aq)} + 8\ H_2O_{\ (l)} \quad \textbf{(EQ 11.18)}$$

The $Fe(OH)_3$ formed above is dissolved, using HCl:

$$Fe(OH)_{3\ (s)} + 3\ H^{+}{}_{(aq)} \rightarrow Fe^{3+}{}_{(aq)} + 3\ H_2O_{\ (l)} \quad \textbf{(EQ 11.19)}$$

The presence of the iron ion is confirmed by reaction with KSCN which forms a deep-red soluble iron-thiocyanate complex ion (thiocyanatoiron(II) ion):

$$Fe^{3+}{}_{(aq)} + SCN^{-}{}_{(aq)} \rightarrow Fe(SCN)^{2+}{}_{(aq)} \quad \textbf{(EQ 11.20)}$$

Identification of Chromium and Zinc

Chromate and zinc can be tested for in the presence of each other, so the solution to be tested for these is divided in half.

The solution to be tested for chromate is acidified with acetic acid and chromate is then precipitated as lead chromate, a yellow precipitate, by adding lead acetate solution. Lead(II) acetate, $Pb(C_2H_3O_2)_2$, is one of the few covalent salts in solution:

$$CrO_4^{2-}{}_{(aq)} + Pb(C_2H_3O_2)_{2\,(aq)} \rightarrow PbCrO_{4\,(s)} + 2\ C_2H_3O_2^{-}{}_{(aq)} \qquad \textbf{(EQ 11.21)}$$

The solution to be tested for zinc is acidified with HNO_3 which destroys the tetrahydroxozincate ion:

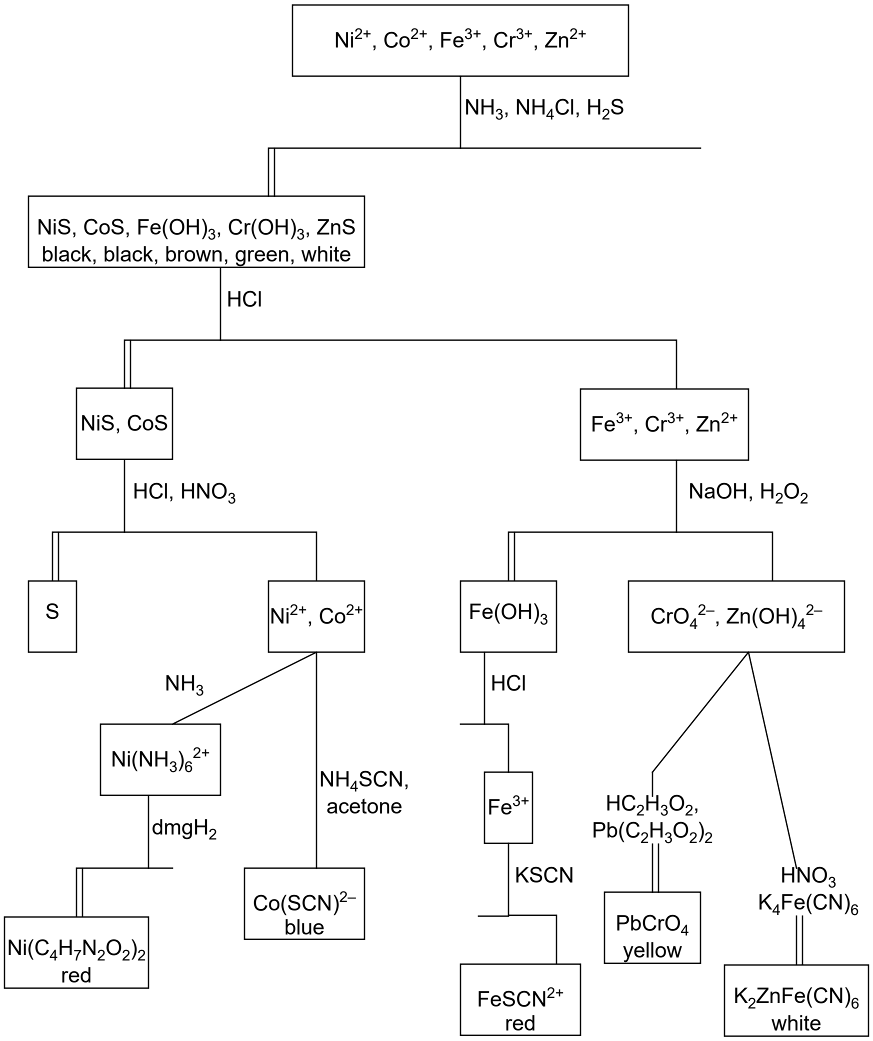
$$Zn(OH)_4^{2-}{}_{(aq)} + 4\ H^+{}_{(aq)} \rightarrow Zn^{2+}{}_{(aq)} + 4\ H_2O_{\,(l)} \qquad \textbf{(EQ 11.22)}$$

Addition of potassium hexacyanoferrate(II), $K_4Fe(CN)_6$, then precipitates the zinc as a mixed complex salt, a pale yellow precipitate:

$$Zn^{2+}{}_{(aq)} + 2\ K^+{}_{(aq)} + Fe(CN)_6^{4-}{}_{(aq)} \rightarrow K_2ZnFe(CN)_{6\,(s)} \qquad \textbf{(EQ 11.23)}$$

Procedure

FIGURE 11.1 **Analytical Group III: The H_2S Basic Group**



NOTE: We are doing an abbreviated form of Group III. The complete Group III also includes Al^{3+} and Mn^{2+}. Time considerations require a shortened form of this group.

Test a known solution simultaneously with your unknown. Do Steps 1, 2 and 6 in hood.

STEP 1: Precipitation of Group III. To 10 drops of the solution to be analyzed, add 10 drops H_2O, then 3 drops 1 *M* NH_4Cl. Add 6 *M* NH_3 until just basic to litmus. Add 2 drops 15 *M* NH_3. Add 8 drops thioacetamide and heat 5 min. in a water bath, stirring occasionally. Cfg and test the ppt (P1) as in step 2.

STEP 2: Separation of Subgroups. Wash ppt P1 with 15 drops H_2O plus 1 drop 1 *M* NH_4Cl. Cfg and discard the washings. To the ppt add 10 drops 1 *M* HCl, stir thoroughly. Cfg immediately and separate the solid (P2) from the solution (S2). Treat the ppt P2 with 4 more drops 1 *M* HCl, stir, cfg, and add the solution to S2. Treat P2 according to Step 6 and S2 according to Step 3.

STEP 3 Separation of Fe from Cr and Zn. To solution S2 add 6 *M* NaOH until basic, then 4 drops more. Add 6-8 drops 3% H_2O_2. Heat 5 min. in a water bath, stir occasionally. Cfg. Decant the solution (S3) into another test tube. Formation of a red brown ppt indicates iron. Treat the ppt (P3) according to Step 4 and the solution S3 according to Step 5.

STEP 4: Test for Iron. To ppt P3 add 10 drops H_2O and 5 drops 6 *M* HCl, stir to dissolve. To the solution add 2 drops 0.2 *M* KSCN. Formation of a deep red solution confirms iron.

STEP 5: Tests for chromium and zinc. Divide solution S3 into two parts. (A yellow solution indicates chromium). To one part add 6 *M* $HC_2H_3O_2$ until acidic, then add 2 drops 0.1 *M* $Pb(C_2H_3O_2)_2$. Formation of a yellow ppt of $PbCrO_4$ proves chromium. To the second portion of S3 add 6 *M* HNO_3 until acidic, then add 5 drops 0.1 *M* $K_4Fe(CN)_6$. Formation of an off-white ppt of $K_2ZnFe(CN)_6$ proves zinc.

STEP 6: Dissolving NiS and CoS. Wash ppt P2 from step 2 with 10 drops H_2O, cfg and discard washings. Now add 3 drops 12 *M* HCl and 1 drop 15 *M* HNO_3, heat in water bath to dissolve the NiS and CoS. Add 5 drops H_2O. Cfg and discard any ppt. Divide the solution (S4) in half, treating one half as in Step 7 and the other half as in Step 8.

STEP 7: Nickel Test. To one half of S4 add 6 *M* NH_3 until basic, then add 1 more drop. Add 3 drops 1% dimethylglyoxime in 95% ethanol. Formation of a bright red ppt of $Ni(C_4H_7N_2O_2)_2$ proves nickel.

STEP 8: Cobalt Test. To one half of S4 add 6 *M* NH_3 until basic, then add 1 drop 6 *M* HCl. Add a few crystals of NH_4SCN to the test tube. Now add an equal volume of acetone and stir. The development of a blue-green color proves cobalt. (If the solution becomes red, iron(III) is present. Add 1 drop 1 *M* NaF to the solution to remove the iron (or as many drops as are needed to see a color change or clear up the Fe^{2+}). If the resulting solution is blue to green, cobalt is present.)

Post Lab Questions

1. Write the net-ionic equations for the reactions occurring for each cation in the group.
   - a. nickel
   - b. cobalt
   - c. iron
   - d. chromium
   - e. zinc

2. Give the formula of a single reagent that will separate the following pairs in one step.

a. ZnS and CoS (solids)

b. Ni^{2+} and Fe^{3+} (solutions)

c. $Fe(OH)_3$ and $Zn(OH)_2$ (solids)

d. $AgNO_3$ and $Ni(NO_3)_2$ (solutions)

3. What color is each of the following?

a. $Fe(OH)_3$ solid

b. $PbCrO_4$ solid

c. $Co(SCN)_4^{2-}$ solution

d. $Ni(NO_3)_2$ solution

4. A 0.050 *M* $Co(NO_3)_2$ solution is saturated with H_2S (0.10*M*). Using $K_{spa} = 3$ for CoS, what $[H_3O^+]$ is required to precipitate CoS from the 0.050 *M* $Co(NO_3)_2$ solution?

EXPERIMENT 12

Anion Analysis

Introduction

This experiment looks at the qualitative analysis for some of the common anions. We will look at the following anions:

TABLE 12.1 Anions

sulfate, SO_4^{2-}	sulfide, S^{2-}
phosphate, PO_4^{3-}	carbonate, CO_3^{2-}
chloride, Cl^-	bromide, Br^-
iodide, I^-	nitrate, NO_3^-

The tests for these anions are relatively simple and may be carried out with a minimum of interference from other ions. Anions may be grouped as follows:

Group I: the sulfate group. SO_4^{2-}, CO_3^{2-}, PO_4^{3-}

Group II: halide group. Cl^-, Br^-, I^-, S^{2-}

Group III: nitrate group. NO_3^-

This division of the anions is based on the following facts: (1) in ammoniacal solutions only the anions of Group I are precipitated with Ba^{2+}; (2) in HNO_3 solution only anions of Group II are precipitated with Ag^+. Therefore, the group reagent for Group I is NH_3 and $BaCl_2$, and the group reagent for Group II is HNO_3 and $AgNO_3$. There is no group reagent for Group III as this anion is soluble.

Following the preliminary tests on a sample for anions, specific tests are made for those anions which have not been eliminated as possibilities. The chemistry involved and the basis for these specific tests are summarized below.

Sulfate. This is the only anion of the Group I anions that forms a strong acid. Barium sulfate is insoluble in HCl solution because sulfate is the anion of a strong acid. All the other barium salts of the Group I anions dissolve in strong acid, e.g.:

$$Ba_3(PO_4)_{2\,(s)} + 2\,H^+_{(aq)} \rightleftharpoons 3\,Ba^{2+}_{(aq)} + 2\,HPO_4{}^{2-}{}_{(aq)} \tag{EQ 12.1}$$

Therefore, the test for sulfate ion involves addition of HCl and $BaCl_2$ to the test solution:

$$Ba^{2+}_{(aq)} + SO_4{}^{2-}{}_{(aq)} \rightleftharpoons BaSO_{4\,(s)} \tag{EQ 12.2}$$

forming barium sulfate, a white precipitate.

Sulfide. The sulfide ion is stable only in basic solutions. Adding acid to a solution containing sulfide ion produces H_2S gas:

$$2\,H^+_{(aq)} + S^{2-}_{(aq)} \rightleftharpoons H_2S_{(g)} \tag{EQ 12.3}$$

The test for sulfide ion involves letting the H2S gas come in contact with moist lead acetate paper forming black lead sulfide:

$$H_2S_{(g)} + Pb^{2+}_{(aq)} \rightleftharpoons PbS_{(s)} \tag{EQ 12.4}$$

Hydrogen sulfide also has a characteristic “rotten egg” odor.

The sulfide ion can be destroyed by reaction with strong oxidizing agents such as sulfite ion or nitric acid:

$$2\,S^{2-}_{(aq)} + SO_3{}^{2-}{}_{(aq)} + 6\,H^+_{(aq)} \rightleftharpoons 3\,S_{(s)} + 3\,H_2O_{(l)} \tag{EQ 12.5}$$

$$3\,S^{2-}_{(aq)} + 2\,NO_3{}^{-}{}_{(aq)} + 8\,H^+_{(aq)} \rightleftharpoons 3\,S_{(s)} + 2\,NO_{(g)} + 4\,H_2O_{(l)} \tag{EQ 12.6}$$

Chloride bromide, iodide. These ions are, like the sulfate ion, the anions of strong acids. They form insoluble salts with silver ion in nitric acid. The colors of the silver salts are indicative of the anion present, but confirmatory tests are also needed. Silver chloride is white, silver bromide is pale yellow, and silver iodide is yellow.

We can dissolve the AgCl by addition of aqueous ammonia solution forming the diamminesilver(I) complex ion:

$$AgCl_{(s)} + 2\,NH_{3\,(aq)} \rightleftharpoons Ag(NH_3)_2{}^+{}_{(aq)} + Cl^-_{(aq)} \tag{EQ 12.7}$$

The AgBr is slightly soluble in ammonia solution, so concentrations must be carefully controlled. The AgI does not dissolve in ammonia. Bromide or iodide ions may be confirmed by oxidation with free chlorine generating free bromine or iodine.

$$2\,Br^-_{(aq)} + Cl_{2\,(g)} \rightleftharpoons Br_{2\,(l)} + 2\,Cl^-_{(aq)} \tag{EQ 12.8}$$

$$2\,I^-_{(aq)} + Cl_{2\,(g)} \rightleftharpoons I_{2\,(s)} + 2\,Cl^-_{(aq)} \tag{EQ 12.9}$$

The free halogens are more soluble in hexane than in water and take on a distinctive color, bromine is red-brown and iodine is violet. By mixing the aqueous test solution with the hexane layer and observing the resultant color, the presence of bromide or iodide in the original solution may be confirmed.

There are methods of distinguishing bromide and iodide in the presence of each other. But time limitations will not let us do that testing.

Carbonate. Carbonate forms the weak acid, carbonic acid, which is not very soluble and breaks down forming water and carbon dioxide:

$$2\ H^+_{(aq)} + CO_3^{2-}{}_{(aq)} \rightleftharpoons H_2CO_{3\,(aq)} \rightleftharpoons H_2O_{(l)} + CO_{2\,(g)} \qquad \textbf{(EQ 12.10)}$$

Addition of a strong acid to a solution containing carbonate, results in the formation of a colorless, odorless gas. This effervescence is sufficient to confirm carbonate of the anions we are testing for. If sulfite ion were present, further testing would be necessary as a similar reaction occurs with sulfite.

Nitrate. We cannot use a precipitation method to test for the nitrate ion as all nitrate salts are soluble. The "brown-ring" test for nitrate ion involves its reduction by ferrous ion in concentrated sulfuric acid:

$$NO_3^-{}_{(aq)} + 4\ H^+_{(aq)} + 3\ Fe^{2+}_{(aq)} \rightleftharpoons 3\ Fe^{3+}_{(aq)} + NO_{(g)} + 2\ H_2O_{(l)} \qquad \textbf{(EQ 12.11)}$$

The nitric oxide complexes with excess ferrous ion forming the brown-ring $FeNO^{2+}$ complex:

$$Fe^{2+}_{(aq)} + NO_{(g)} \rightleftharpoons FeNO^{2+}_{(aq)} \qquad \textbf{(EQ 12.12)}$$

It is essential that an excess of ferrous ion (Fe^{2+}) be used and that concentrated sulfuric acid is used. The nitrate test has several interferences. **If bromide or iodide is present, the concentrated sulfuric acid will oxidize the halide ion to the free halogen, giving a false positive color**:

$$2\ Br^-_{(aq)} + SO_4^{2-}{}_{(aq)} + 4\ H^+_{(aq)} \rightleftharpoons Br_{2\,(l)} + SO_{2\,(g)} + 2\ H_2O_{(l)} \qquad \textbf{(EQ 12.13)}$$

Phosphate. This is the anion of a moderately weak, nonvolatile acid. The phosphate ion is precipitated by reaction with ammonium molybdate reagent forming a mixed salt, ammonium phosphomolybdate:

$$3\ NH_4^+{}_{(aq)} + 12\ MoO_4^{2-}{}_{(aq)} + PO_4^{3-}{}_{(aq)} + 24\ H^+_{(aq)} \rightleftharpoons (NH_4)_3PO_{4\,(aq)} + 12\ MoO_{3\,(s)} + 12\ H_2O_{(l)} \qquad \textbf{(EQ 12.14)}$$

Sulfide ion interferes with this test but can be removed first by acidifying the solution with HCl and boiling it.

Experimental Procedure - Preliminary Tests

Prepare a solution of your anion unknown by dissolving about 0.2 g of your sample in 25 mL distilled water. (0.2 g is about 1/4 to 1/2 inch on the end of a spatula.) For each anion to be tested, run a known solution along with your unknown solution. Use a sodium or potassium solution of the anion being tested. Use a fresh unknown sample for each test unless directed otherwise.

Group I anions. To 10 drops of unknown solution, add 6 *M* NH_3 until basic and then 4 drops $BaCl_2$ solution. Formation of a precipitate confirms the presence of ions of this group.

Group II anions. To 10 drops of unknown solution, add 6 *M* HNO_3 until acidic then add 4 drops more. Add 3 drops $AgNO_3$ solution. Formation of a precipitate confirms the presence of anions of this group.

Group III anions. No preliminary test is available for this group.

After completion of the preliminary tests, run the specific anion tests for the anion groups found present in your sample.

Experimental Procedure - Specific Tests

Sulfate test. To 5 drops of solution, add 2 drops 6 *M* HCl and 2 drops $BaCl_2$ solution. A white ppt proves sulfate.

Sulfide test. To 1 mL of test solution, add 6 *M* HCl until acidic, then add 3 drops excess 6 *M* HCl. Note any odor of H_2S (rotten eggs). Place a strip of moistened lead acetate paper over the mouth of the test tube and heat in a water bath for several minutes. A darkening of the lead acetate paper confirms S^{2-} ion.

Phosphate test.

NOTE: Sulfide ion interferes with this test and must be removed first by making the 10 drops test solution distinctly acidic with HCl and heating with stirring for 3 minutes to remove sulfide as H_2S gas.

Mix 5 drops of 0.5 *M* $(NH_4)_2MoO_4$ reagent with 5 drops 6*M* HNO_3 and add 10 drops of the test solution. A yellow ppt of $(NH_4)_3PO_4 \bullet 12\ MoO_3$ indicates the presence of phosphate. If a ppt does not form immediately, heat in a water bath for a few minutes. Sulfide ion interferes with this test and must be removed first by making the 10 drops test solution distinctly acid with HCl and heating with stirring for 3 minutes to remove sulfide as H_2S gas.

Chloride test. To 10 drops of test solution, add 6 *M* HNO_3 until acid to litmus. (If your solution contains sulfide ion, add 2 more drops HNO_3 and heat for 3 minutes with stirring to remove H_2S.) Add 5 drops 0.1 *M* $AgNO_3$. Formation of a ppt confirms the presence of Cl^-, Br^-, or I^-. No ppt means these 3 anions are absent. (AgCl is white, AgBr is pale yellow, and AgI is light yellow.) Centrifuge and discard the supernate. To the ppt, add 10 drops H_2O and 2 drops 6 *M* NH_3 and mix. Cool the test tube and cfg if any ppt remains. To the clear supernate, add 6 *M* HNO_3 until acidic. The formation of a white ppt confirms AgCl.

Bromide & iodide test.

CAUTION: Use Cl_2/H_2O in the hood!

NOTE: Make sure that your Cl_2 is saturated, by adding 12 M HCl drop wise to the Cl_2 while the Cl_2 is being stirred using the magnetic stir bar until it turns a yellowish-green. Be sure not to over flow your reagent bottle!

Because of the difficulty of detecting these ions in the presence of each other and our limited time, your sample will not contain both of these ions. To10 drops of test solution, add 6 *M* HNO_3 until acidic, then add 15 drops hexane and 10 drops of chlorine water.

Mix well and note the color of the hexane layer. Br_2 is red-brown and I_2 is violet in hexane.

Carbonate test. To 10 drops of test solution, add 4-5 drops 6 *M* HCl and look for effervescence of CO_2 gas. (Looks like soda-water fizzing.) If you are uncertain, use a small amount of solid known and add 4-5 drops 6 *M* HCl and look for effervescence. Of the anions we are studying, only carbonate effervesces.

Nitrate test. If Br^- or I^- ion is present treat 10 drops of test solution with 1 mL of saturated $AgC_2H_3O_2$ solution to ppt out AgBr or AgI. Cfg and use the clear supernate for the nitrate test. If neither Br^- nor I^- are present, use 10 drops of test solution. Add 5 drops freshly prepared solution (made by dissolving a small amount solid $FeSO_4$ in 2 mL H_2O) and mix. Acidify with 3 *M* H_2SO_4, mix thoroughly. Incline the test tube at a 45° angle and pour about 1 mL (a dropper full) of concentrated H_2SO_4 (18 *M*) down the side of the test tube. The concentrated H_2SO_4 will form a layer in the bottom of the tube because of its greater density. Avoid mixing. Let the test tube stand for 3-5 minutes. Look for the presence of a brown ring at the interface of the concentrated H_2SO_4 layer and the test solution layer.

Post Lab Questions

1. In the test for SO_4^{2-}, explain why the addition of acid will dissolve other insoluble barium salts. Write the equation for the reaction of $BaCO_3$ in acid solution.

2. Why do Br^- and I^- interfere with the NO_3^- test? Explain fully using bromide as an example, including equations.

3. Explain why an excess of Fe^{2+} is necessary for the NO_3^- test.

4. Tell how you could distinguish chemically between the following pairs of substances in one or two steps. In each case, tell what you would observe. Include equations for reactions occurring.
   a. HCl and H_2SO_4

   b. NaBr and Na_2CO_3

   c. $BaSO_4$ and $BaCO_3$

d. KNO_3 and K_3PO_4

5. In the chart below, indicate what happens to each of the anions when its sodium salt is treated with (1) NH_3 and $BaCl_2$ solutions, and (2) HNO_3 and $AgNO_3$ solutions. Give the formulas of the products formed.

TABLE 12.2

Anion	**$BaCl_2$+ NH_3**	**HNO_3 + $AgNO_3$**
Br^-		
NO_3^-		
SO_4^2		
Cl^-		
PO_4^{3-}		
CO_3^{2-}		
I^-		
S^{2-}		

6. Write the net ionic equations for the reactions involved in the testing of each of the anions.

a. sulfate

b. sulfide

c. phosphate

d. chloride

e. bromide

f. iodide

g. carbonate

h. nitrate

EXPERIMENT 13 *Five Solution Analysis*

Introduction

You will be provided with five test tubes, each containing a solution of an unknown compound. Each tube will be coded, and you are to identify each substance. Each of the five tubes will contain one of the following:

1. An acid, either HCl, HNO_3, or H_2SO_4
2. A base, either NaOH, NH_3, or Na_2S
3. A chloride salt, either NaCl, $BaCl_2$, or $CuCl_2$
4. A nitrate salt, either $AgNO_3$, $Cu(NO_3)_2$, or $Fe(NO_3)_3$
5. A sodium salt, either NaI, Na_2SO_4, or Na_2CO_3

Identify each unknown by the unknown number.

In your report includes a description of all steps you do for each sample, the observed results, and your conclusions. Write balanced net ionic equations for all observed reactions for each unknown solution.

YOU HAVE ONLY ONE LAB PERIOD TO COMPLETE THIS EXPERIMENT.

You should plan **before coming to lab** how you will analyze your unknown solutions. Consider the following along with any other information that you deem important:

1. acid-base nature of each solution;
2. color of each solution;
3. potential insoluble salts each solution will form, reagent needed to produce the given salt, and color it would be;
4. odor of each solution.

You may use any reagents present in the laboratories.

CAREFUL PREPLANNING CAN GREATLY SIMPLIFY THE WORK NEEDED TO COMPLETE THIS EXPERIMENT.

Outline your analysis procedure on the first page of the lab sheet **before coming to class**. You will not be allowed to disrupt the work of another student to try to compensate for lack of preparation on your part:

Observations and Tests to Consider

Odor. Many solutions have characteristic odors, e.g., HCl, NH_3, and Na_2S. If you are not familiar with these, **carefully** check the odors of known test solutions by fanning a little of the vapor above an open bottle toward your nose. Do **not** put the bottle directly under your nose as too much vapor can be inhaled.

Color. Solutions of some metal cations have characteristic colors. If you are not familiar with these, check the test solutions of these cations to observe the respective colors. See Table 13.1 on page 109.

Acid-Base Nature. Whether a solution is acidic or basic can be determined by litmus paper. Range specific pH paper can be used to determine pH usually within 1 pH unit. Some salts result in acidic or basic solutions as a result of the hydrolysis of cations or weak acid anions. (Some metal salts must be dissolved in acid solution to be soluble, so be careful of using pH as a lone criterion to identify a substance.)

We can generally distinguish four classes of compounds which give acidic or basic solutions at the approximately 0.1 *M* concentrations we are using. Remember that pH = –log [H^+]. Therefore, low pH values indicate higher [H^+] concentrations. Neutral solutions have pH = 7. High pH values indicate lower [H^+] concentrations and higher [OH^-] concentrations.

- Strong Acids: pH < 3. For example, HCl, HNO_3, H_2SO_4, $HClO_4$, etc. These are strong acids with nearly complete ionization occurring according to:

$$HX_{(aq)} \rightleftharpoons H^+_{(aq)} + X^-_{(aq)} \quad \textbf{(EQ 13.1)}$$

- Acid Salts: 1 < pH < 7. For example, NH_4Cl, $Fe(NO_3)_3$, $ZnCl_2$, etc. The cations hydrolyze with water producing H^+ ion.

$$NH_4{}^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_{3\,(aq)} + H_3O^+{}_{(aq)} \quad \textbf{(EQ 13.2)}$$

or

$$Fe^{3+}{}_{(aq)} + 2\ H_2O_{(l)} \rightleftharpoons Fe(OH)_2{}^+{}_{(aq)} + 2\ H^+{}_{(aq)} \quad \textbf{(EQ 13.3)}$$

Some metal cations (especially +3 or higher charges) hydrolyze so extensively that the metal hydroxide precipitates out of solution. To keep such cations in solution, a strong acid must be added.

- Basic Salts: 7 < pH < 11. For example, Na_2CO_3, Na_2S, NaCN, etc. These salts contain the anion of a weak acid which hydrolyzes producing OH^- ion:

$$CN^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons HCN_{(aq)} + OH^-{}_{(aq)} \quad \textbf{(EQ 13.4)}$$

$$S^{2-}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons HS^-{}_{(aq)} + OH^-{}_{(aq)} \quad \textbf{(EQ 13.5)}$$

Na_2S hydrolyzes to such an extent that we are considering it a strong base in this experiment.

- Bases: pH > 11. For example, NaOH, NH_3, $Ba(OH)_2$, etc. These compounds ionize partly or completely producing hydroxide ion:

$$NH_{3\,(aq)} + H_2O_{\,(l)} \rightleftharpoons NH_4{}^{+}{}_{(aq)} + OH^{-}{}_{(aq)} \quad \textbf{(EQ 13.6)}$$

$$NaOH_{\,(aq)} \rightleftharpoons Na^{+}{}_{(aq)} + OH^{-}{}_{(aq)} \quad \textbf{(EQ 13.7)}$$

Precipitation of Insoluble Salts. The formation of a precipitate when two solutions are mixed indicates that an insoluble compound has been formed. The solubility rules enable you to predict what salts are insoluble for a given cation or anion and, therefore, determine what reagent to add to test for a given ion. Table 13.2 on page 110 gives the colors of some of the various insoluble salts.

For example, if you suspect a solution contains Pb^{2+} ion, addition of I^{-} ion would precipitate yellow PbI_2 and addition of $SO_4{}^{2-}$ ion would precipitate white $PbSO_4$.

Evolution of Gases. The addition of an acid to a solution containing $CO_3{}^{2-}$ or $SO_3{}^{2-}$ produces CO_2 and SO_2 gas respectively:

$$CO_3{}^{2-}{}_{(aq)} + 2\,H^{+}{}_{(aq)} \rightleftharpoons H_2CO_{3\,(aq)} \rightleftharpoons H_2O_{\,(l)} + CO_{2\,(g)} \quad \textbf{(EQ 13.8)}$$

Addition of acid to a sulfide solution produces H_2S, detected by its odor. Addition of strong OH^{-} to an $NH_4{}^{+}$ solution produces NH_3, detected by its odor.

Confirmatory Tests. The presence of ammonia is confirmed by making use of its volatility and its weakly basic character. The test tube with the solution is warmed in a water bath while a strip of wet, red litmus paper is placed across the top of the test tube. The ammonia vapor reacts with the water on the litmus paper and turns the red paper blue:

$$NH_{3\,(aq)} + H_2O_{\,(l)} \rightleftharpoons NH_4{}^{+}{}_{(aq)} + OH^{-}{}_{(aq)} \quad \textbf{(EQ 13.9)}$$

Be sure that the litmus does not touch the solution directly.

TABLE 13.1 **Colors of Aqueous Solutions of Some Common Cations**

Colorless Ions	Colored Ions
Ag^{+} Al^{3+}	Cu^{2+} blue
$Hg_2{}^{2+}$ Zn^{2+}	Fe^{3+} yellow
Pb^{2+} Mn^{2+}	Ni^{2+} green
Hg^{2+} Ca^{2+}	Co^{2+} pink
Bi^{3+} Sr^{2+}	Cr^{3+} blue-violet
Sn^{2+} Ba^{2+}	
Cd^{2+} Mg^{2+}	
As^{3+}	
Sb^{3+} Na^{+}	
$NH_4{}^{+}$	

TABLE 13.2 Colors of Some Insoluble Salts

Bromides: Br^-	**Iodides: I^-**
Ag^+, Very pale yellow; heavy; curdy	Ag^+, Pale yellow; heavy; curdy
Pb^{2+}, White	Pb^{2+}, Bright yellow
	Brown (Cu^{2+} reduced by I^- to Cu^+)
Carbonates: CO_3^{2-}	**Oxalates: $C_2O_4^{2-}$**
Ag^+, White	Ag^+, White, heavy
Ba^{2+}, White	Ba^{2+}, White
Cu^{2+}, Light blue	Cu^{2+}, Pale blue
Fe^{3+}, Light orange-brown gelatinous	Ni^{2+}, Very pale green, gelatinous
Ni^{2+}, Pale green; gelatinous	
Pb^{2+}, White	
Chlorides: Cl^-	**Phosphates: PO_4^{3-}**
Ag^+, White; heavy precipitate	Ag^+, Light yellow
Pb^{2+}, White; moderately soluble; soluble in hot solution	Ba^{2+}, White, gelatinous
	Ca^{2+}, White gelatinous
Chromates: CrO_4^{2-}	**Sulfates: SO_4^{2-}**
Ag^+, Dark orange-red	Ba^{2+}, White
Ba^{2+}, Light yellow	Pb^{2+}, White
Cu^{2+}, Orange-brown	
Pb^{2+}, Bright yellow	
Hydroxides: OH^-	**Sulfides: S^{2-}**
Ag^+, With NaOH, grey-brown suspension	Ag^+, Black
With NH_3, grey-brown; dissolves in excess NH_3 to colorless solution	Cu^{2+}, Black
Cu^{2+}, With NaOH, pale blue	Fe^{3+}, Black
With NH_3, pale blue; dissolves in excess NH_3 to deep blue solution	Ni^{2+}, Black
Fe^{3+}, Rust-colored	**Sulfites: SO_3^{2-}**
Ni^{2+}, With NaOH, pale green; gelatinous;	Ag^+, White, curdy
With NH_3 pale green gelatinous; dissolves in excess NH_3 to blue solution	Ba^{2+}, White

EXPERIMENT 14

Qualitative Analysis: General Unknown

Objective

The objective of this lab is to use the knowledge and techniques you have already gained with respect to the qualitative analysis of cations to separate and identify the metal ions in an unknown solution.

Introduction

At this point, you have already done a considerable amount of work, using your knowledge of precipitation, redox reactions and complex ion formation, and using prepared schemes to separate and identify mixtures of cations. In this capstone lab, you will apply this knowledge to generate a scheme, and to separate and identify the species in a set of metal ions specifically assigned to you. The possible ions include: Ag^+, Ni^{2+}, Ba^{2+}, Zn^{2+}, Fe^{3+}, Cr^{3+}, Pb^{2+}, Hg_2^{2+}, Cu^{2+}, Bi^{3+}, Cd^{2+}, Hg^{2+}, Sn^{4+}, and Co^{2+}.

Each student will be given their own individual set of seven metal ions from which a subset will be given to them as their unknown solution. Your job will be to generate a scheme which, in principle, should produce from this unknown seven separate samples with a precipitate, a characteristic color or some other property which will definitely identify all seven metal ions in your given unknown list.

Procedure

Your first task is to present to your instructor your separation scheme. It is quite likely that this scheme will include some sort of sulfide separation, either under acidic or basic conditions, although, in principle, this is not a requirement. You have a limited permission to include whatever chemical tests you like, even if it is not in the prescribed list of experiments you have already done. However, if you want to use some reagent other than the ones you have already used, you must get permission from your instructor. Unless given permission by you instructor, the scheme must actually separate the seven ions. In other words, you cannot simply split a solution in two and do two separate special tests as part of your scheme unless that was done in a previous lab.

After your scheme has been approved and signed by your instructor, you are required to make a “known” solution containing the seven ions on your list. In order to do this, you will need to use the more concentrated metal ion solutions (0.50 M rather than 0.10 M) provided in the lab. This will allow you to produce a known with metal concentrations just a little lower than the 0.10 M concentration these ions have had in previous lab work.

Next, you must perform your scheme on both your “known” and your unknown. After doing this, you may do whatever additional tests you like until you are confident you have identified the ions in your unknown. This is when your creativity and ability to think on your feet comes in. This the fun part of the lab. You may want to create a scheme for a sub group of your ions. You may want to use a special test in the middle of your scheme rather than at the end. After you do your scheme on your own and unknown, all restrictions are removed, except you must get permission to do experiments involving substances not already available in the lab. Do not stop testing until you feel fairly confident you now what was in your unknown. Your sample will have between two and five of the seven ions.

Results

The lab write-up will simply include your signed scheme, all the pages of data and observations from the lab and a list of the ions you believe are in your assigned unknown.

EXPERIMENT 15

Determining the Identity of an Unknown Solution

Background

This experiment will test your skills of deduction, observation, and knowledge of inorganic reactions. You will be given eleven disposable tubes, each containing a colorless aqueous solution from the list below. Your job is to correctly identify which solution is contained in each of the test tubes. No other reagents may be used in your study except pH paper and the substances themselves.

TABLE 15.1 Reagents available for use

NaOH	poisonous, corrosive (caustic)
H_2SO_4	poisonous, corrosive
Na_2CO_3	
HCl	poisonous, corrosive
$BaCl_2$	poisonous
H_2O	
H_2O_2	oxidizer, corrosive
NaI	irritant
$NaIO_3$	oxidizer
Na_2SO_3	reducing agent
$Zn(NO_3)_2$	strong oxidizer, irritant

In order to determine which solution is in each test tube, you will probably want to first subdivide the solutions into three groups according to pH characteristics. Using universal indicator paper, determine the approximate pH of each solution. Be careful in using this for sole identification in your unknown since pH depends also on solution concentration.

A second step might be to do flame tests on the samples. Using a CLEAN nichrome or platinum wire, carefully test the flames of each to find the $BaCl_2$ solution (what color should that flame be?) and the sodium salts. You must clean the wire thoroughly between samples so as to avoid carrying the flame color over into the next sample. Na^+ is somewhat difficult to remove from the wire. To do so, get the wire glowing hot and dip it into some HCl (this is the only time a reagent outside of the matrix may be used in this experiment). Repeat this step until the HCl flame is essentially colorless. Then move on to your next sample.

A third step may involve mixing the various solutions and studying the results. Both precipitation and redox chemistry will be important. A matrix with eleven columns and eleven rows can be created to report this information. The observations about the resulting mixture of two solutions is recorded in the space connecting these two. Obviously, 121 mixtures are not necessary. If solution A is mixed with B, it is not necessary to mix B with A. Also you need not mix A with A. Therefore, a maximum of 55 mixtures will be necessary.

When observing the results of mixtures, note precipitates (if any) and their colors and textures. Also be alert for gas evolution and/or heat changes. Remember, the reaction of a strong acid with a strong base is often noticeable only by the presence of heat evolved during the neutralization.

Prelaboratory Questions

1. Using a solubility table, acid/base information, and an electrochemical half reaction activity series, predict the expected results for each mixing. Your instructor will check this for you when you are finished. Consider both cations with both anions in the mix when predicting results. Create a 11×11 matrix in your notebook and record the predicted observations. You need not do duplicates (A with B and also B with A) so you will actually create a triangle of reactions for a total of 55 mixtures.

2. For each original solution, predict the pH category (acid, base, or neutral) and the flame test color.

3. Consider the mixture of NaI and $NaIO_3$ in acid. What do you expect? Balance the redox equation.

4. What will happen if Na_2CO_3 is added to the products in Step 3, above? What if Na_2SO_3 is added instead? Explain with balanced equations.

5. Consider the mixture of NaI with H_2O_2 in acid. What do you expect? Balance the equation.

6. What will happen to the products in Step 5, above, if Na_2SO_3 is then added? Balance the equation.

7. Which of the eleven solutions are likely to be the most hazardous with respect to eye exposure?

Procedure

During the first lab period, the eleven known solutions will be provided for you. Using a spot plate, complete the 55 mixes and carefully record observations. Check your results against your predictions from the prelab, and solve any discrepancies. Be certain to use a contrasting colored background so as not to miss white precipitates. Be very careful to avoid cross contamination of your solutions. All solutions must be disposed of in the appropriate waste container in the fume hood. Do NOT wash any down the sinks!

With a little common sense and intelligence, the number of actual mixes can be greatly reduced. Carefully considering the substances in the list can create answers to the problem involving a much smaller number of solution mixes. You will be asked as a post lab question to find the minimum number needed. You will want to consider this now, however to save work for yourself.

From your work above, create a scheme of steps that will allow you to identify each test tube. Some solutions will be identified because of their reactions and others because of their lack of reactivity.

During the second lab period, the known solutions will be removed and you will be given eleven disposable tubes, each containing one of the eleven solutions above. Your job is to identify each one. We will again use spot plates for the analysis to minimize waste. Be certain to use a contrasting colored background so as not to miss white precipitates. Be very careful to avoid cross contamination of your solutions. You will be allowed 3 hours for the analysis. The only other chemicals available to you will be pH test paper and HCl (for cleaning the flame test wire). When completed, create a summary table indicating the identity of the solution in each of the eleven test tubes. Dispose of all solutions properly in the waste container for this experiment.

Post Laboratory Question

1. What is the minimum number of mixes necessary to identify the bottles? Support your answer with details for the analysis. Do not use pH test color to distinguish strong bases from weak bases (or strong acids from weak acids) since this depends on the concentrations of the solutions given. Assume in your answer, that you are very unlucky (example - if you are looking for a precipitate of A with B, C, or D, you will find it on the third mix).

EXPERIMENT 16 *Electrochemistry*

Background

Principles of Galvanic (Voltaic) Cells

The standard cell potential $E°$ are generally represented as standard reduction potentials. To calculate the cell potentials from standard reduction potentials the following equation is often used:

$$E_{cell}° = E_{cathode}° - E_{anode}° \qquad \textbf{(EQ 16.1)}$$

For the reaction:

$$Cl_{2\,(g)} + 2\,Br^{-}_{(aq)} \rightarrow 2\,Cl^{-}_{(aq)} + Br_{2\,(l)} \quad E° = 0.30\text{ V} \qquad \textbf{(EQ 16.2)}$$

notice that chlorine gas is reduced and the bromide ion is oxidized. Since reduction occurs at the cathode and oxidation occurs at the anode the standard cell potential be calculated:

$$Cl_{2\,(g)} + 2\,e^{-} \rightarrow 2\,Cl^{-}_{(aq)} \quad E° = 1.36\text{ V} \qquad \textbf{(EQ 16.3)}$$

$$Br_{2\,(l)} + 2\,e^{-} \rightarrow 2\,Br^{-}_{(aq)} \quad E° = 1.06\text{ V}$$

$$E_{cell}° = 1.36\ V - 1.06\ V = 0.30\ V \qquad \textbf{(EQ 16.4)}$$

Thus $E°$ for any cell reaction can be calculated by subtracting the cathode from the anode reaction. The cell voltages $E°$ refer to the voltages observed when all species are in their standard states (approximately 1 *M* for species in solution and 1 atm pressure for gases). Most commonly, $E°$ values are tabulated for 298 K.

Half-cell potentials can be calculated from cell potentials and from the convention that $E° = 0$ V for the half-cell at all temperature is:

$$2\,H^{+}_{(aq)} + 2\,e^{-} \rightarrow H_{2\,(g)} \quad E° = 0\text{ V} \qquad \textbf{(EQ 16.5)}$$

Electrical conductivity is an intensive property. Hence, electrical potentials do not depend on the number of molecules. ions, or electrons. This is why individual cells of the same kind, such as dry cells of penlight size AA, flashlight size D, or lantern size 6 all have the same $E°$ = 1.5 V. Thus, from the half-cell reactions above, the two following cell reactions have the same $E°$.

$$\mathrm{Zn}_{(s)} + \mathrm{Cl}_{2\,(g)} \rightarrow \mathrm{Zn}^{2+}{}_{(aq)} + 2\ \mathrm{C1}^{-}{}_{(aq)}\ E° = +0.76\ \mathrm{V} - (-1.36\ \mathrm{V}) = +2.12\ \mathrm{V} \qquad \textbf{(EQ 16.6)}$$

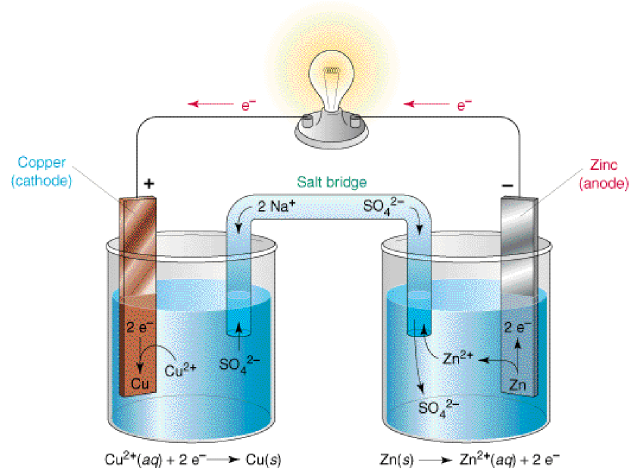
$$½\ \mathrm{Zn}_{(s)} + ½\ \mathrm{Cl}_{2\,(g)} \rightarrow ½\ \mathrm{Zn}^{2+}{}_{(aq)} + \mathrm{Cl}^{-}{}_{(aq)}\ E° = +0.76\ \mathrm{V} - (-1.36\ \mathrm{V}) = +2.12\ \mathrm{V} \qquad \textbf{(EQ 16.7)}$$

When a cell reaction is written so that $E°$ is positive, the reaction will proceed spontaneously from left to right if all components are in standard states. The reaction can occur simply by mixing the reagents or by separating the half-cells so that the potential can be measured. In the latter case the reaction actually occurs in the spontaneous direction, but very slowly since the voltmeter has a very high resistance to electric current. When the reagents are separated so that a measurable voltage is observed, the electrochemical cell is called a voltaic (or galvanic) cell.

It is useful to learn how to name all the components and processes occurring in a voltaic cell. Consider the example in Figure 16.1. For the copper electrode the electrode, the electrode process is cathodic. For the zinc electrode, the electrode process is anodic. The line or shorthand notation for this cell is:

$$\mathrm{Zn}_{(s)}\,|\,\mathrm{Zn}^{2+}{}_{(aq)}\,(1\ M)\ ||\ \mathrm{Cu}^{2+}{}_{(aq)}\,(1\ M)\,|\,\mathrm{Cu}_{(s)}$$

FIGURE 16.1



Cu-Zn

The cell reaction is

$$\mathrm{Zn}_{(s)} + \mathrm{Cu}^{2+}{}_{(aq)} \rightarrow \mathrm{Zn}^{2+}{}_{(aq)} + \mathrm{Cu}_{(s)} \quad E° = 0.34 - (-0.76\ \mathrm{V}) = 1.10\ \mathrm{V} \qquad \textbf{(EQ 16.8)}$$

For every zinc atom oxidized, one copper ion is reduced and two electrons flow through the wire. Since both beakers must maintain a neutral charge, ions must flow through the Na_2SO_4 salt bridge; either a zinc ion from right to left, or a sulfate ion from left to right. In actuality, of course, both Zn^{2+} and SO_4^{2-} migrate into the salt bridge, and Na^+ and SO_4^{2-} migrate out of it. After many hours of operation, the salt bridge will contain many ions from both beakers; but for each electron passed through the wire, one net charge will transfer between beakers to maintain electrical neutrality. Note the following points:

1. The sulfate ion can be replaced by any other anion that does not precipitate Zn^{2+} or Cu^{2+}or otherwise participate in a reaction: Cl^- or NO_3^- can be used.

2. The copper electrode can be replaced by an inert, conducting substance such as platinum, gold, or carbon (graphite). In any case, copper metal will be deposited on the cathode.
3. The two independent half-cells connected by a salt bridge can simply be mixed together. If this is done, the reaction will proceed essentially to completion. Separation into two half-cells is merely a convenient way of illustrating how useful the half-cell concept is.

Voltaic Cells Procedure

You will make a complete cell of the type shown in Figure 16.1. Your instructor will assign students to prepare cells from part A and part B.

Part A. For this cell we will use zinc nitrate and copper(II) nitrate instead of the sulfates as shown in Figure 16.1.

1. Place 30 mL of 0.1 M $Zn(NO_3)_2$ solution and 30 mL of 0.1 M $Cu(NO_3)_2$ solution in separate 100 mL beakers.
2. Obtain a zinc strip and a copper strip from the storage shelf: clean both sides of the copper strip with sandpaper.
3. Obtain a salt bridge from the stockroom.
4. Insert the strips in the solutions of their own ions. Label the diagram with the appropriate electrode names, processes, and signs.
5. Obtain a voltmeter from your instructor. Identify its positive and negative terminals. Attach it to the appropriate electrodes (do not guess) and read the voltage.
6. Now short-circuit the cell with a single piece of wire with alligator clips at each end. What chemical reaction is taking place? Which way are electrons flowing? Record in your notebook any physical change occurring that confirms that the chemical reaction is taking place?
7. Set the cell-aside, leaving it short-circuited until the end of the period. Before leaving the laboratory, disconnect the short circuit. Note the physical condition of the electrodes and the color of the solution and read the voltage across the electrodes with the voltmeter.

Part B. You will prepare two or three labeled 100 mL beakers representing each of the following half-cells (each should contain 25 to 30 mL of total solution).

The stockroom will provide 0.1 M $Zn(NO_3)_2$, 0.1 M $Cu(NO_3)_2$, 0.1 M $Cd(NO_3)_2$, 0.1 M $Pb(NO_3)_2$, 0.1 M $AgNO_3$, 0.1 M Br_2/0.1M KBr,[1] 0.1 M I_2/0.1 M KI solutions. As well as Zn, Cu, Cd, Pb, and C or Pt[2] electrodes.

Proceed systematically to set up cells to measure the potentials of the reactions listed in Table 16.1 on page 123. (Your instructor will tell you which cells to set up if there is not time to do them all.)

Your instructor will assign the following diagrams:

TABLE 16.1 Half Cells with Solutions and Electrodes:

	Half Cell	Half Cell
Diagram #1	$Pb_{(s)} \mid Pb(NO_3)_{2\,(aq)}$	$Cu_{(s)} \mid Cu(NO_3)_{2\,(aq)}$
Diagram #2	$Cd_{(s)} \mid Cd(NO_3)_{2\,(aq)}$	$Cu_{(s)} \mid Cu(NO_3)_{2\,(aq)}$
Diagram #3	$Pt_{(s)} \mid Br_{2\,(aq)}, Br^-_{(aq)}$	$Cu_{(s)} \mid Cu(NO_3)_{2\,(aq)}$

---

[1] Actually contains halogen, mostly as a complex ion from the equilibrium $X^- + X_2 \rightleftharpoons X_3^-$

[2] Use Pt foil for the electrode. The wire does not have enough surface area.

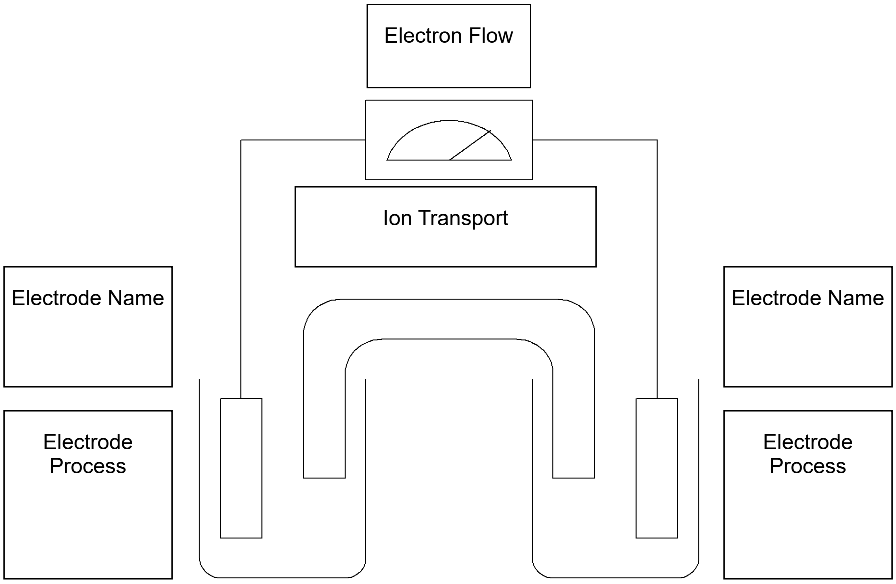
TABLE 16.1 Half Cells with Solutions and Electrodes:

	Half Cell	Half Cell
Diagram #4	Pt $_{(s)}$ | $I_{2\,(aq)}$, $I^-_{(aq)}$	Cu $_{(s)}$ | $Cu(NO_3)_{2\,(aq)}$
Diagram #5	Ag $_{(s)}$ | $AgNO_{3\,(aq)}$	Cu $_{(s)}$ | $Cu(NO_3)_{2\,(aq)}$
Diagram #6	Pt $_{(s)}$ | $Br_{2\,(aq)}$, $Br^-_{(aq)}$	Pt $_{(s)}$ | $I_{2\,(aq)}$, $I^-_{(aq)}$
Diagram #7	Pb $_{(s)}$ | $Pb(NO_3)_{2\,(aq)}$	Cd $_{(s)}$ | $Cd(NO_3)_{2\,(aq)}$
Diagram #8	Ag $_{(s)}$ | $AgNO_{3\,(aq)}$	Pb $_{(s)}$ | $Pb(NO_3)_{2\,(aq)}$
Diagram #9	Ag $_{(s)}$ | $AgNO_{3\,(aq)}$	Cd $_{(s)}$ | $Cd(NO_3)_{2\,(aq)}$
Diagram #10	Cu $_{(s)}$ | $Cu(NO_3)_{2\,(aq)}$	Cu $_{(s)}$ | $Cu(NO_3)_{2\,(aq)}$
Diagram #11	Pt $_{(s)}$ | $Br_{2\,(aq)}$, $Br^-_{(aq)}$	Pb $_{(s)}$ | $Pb(NO_3)_{2\,(aq)}$
Diagram #12	Pt $_{(s)}$ | $I_{2\,(aq)}$, $I^-_{(aq)}$	Pb $_{(s)}$ | $Pb(NO_3)_{2\,(aq)}$

For each voltaic cell refer to "Questions and Data Interpretation" on page 131 for data work-up.

When you have finished this experiment, return all the metal electrodes to the appropriate containers. Salt bridges should be stored for future use in large beakers partly filled with 0.1*M* KNO_3 solution.

FIGURE 16.2 Example Diagram



Corrosion

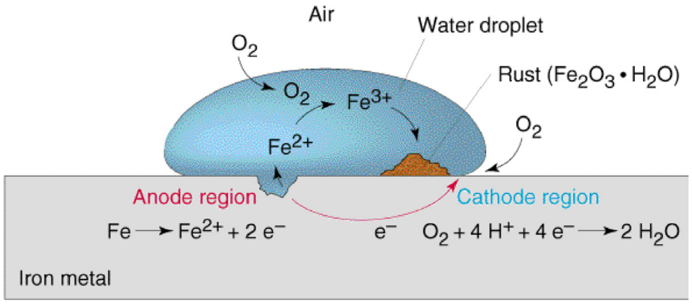
Metals are materials from which automobiles, ships, bridges, airplanes, pipes, and many other modern essentials are constructed. Metals are usually exposed to air. Water, salt, and other chemical species that cause them to corrode. Prevention of corrosion is one of the most important applications of chemistry, since enormous amounts of effort and sums of money are invested in the protection of metals from the environment. To a chemist, corrosion is the oxidation of metals by atmospheric oxygen, typically in conjunction with water and salts. The prevention of corrosion is a fascinating application of electrochemistry.

A typical corrosion process is illustrated in Figure 16.3. A piece of iron is in contract with a drop of water and with the atmosphere. If the iron were very pure it would be quite resistant to corrosion, because its uniform composition would necessitate that oxidation of the iron and reduction of the oxygen take place at the same site or at similar sites. But most commercial samples of iron contain impurities or lattice defects which render the sites cathodic (susceptible to reduction of oxygen) or anodic (susceptible to oxidation of iron). For example, a tiny crystal of another metal present in the iron as an impurity, or another metal intentionally, fastened to the iron, typically serves as a cathodic site. As Figure 16.3 shows, the cathodic and anodic processes generally take place at different sites because a galvanic cell is set up with electrons traveling through the iron itself.

The cathodic region will be indicated by a pink color from the phenolphthalein and should also show the reaction:

$$O_{2\,(g)} + 2\,H_2O_{\,(l)} + 4e^{-} \rightarrow 4\,OH^{-}_{(aq)} \qquad \textbf{(EQ 16.9)}$$

FIGURE 16.3



Corrosion of a metal can be inhibited or prevented in three different ways:

1. The metal can be alloyed with another metal, typically a less reactive one: (The alloy may also impart desirable mechanical properties to the metal.) Stainless steel is such an alloy.
2. The metal can be given a protective coating which is more difficult to oxidize than the metal itself. For example, silver is plated onto forks, knives, and spoons to protect the underlying metal from being attacked by air and food chemicals. Tin-plating of iron affords a protective coating, because tin is less easily oxidized than iron:

$$Sn_{\,(s)} \rightarrow Sn^{2+}_{(aq)} + 2\,e^{-} \quad E° = +0.14\text{ V} \qquad \textbf{(EQ 16.10)}$$

$$Fe_{\,(s)} \rightarrow Fe^{2+}_{(aq)} + 2\,e^{-} \quad E° = +0.44\text{ V} \qquad \textbf{(EQ 16.11)}$$

   Aluminum is a metal that ought to be very easily oxidized, but it forms a tightly adhering thin coat of oxide, which protects it against further oxidation. A nonmetallic coating such as paint also protects a metal from corrosion.

3. The metal can be placed in electrical contact with another metal that is more easily oxidized than the metal being protected. The more easily oxidized metal will then be oxidized first. For example, if you own a boat. You can protect its metal hull by fastening a block of magnesium to the hull. The magnesium block and the iron hull form a galvanic cell with the magnesium (the Anode) being oxidized and the oxygen being reduced at the iron. Since the iron is protected by being made the cathode, this method of corrosion protection is called cathodic protection. The magnesium block is referred to as a sacrificial anode.

Other examples of corrosion and corrosion protection are described in your text. In this experiment, you will demonstrate corrosion of iron. Then you will protect the iron from corrosion by methods 2 and 3 above. You will also demonstrate the effect of removing the protective coating of oxide from a piece of aluminum.

Corrosion Action and Cathodic Protection Procedure

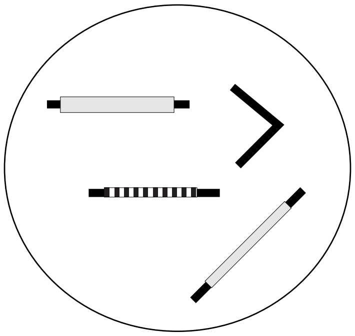
To observe the sites on an iron surface where the anode and cathode reactions in Figure 16.3 occur, you will place several iron nails, in a gel, where chains of gelatin molecules immobilize an aqueous solution. The gel serves to keep the iron nails motionless, and you will add indicators for Fe^{2+} and OH^- to the gel to determine where these ions are produced.

1. Prepare the gel by weighing out approximately 1 g of powdered agar and 2 g of NaCl. Heat 100 cm^3 of deionized water to a gentle boil. Stop heating the water, add the salt and agar, and stir until the entire agar has dissolved.
2. Add the 2 mL of phenolphthalein indicator solution, 1 drop 6 *M* HCl solution, and 1 mL of 0.01 *M* potassium hexacyanoferrate(III), $K_3Fe(CN)_6$ solution, while stirring. When all the ingredients have dissolved or are mixed, set the solution aside to cool slowly.
3. While the agar solution is cooling, prepare four clean iron nails as follows:
   a. A nail with one or more very sharp bends (use pliers).
   b. A nail wrapped near its head with several turns of bare copper wire or piercing a piece of copper foil.
   c. A nail piercing a piece of zinc foil in two or more places, with zinc crimped tightly around the nail with a pair of pliers.
   d. A nail piercing a piece of tinfoil as in Step “c” above.

> ⚠ Handle the nails as little as possible with bare hands to avoid coating them with oil from your skin!
>
> When you are done discard the cooled agar in the trash can, not down the sink, which clogs the it.

4. Clean all four nails for 1 minute in 0.5 *M* oxalic acid solution to remove oxide from the iron. Using forceps or tongs rinse the nails thoroughly in water and place them in a petri dish (See Figure 16.4). Carefully pour the warm agar solution over the nails until they are just covered. (If the agar is too viscous. it should be repeated.) Seal the lid of the petri dish with a bit of tape and let sit until the next lab period.

FIGURE 16.4



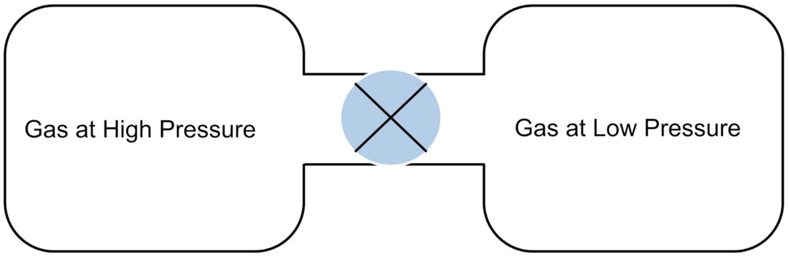
Observations of corrosion of iron nails. At the end of the laboratory period, or during the next laboratory period if no colors are observed at the end of the laboratory period, make a drawing of each iron nail in “Corrosion” on page 133. Indicate the regions of corrosion of the nails and any colors in the gel.

Concentration Cell Principles

In this experiment you will observe the effects of varying the concentration of a species participating in an electrochemical oxidation-reduction reaction both in a qualitative (Le Châtelier) and quantitative (Nernst equation) fashion.

If two identical cylinders contain the same gas at different pressures, and if the cylinders are connected, gas will flow from the cylinder at higher pressure to the one at lower pressure (Figure 16.5). If a gas turbine is connected between the cylinders. the system will turn the turbine and produce useful work until the pressures are equal.

FIGURE 16.5

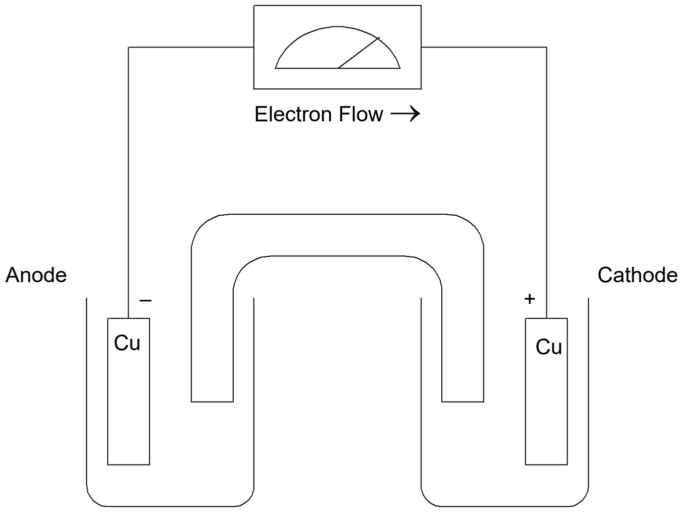


A parallel situation exists when two half-cells differing only in the concentration of one species are connected by a salt bridge.

This cell, a concentration cell as in Figure 16.6 on page 128, will undergo the two half-reactions shown until (like the gas cylinders in Figure 16.5) the concentrations of Cu^{2+} (like the gas pressures) are equal. Actually, the activities of Cu^{2+} must be identical, but it is not a bad approximation to consider the solutions ideal, with concentrations equaling activities.

Refer to “Questions and Data Interpretation” on page 131 for data work-up.

FIGURE 16.6



$Cu_{(s)} \rightarrow Cu^{2+}{}_{(aq)} + 2e^-$ $\quad$ $Cu^{2+}{}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

Net Reaction: $Cu^{2+}{}_{(aq)}\,(0.1M) \rightarrow Cu^{2+}{}_{(aq)}\,(0.001M)$

When an electrochemical cell contains species that are not at unit activities (approximately 1 *M* for dissolved species and 1 atm for gases), the cell voltage, *E*, can be found from the **Nernst equation**. For the hypothetical reaction:

$$r\,A + s\,B \rightarrow p\,C + q\,D \qquad \textbf{(EQ 16.12)}$$

Equation 16.13 can be written:

$$E = E° - \frac{RT}{nF}\ln\frac{[C]^p[D]^q}{[A]^r[B]^s} \qquad \textbf{(EQ 16.13)}$$

where R = the gas constant. 8.314 J/mol K; T = temperature (in Kelvins); n = number of electrons transferred for the species indicated in the equation; and F = Faraday's constant, 96485 C/mol or 96485 J/V mol.

When the temperature is 298.15 K and natural logarithms are converted to common logarithms (In $x = 2.303 \log_{10} x$), Equation 16.13 becomes:

$$E = E° - \frac{0.0592}{n}\log\frac{[C]^p[D]^q}{[A]^r[B]^s} \qquad \textbf{(EQ 16.14)}$$

In a concentration cell the reaction is simply the equivalent of mixing the more concentrated solution with the more dilute solution:

$$A_{(s)} + A^{n+}{}_{(aq)}\,(M_{conc}) \rightarrow A_{(s)} + A^{n+}{}_{(aq)}\,(M_{dil}) \qquad \textbf{(EQ 16.15)}$$

$$A_{(s)}\,|\,A^{n+}{}_{(aq)}\,(M_{dil})\,||\,A^{n+}{}_{(aq)}\,(M_{conc})\,|\,A_{(s)} \qquad \textbf{(EQ 16.16)}$$

Since the two half-reactions are the same, $E°_{anode} = E°_{cathode}$, so that $E° = 0$ and the Nernst equation becomes simply:

$$E = -\frac{0.0592}{n}\log\frac{[\mathrm{A}^{n+}\ M_{\mathrm{dil}}]}{[\mathrm{A}^{n+}\ M_{\mathrm{conc}}]} \qquad \textbf{(EQ 16.17)}$$

Concentration Cell Procedure

1. Set up a simple concentration cell by using a Cu 0.1 *M* $Cu(NO_3)_2$ half-cell such as that prepared for the "Voltaic Cells Procedure" on page 123, and a second half-cell prepared as follows.
   - a. Take 25 to 30 mL (the same volume as before) of 0.1 *M* KNO_3 solution and add exactly 1 drop of 0.1 *M* $Cu(NO_3)_2$ solution to this solution.
   - b. Clean a Cu strip with sandpaper and insert it into the beaker. Connect the two half-cells by a salt bridge and measure the cell voltage.
2. Now add 11 drops of 0.1 *M* Na_2S solution to the second more dilute, half-cell. Since CuS is very insoluble, the addition of Na_2S has the effect of decreasing $[Cu^{2+}]$ to an extremely small value.
3. Measure the cell voltage again. Diagram the cell as with the others, labeling the electrode signs and processes. Measure the temperature of the solutions.

Questions and Data Interpretation

Voltaic Cells Data

Part A. Chemical reaction in the single-cell setup (Figure 16.1):

1. Label all electrode names (anode/cathode), processes (oxidation/reduction), half-reactions and signs on the “Electrochemical Cell Summary Sheet” on page 137. Show the direction of electron flow and initial cell voltage.
2. Record the appearance of cell after discharge, and give an explanation of its appearance for the Zn-Cu cell.

3. Record the final cell voltage of the Zn-Cu cell. Explain why it has changed. If it is not zero, explain why it will eventually become zero.

Part B. For each pair of half-cells label all items shown in Figure 16.2: electrode names, direction of electron flow, half-cell reactions, and ion transport across the salt bridge. See “Electrochemical Cell Summary Sheet” on page 137. Show the observed voltage and the voltmeter signs for each cell. Use the handout to report the findings that you recorded in your notebook.

Voltaic Cells Data Interpretation

1. For each cell in “Part B” on page 123 calculate $E°$ from a textbook table of half-cell potentials. Compare your values with those observed. If all your solutions were 0.1 M, the net difference between your observed E and $E°$ should be negligible.
2. The cell in Figure 16.1 on page 122 can be described as follows:

$$\underbrace{Zn_{(s)} \,|\, Zn^{2+}_{(aq)}}_{\text{anode}} \,||\, \underbrace{Cu^{2+}_{(aq)} \,|\, Cu_{(s)}}_{\text{cathode}} \qquad E° = 1.10\ \text{V}$$

> **Note:** $E°$ is positive if electrons flow from left to right in the external wire. Here vertical lines represent a phase boundary, and double vertical lines represent a salt bridge.

Calculate the cell potential of the following cells, using *both* your data and a textbook table of half-cell potentials. Include signs for each $E°$

a. $Zn_{(s)} \mid Zn(NO_3)_{2\,(aq)} \parallel Cd(NO_3)_{2\,(aq)} \mid Cd_{(s)}$

Calculated cell potential using your data:

Calculated cell potential using textbook data:

b. $Ag_{(s)} \mid AgNO_{3\,(aq)} \parallel Br_{2\,(aq)}, Br^{-}_{(aq)} \mid Pt_{(s)}$

Calculated cell potential using your data:

Calculated cell potential using textbook data:

Voltaic Cells Questions

1. Is it necessary for you to take into account how many electrons are transferred per atom or ion when calculating a cell potential $E°_{cell}$?

2. Would the cell voltage change significantly if the right-hand half-cells contained twice their volume of a solution of the same concentration? Why? What if each electrode were made from cylindrical wires instead of flat sheets?

3. Why do you suppose your observed cell voltages are usually less than calculated $E°$ values? (Do not assume that meter inaccuracy is a satisfactory reason.)

4. Fill in the blanks in the table below :

TABLE 16.2

Cell Type	Process	ΔG°	Negative Electrode	Positive Electrode
Voltaic	Discharge	Less than 0	Anode	Cathode
		(Spontaneous)	(Oxidation)	( )
Electrolytic	( )	( ) than 0	( )	( )
		( )	( )	( )

Corrosion

1. Compare the reduction potentials of tin, iron, and zinc by looking up the *E*° values for each half-cell reaction, $M^{2+}{}_{(aq)} + 2\ e^{-} \rightarrow M_{(s)}$, in your textbook. Which metal, tin or zinc affords cathodic protection to iron, and which acts as an inert coating? Suppose that galvanized (zinc-plated) and tin-plated iron sheets are scratched. Which will corrode more readily?

2. You own a boat with an iron hull. Is it wise to attach fittings of copper to the iron deck? Why or why not? If you wish to use copper fittings, how should they be attached?

3. The gel surrounding the iron nails contains two corrosion indicators. A pink coloration occurs when the acid-base indicator phenolphthalein is in the presence of excess OH^-. A blue coloration occurs when Fe^{2+} reacts with the hexacyanoferrate(III) anion to produce a precipitate called Prussian blue, $KFe(III)Fe(II)(CN)_6 \cdot x\ H_2O$.
   - a. Based on your observations, make a large drawing of each nail and write the appropriate half-reaction near each corresponding site.
   - b. Indicate whether oxidation or reduction is taking place at each site and indicate its electrode name (cathode or anode).
   - c. Show the likely path of electron flow.
   - d. List the reasons for the corrosion (or lack of corrosion) of the iron in each nail. For nails in which the iron is protected from corrosion, explain how and why it is protected.

Bent iron nail

Iron nail with copper wire

Iron nail with zinc

Iron nail with tin foil

Concentration Cell Data

1. Record the cell voltage and observed changes in the cell upon addition of the Na_2S solution. Record the voltage after the addition of the Na_2S solution. Be sure to diagram the cell as in each of the previous parts: showing electrode signs, electrode processes, etc.

2. One drop has a volume of about 0.05 mL, thus the concentration of Cu^{2+} in the dilute half-cell is about (0.05 mL/25 mL)(0.1 *M*) = 2×10^{-4} *M*. Use Equation 16.17 to calculate it at 298 K and compare it with your observed value. Why might they differ?

3. After adding 11 drops (0.5 mL) of Na_2S solution, $[S^{2-}]$ is about (0.5 mL/25 mL)(0.1 *M*) = 2×10^{-3} *M*
    a. Calculate $[Cu^{2+}]$ from the solubility product constant:

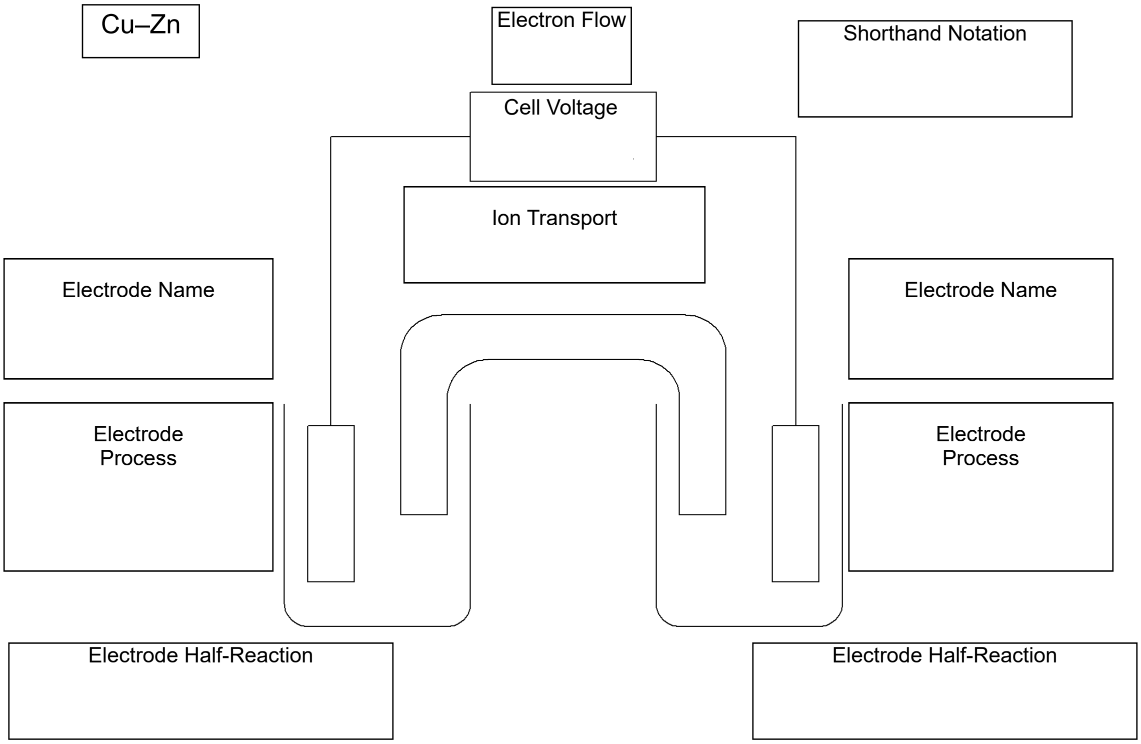
$$K_{sp} = 8\times10^{-37} = [Cu^{2+}][S^{2-}] \qquad \textbf{(EQ 16.18)}$$

    b. Then calculate *E* and again compare it with the *E* observed after you added Na_2S solution to the dilute Cu^{2+} half-cell.

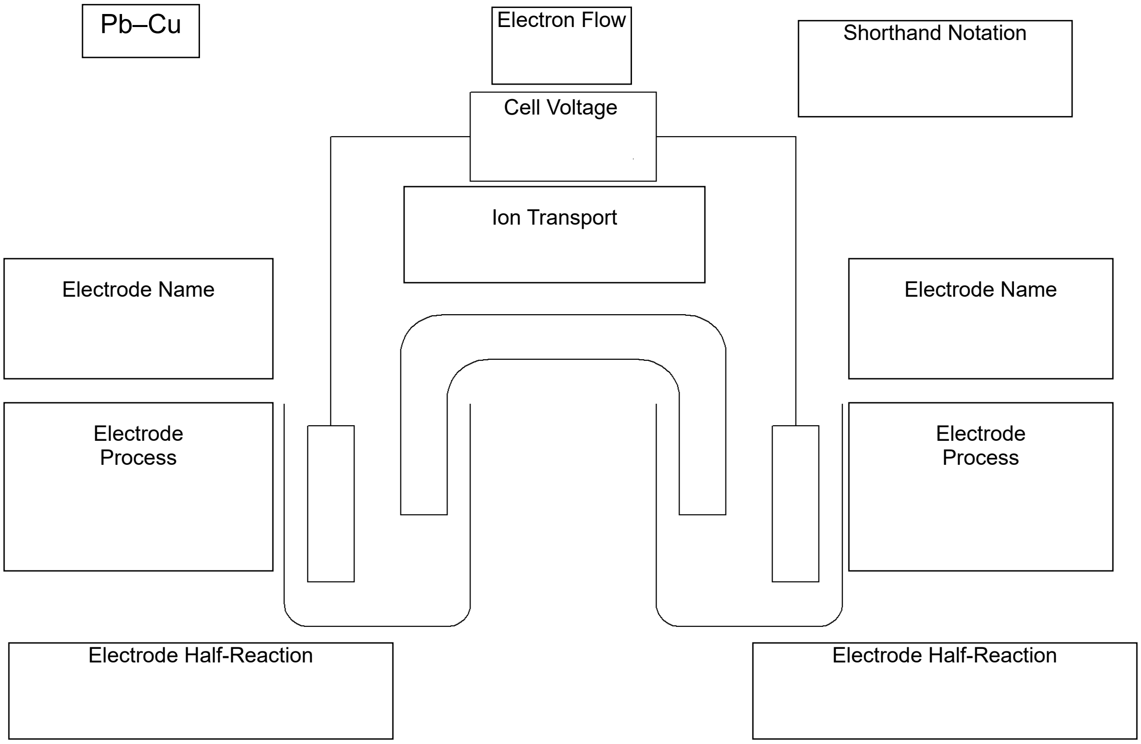
4. Suppose you had solutions 1 *M* in $Hg(NO_3)_2$ and Na_2S available. K_{sp} HgS = 1.6×10^{-34}. What is the highest E you could achieve with a Hg–Hg^{2+} concentration cell? What would be the constituents of each half-cell? Neglect the fact that S^{2-} hydrolyzes extensively in water.

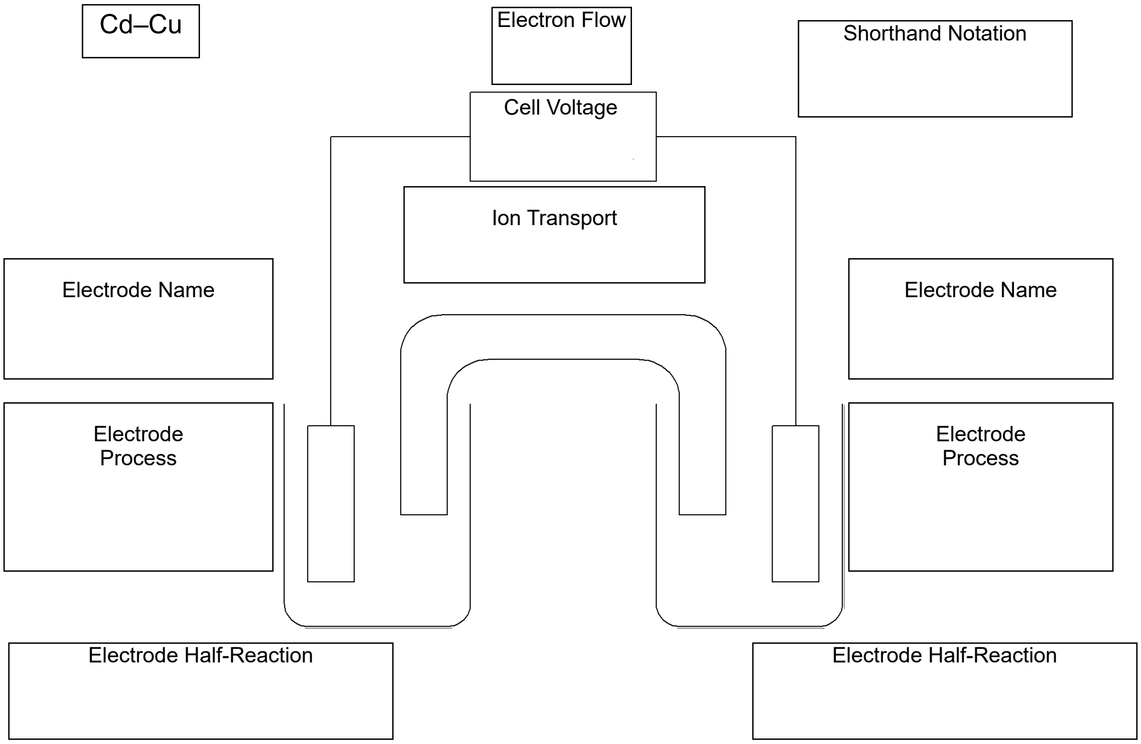
Electrochemical Cell Summary Sheet

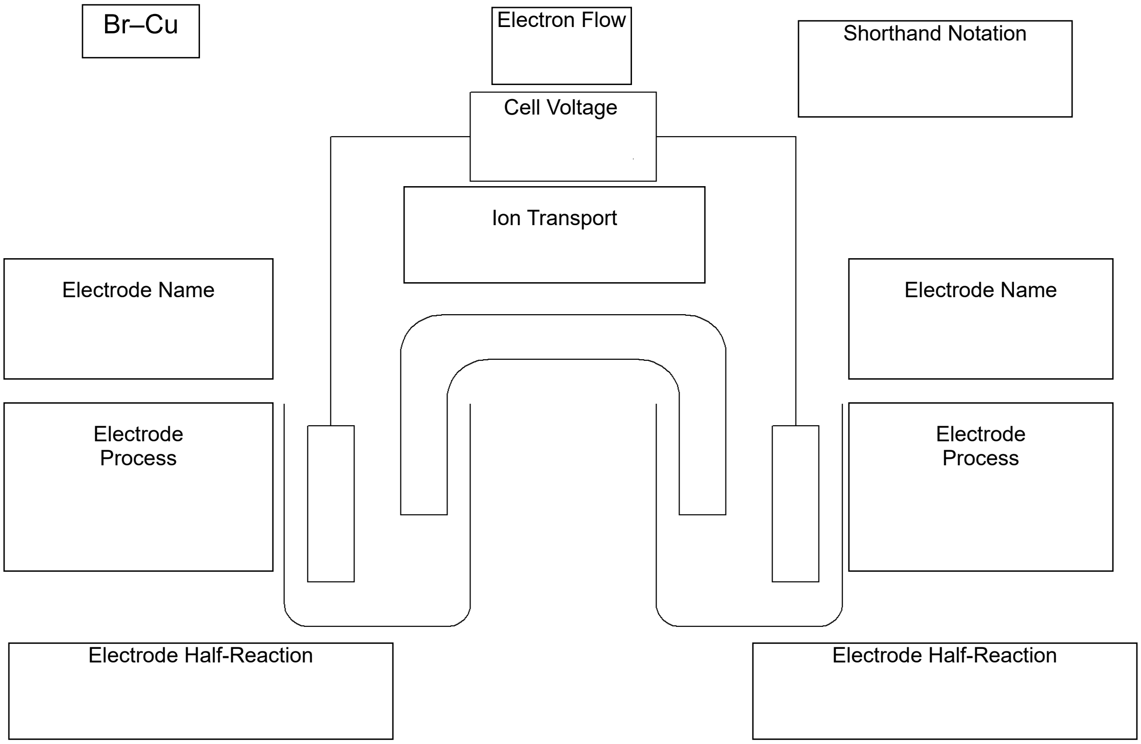
Cu–Zn



Pb–Cu




Cd–Cu
Electron Flow
Shorthand Notation
Cell Voltage
Ion Transport
Electrode Name
Electrode Name
Electrode Process
Electrode Process
Electrode Half-Reaction
Electrode Half-Reaction


Br–Cu
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Ion Transport
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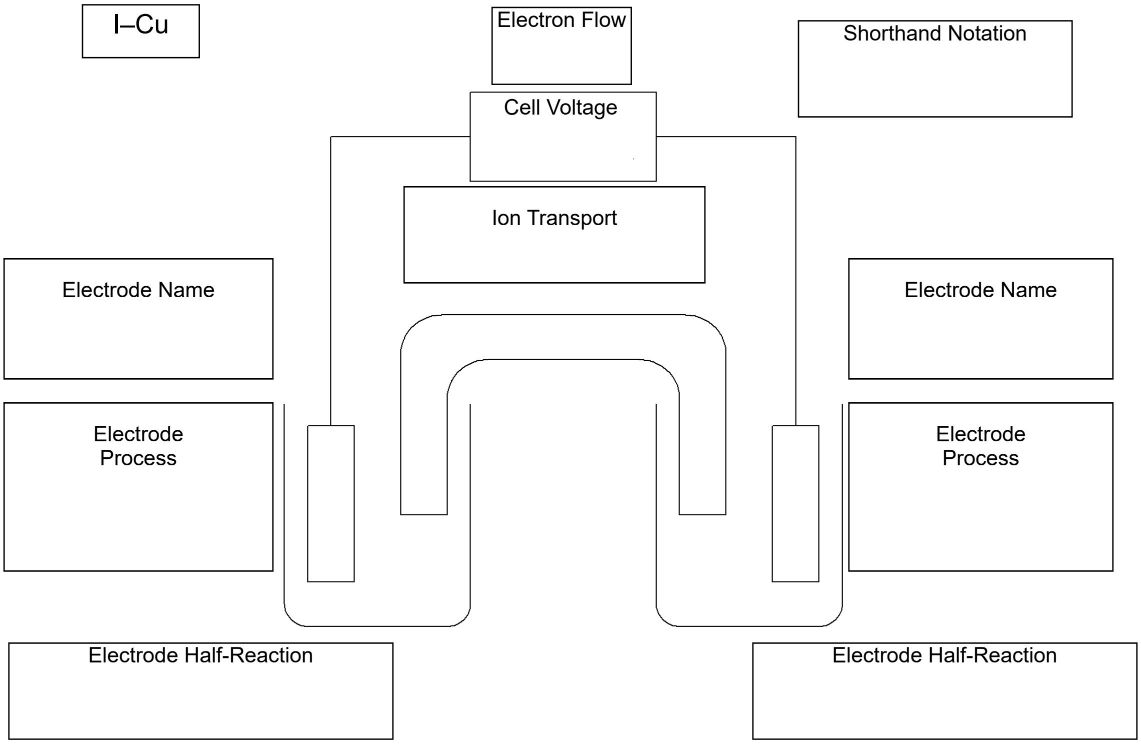
Electrode Name
Electrode Process
Electrode Process
Electrode Half-Reaction
Electrode Half-Reaction


I–Cu
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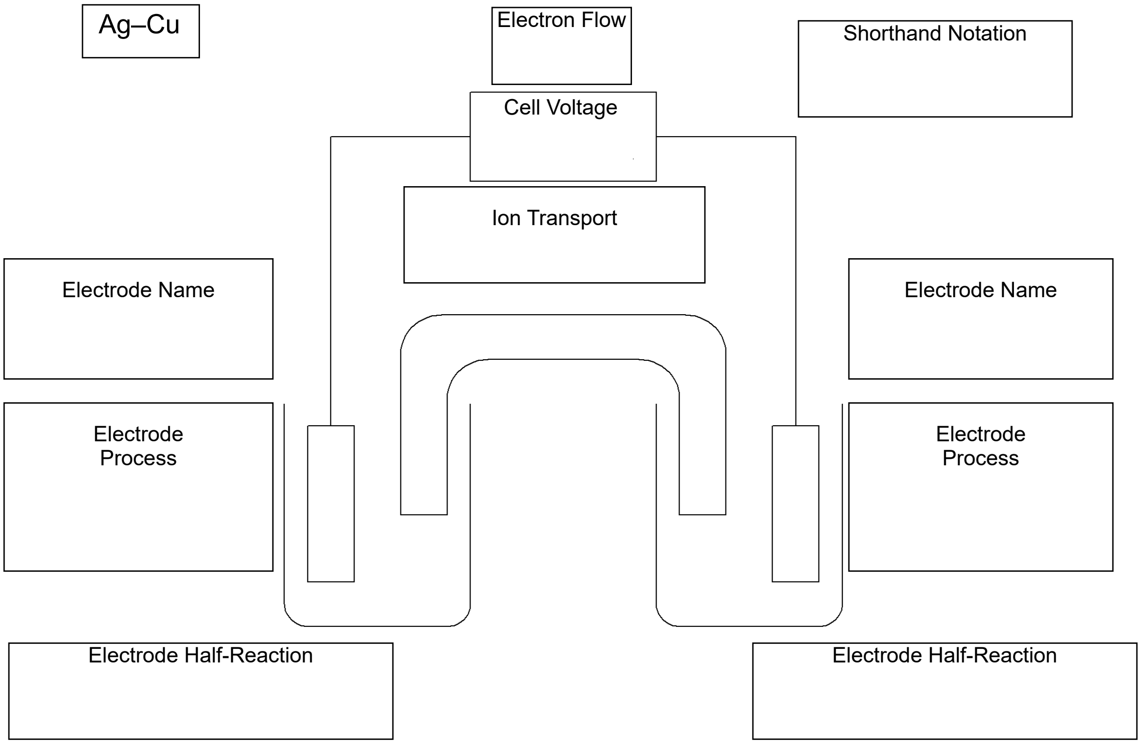
Cell Voltage
Ion Transport
Electrode Name
Electrode Name
Electrode Process
Electrode Process
Electrode Half-Reaction
Electrode Half-Reaction


Ag–Cu
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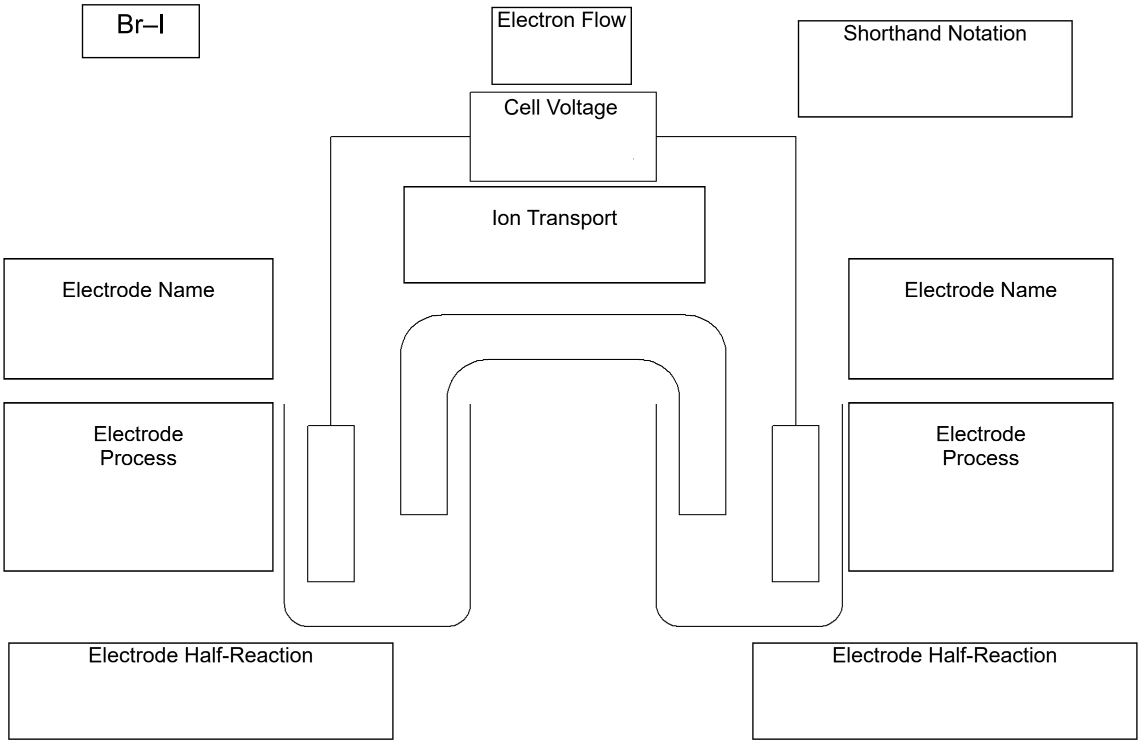
Electrode Half-Reaction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Cell Voltage
Ion Transport
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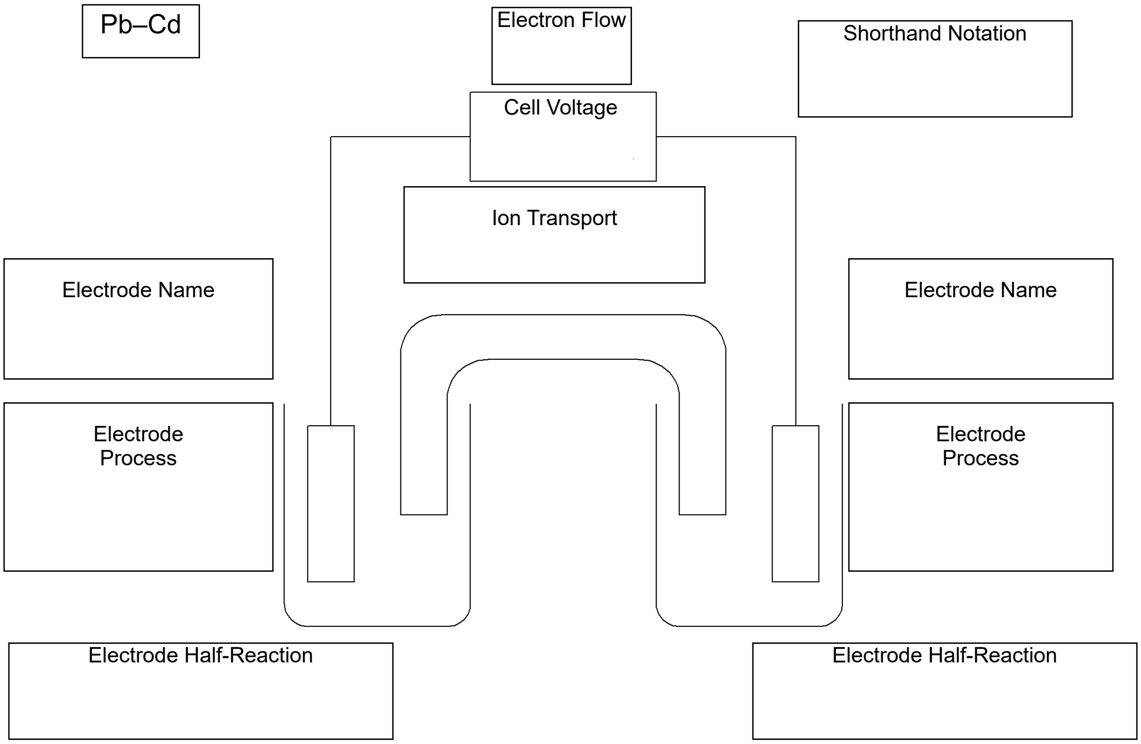
Electrode Half-Reaction
Electrode Half-Reaction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Shorthand Notation
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Ion Transport
Electrode Name
Electrode Name
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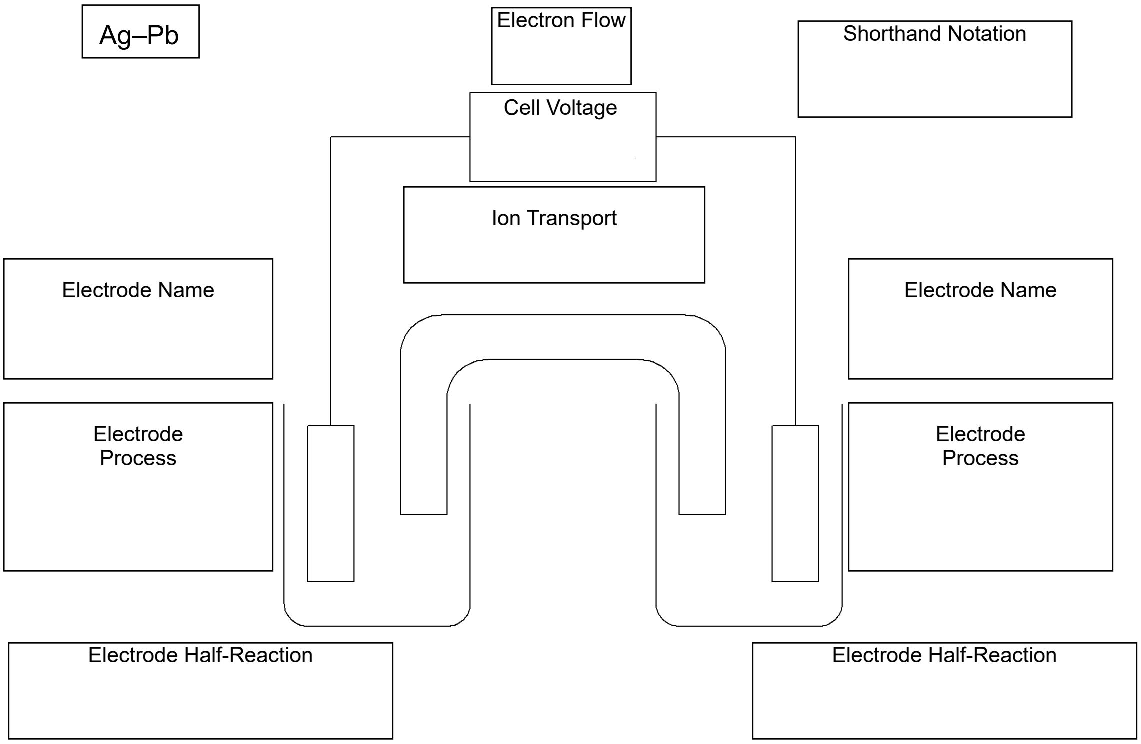
Electrode Process
Electrode Half-Reaction
Electrode Half-Reaction

Ag–Pb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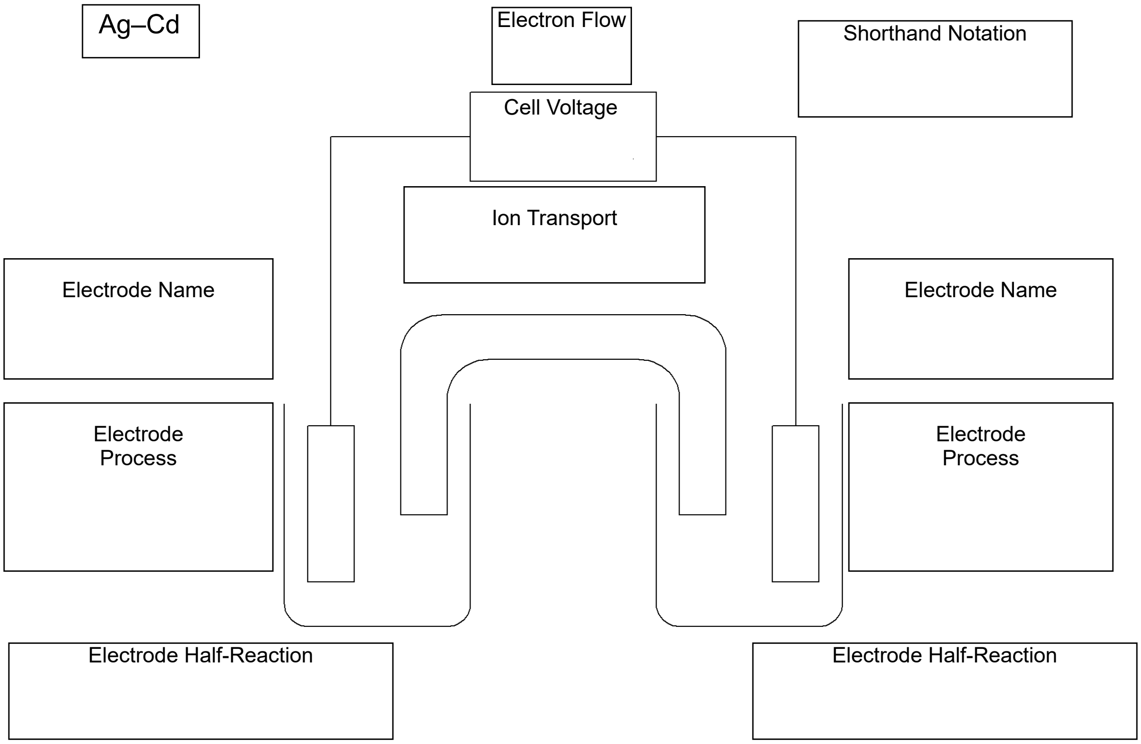
Cell Voltage
Ion Transport
Electrode Name
Electrode Name
Electrode Process
Electrode Process
Electrode Half-Reaction
Electrode Half-Reaction

Ag–Cd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Cell Voltage
Ion Transport
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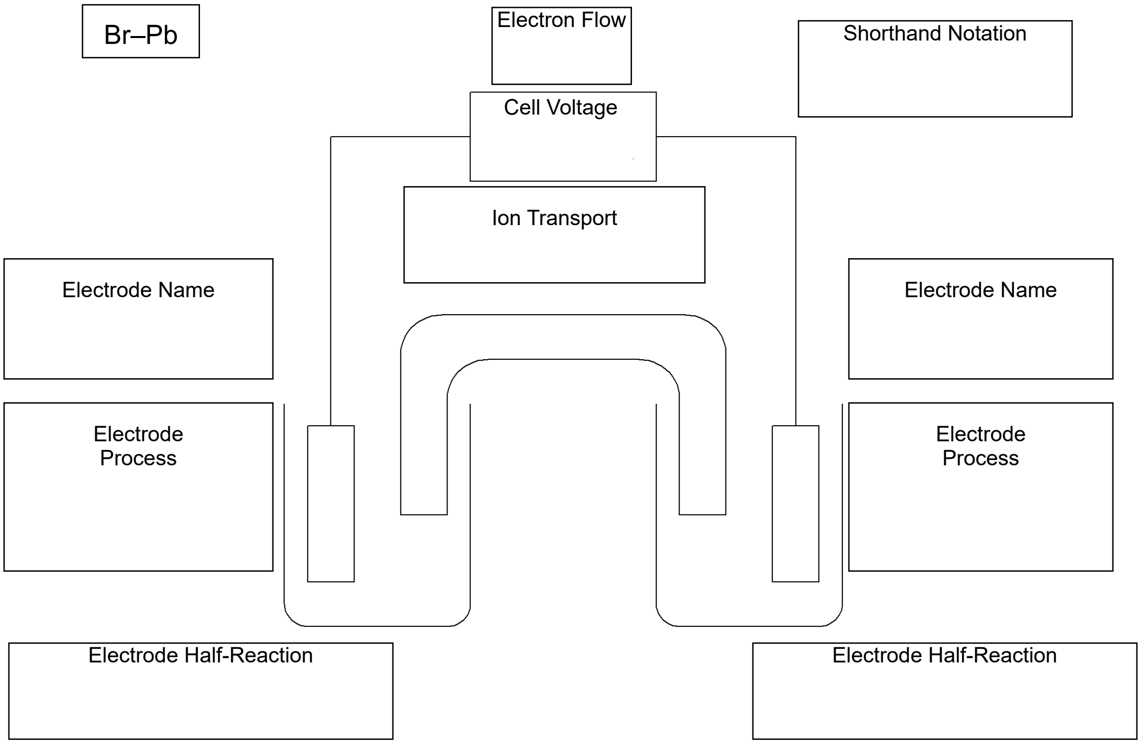
Electrode Name
Electrode Process
Electrode Process
Electrode Half-Reaction
Electrode Half-Reaction


Br–Pb
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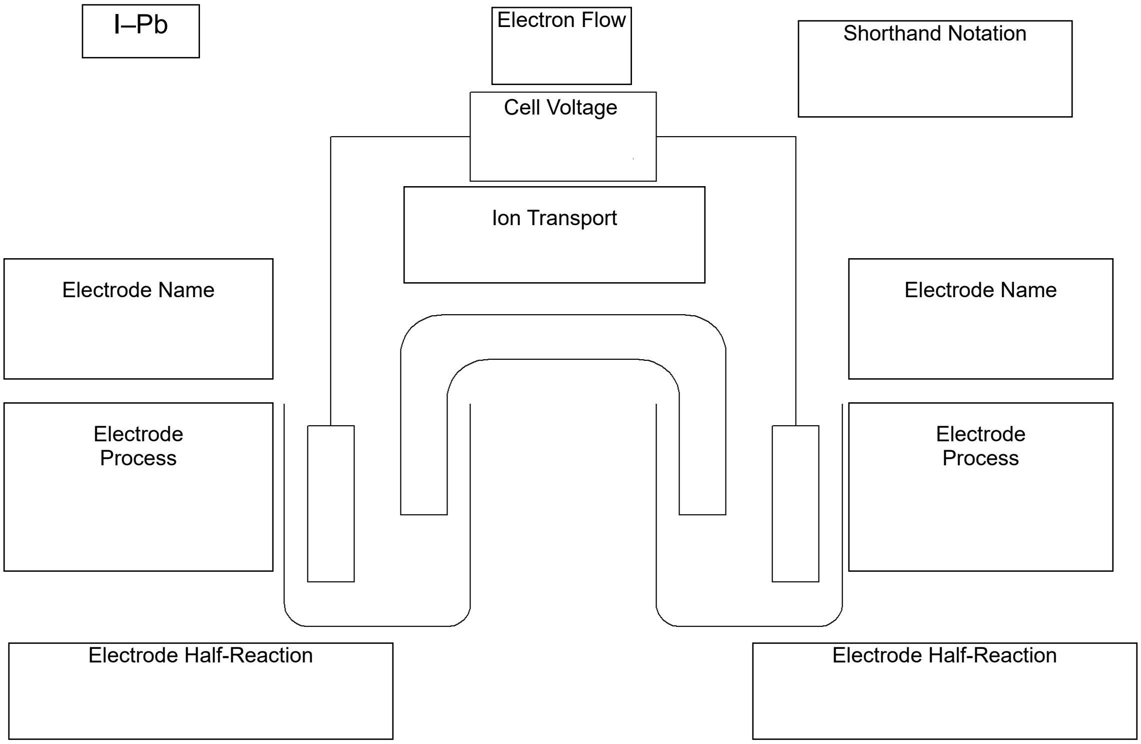
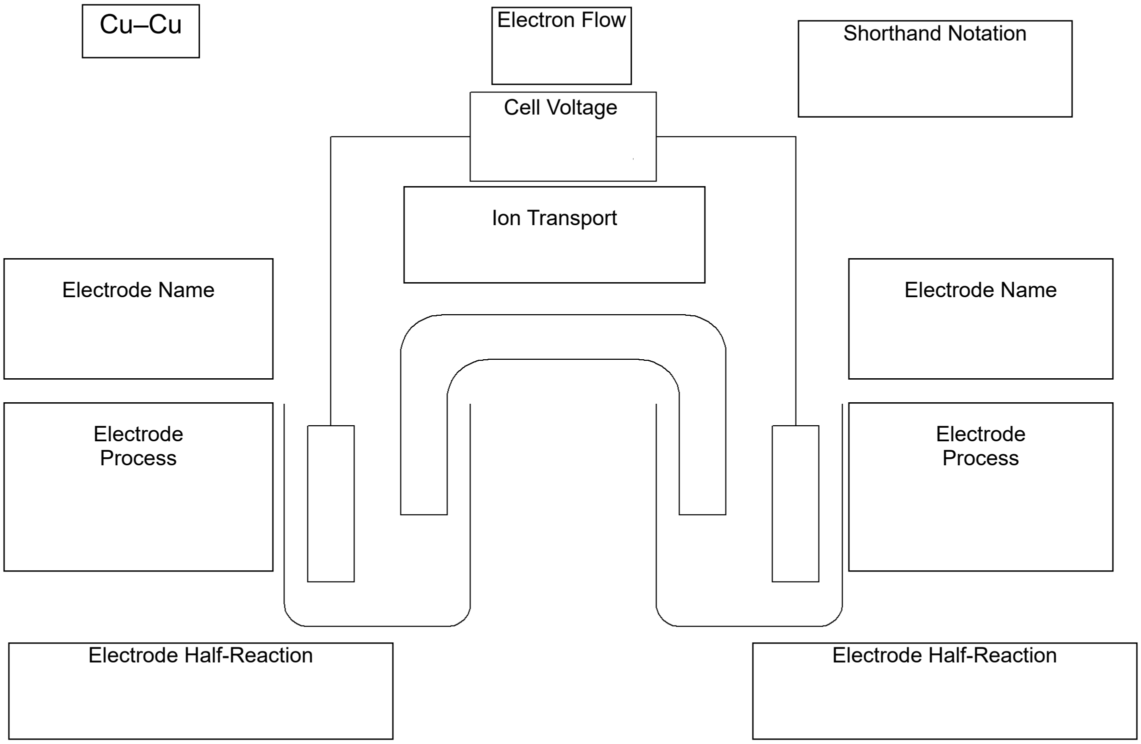
Electrode Half-Reaction


I–Pb
Electron Flow
Shorthand Notation
Cell Voltage
Ion Transport
Electrode Name
Electrode Name
Electrode Process
Electrode Process
Electrode Half-Reaction
Electrode Half-Reaction

Cu–Cu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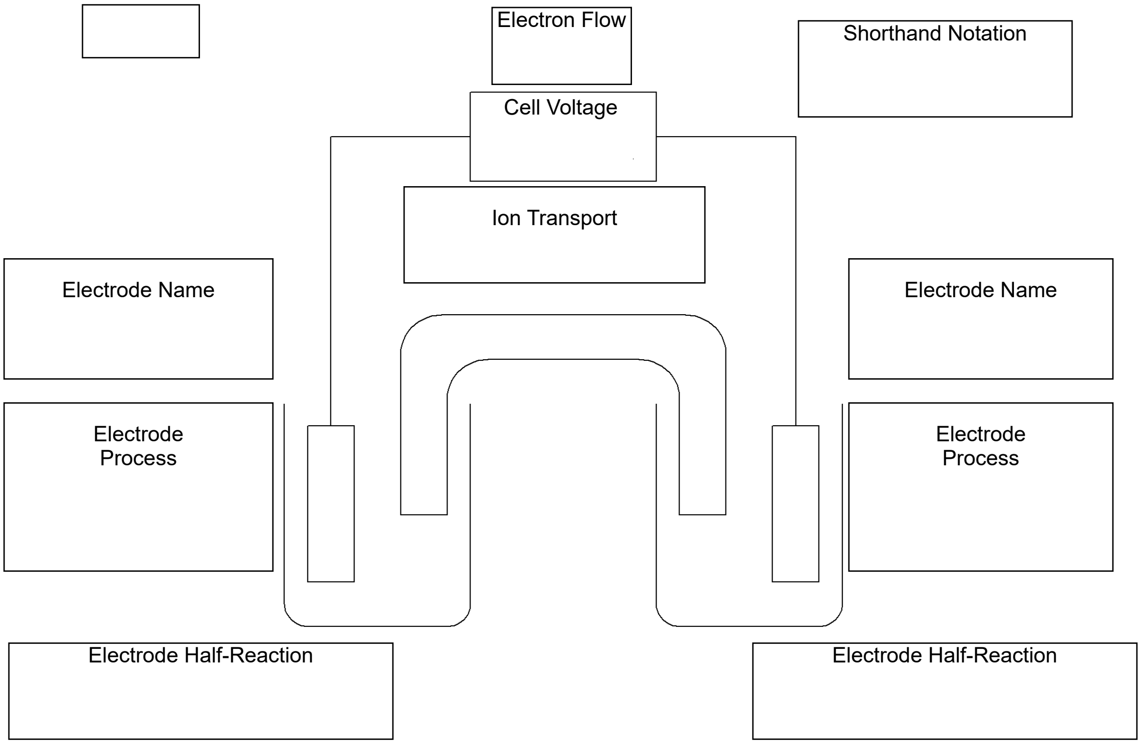
Electrode Half-Reaction
Electrode Half-Reaction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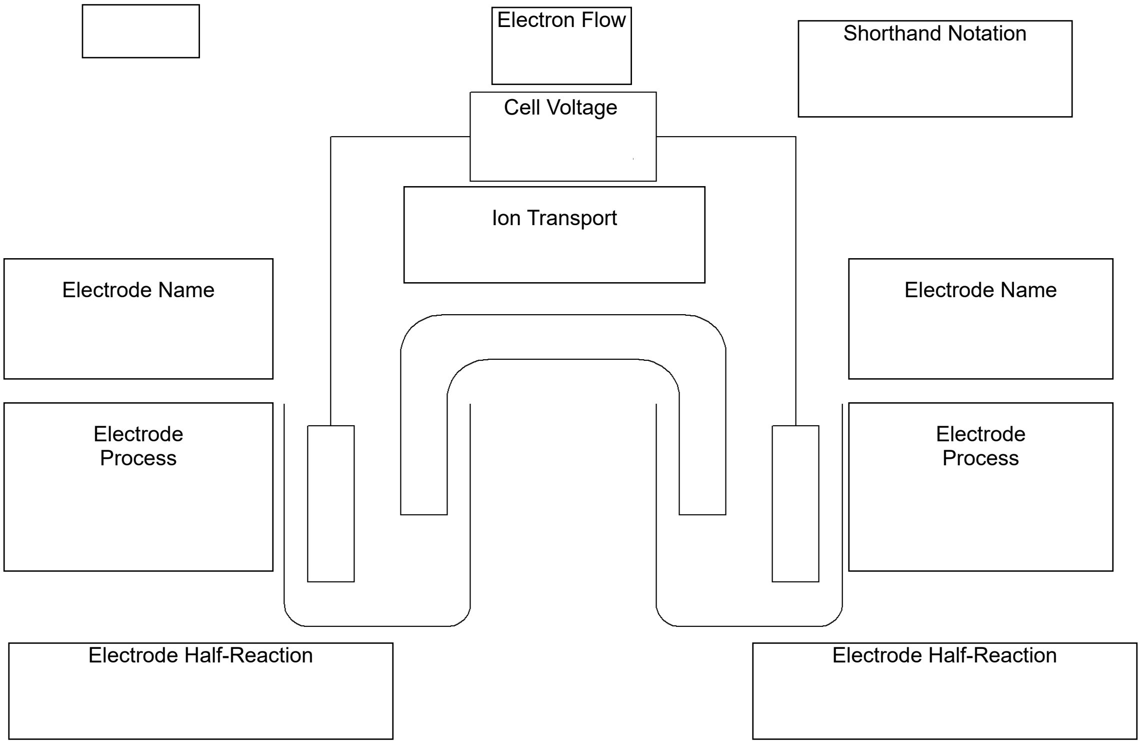
Electrode Process
Electrode Process
Electrode Half-Reaction
Electrode Half-Reaction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Cell Voltage
Ion Transport
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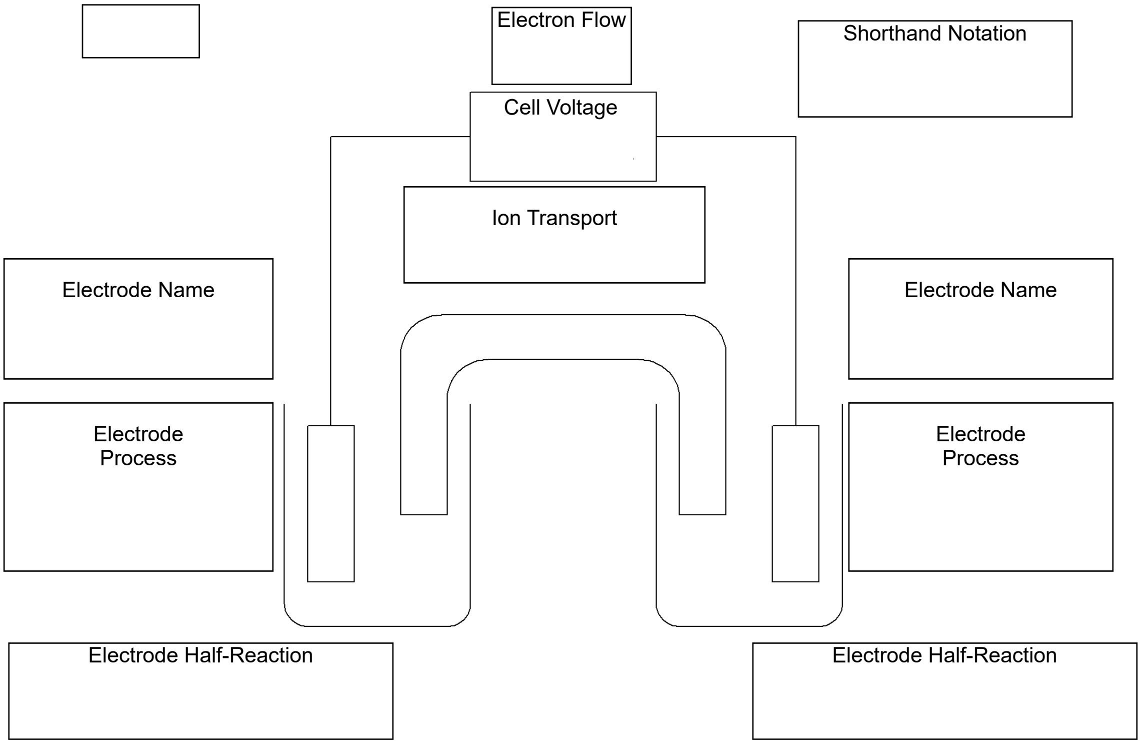
Electrode Half-Reaction

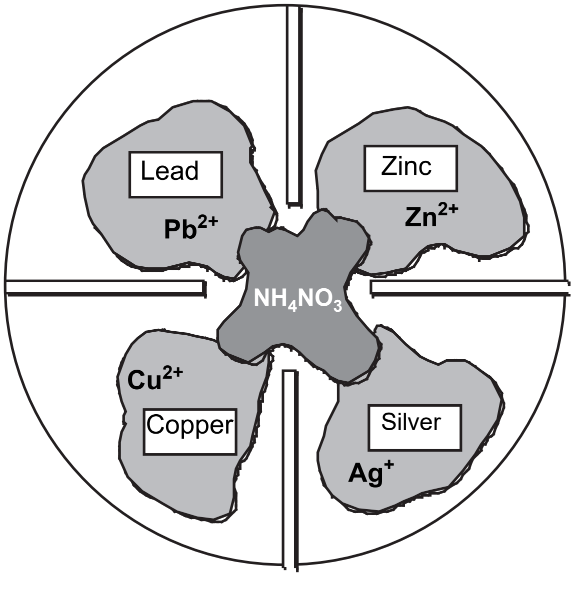

Electron Flow
Shorthand Notation
Cell Voltage
Ion Transport
Electrode Name
Electrode Name
Electrode Process
Electrode Process
Electrode Half-Reaction
Electrode Half-Reaction

EXPERIMENT 17 *Electrochemistry (B)*

Procedure

1. Cut 3-5 mm slits in as stack of three filter papers as shown and place the papers on a clean glass plate. Polish small strips of copper, lead, silver and zinc with steel wool or sand paper to produce a shiny, clean surface. The zinc strip should be amalgamated with a drop of mercuric nitrate solution to insure a clean surface (mercury salts are extremely poisonous so take extra care). Place one of the metal electrode strips on each of the filter paper sectors. Place a few drops of the 1.0 *M* metal ion solutions next to (not on) each of the metal strips, thoroughly wetting the filter paper (caution, avoid contact with silver nitrate!). At the center of the paper add a few drops of 1.0 *M* NH_4NO_3 to serve as a salt bridge for the cells.

FIGURE 17.1



2. Place the black (-) lead from the voltmeter firmly on the lead electrode and the red (+) lead on the copper electrode. This should result in a positive voltage. A positive voltage indicates that the red lead is at the cathode and the black lead is at the anode of a galvanic (spontaneous) cell. Electrons flow into the red lead and out of the black. A negative voltage indicates the reverse. With the black lead still on lead, proceed with the red to silver and to zinc, recording voltage and sign. Calculate the voltages for the remaining cells on the data page before proceeding to measure them. Calculate the standard potentials from the literature values and write the cell reactions for each cell.

TABLE 17.1 **Sample Data Table**

Electrodes (black on first electrode)	**Meas. Voltage**	**Calc. Voltage from Lit. Values**	**%error**	**Cell Reaction**
Pb-Cu				
Pb-Ag				
Pb-Zn				
Cu-Ag				
Cu-Zn				
Cu-Pb				
Ag-Zn				
Ag-Pb				
Ag-Cu				
Zn-Pb				
Zn-Cu				
Zn-Ag				

EXPERIMENT 18

Electrochemistry (C)

Background

Electrolytic Cells Principles

Electrochemical cells include various types:

- Galvanic (voltaic) cells are used to produce electricity from a chemical reaction for which $E° > 0$.
- Concentration cells.
- Fuel cells are galvanic cells that produce electricity from a chemical reaction in which the reactants can be supplied continually.
- Electrolytic cells, in which an external voltage source forces an electrochemical reaction to occur. Such cells are used to electroplate metals (e.g. silver plating jewelry or purifying copper). A battery being charged is also an electrolytic cell.

A lead storage cell is an example of an electrolytic cell. During charging it functions as an electrolytic cell as energy is pumped in; during discharge this energy is extracted. Lead storage cells are important commercially: they are inexpensive. reliable, efficient, and can be reused many times. Their only drawback is their energy density on a weight basis; lead is so dense that lead batteries are very heavy.

If two lead electrodes are immersed in H_2SO_4 solution the lead is oxidized. The product $PbSO_4$, is relatively insoluble in H_2SO_4 solution thus it covers the lead electrodes. If these $PbSO_4$-coated electrodes are then subjected to an external voltage source greater than 2 V, the following reactions occur during the electrolysis:

$$\text{anode: } PbSO_{4\,(s)} + 2\,H_2O_{\,(l)} \rightarrow PbO_{2\,(s)} + 3\,H^+_{\,(aq)} + HSO_4^-{}_{(aq)} + 2\,e^- \quad E° = -1.70\text{ V} \qquad \textbf{(EQ 18.1)}$$

$$\text{cathode: } PbSO_{4\,(s)} + 2\,e^- + H^+_{\,(aq)} \rightarrow Pb_{\,(s)} + HSO_4^-{}_{(aq)} \quad E° = -0.31\text{ V} \qquad \textbf{(EQ 18.2)}$$

Note that the definitions of anode (site of oxidation) and cathode (site of reduction) are the same as in a voltaic cell, but the sign assigned to the electrodes is different. Since electrons are being pumped in during the electrolysis process, the negative electrode is now the cathode. During discharge, the cell reactions are reversed; the cell is a voltaic cell; the positive electrode becomes the cathode (as it is in any voltaic cell.).

Corrosion

Metals are materials from which automobiles, ships, bridges, airplanes, pipes, and many other modern essentials are constructed. Metals are usually exposed to air. Water, salt, and other chemical species that cause them to corrode. Prevention of corrosion is one of the most important applications of chemistry, since enormous amounts of effort and sums of money are invested in the protection of metals from the environment. To a chemist, corrosion is the oxidation of metals by atmospheric oxygen, typically in conjunction with water and salts. The prevention of corrosion is a fascinating application of electrochemistry.

Aluminum is a metal that ought to be very easily oxidized, but it forms a tightly adhering thin coat of oxide, which protects it against further oxidation. A nonmetallic coating such as paint also protects a metal from corrosion.

1. The metal can be placed in electrical contact with another metal that is more easily oxidized than the metal being protected. The more easily oxidized metal will then be oxidized first. For example, if you own a boat. You can protect its metal hull by fastening a block of magnesium to the hull. The magnesium block and the iron hull form a galvanic cell with the magnesium (the Anode) being oxidized and the oxygen being reduced at the iron. Since the iron is protected by being made the cathode, this method of corrosion protection is called cathodic protection. The magnesium block is referred to as a sacrificial anode.

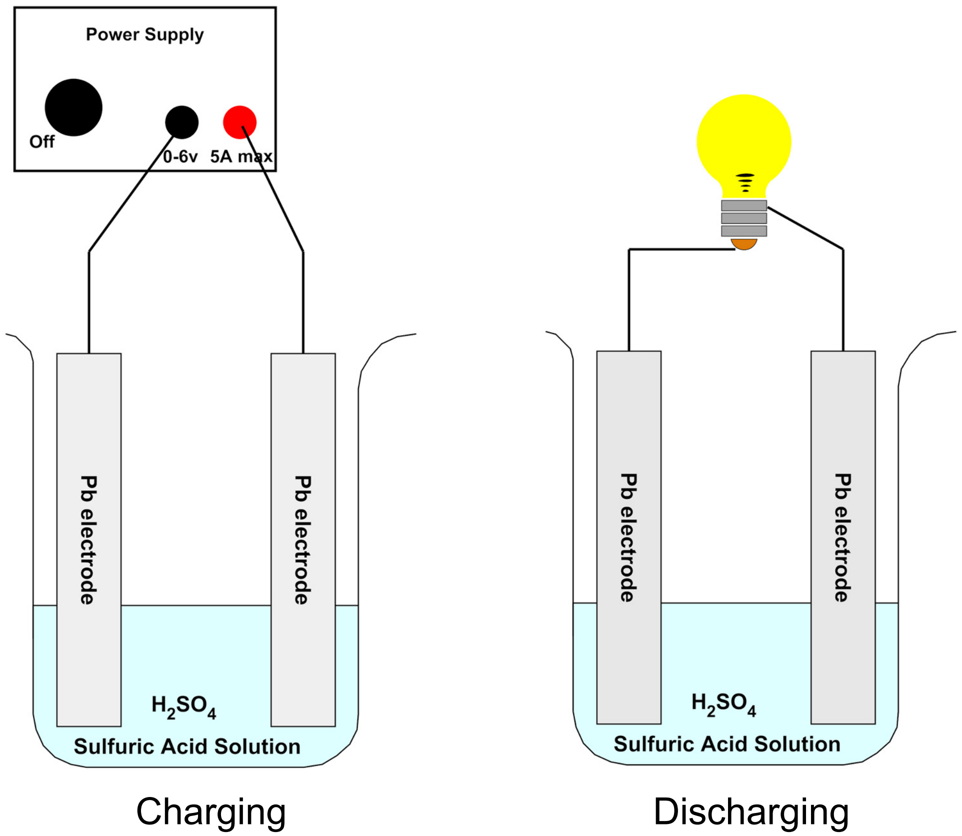
Other examples of corrosion and corrosion protection are described in your text. You will also demonstrate the effect of removing the protective coating of oxide from a piece of aluminum.

Procedure

Electrolytic Cell Procedure

1. Take two lead electrodes and clean them with sandpaper. Place them carefully in a test tube and add concentrated H_2SO_4 until the acid level is just below the point at which the copper wires are attached. This creates a layer of $PbSO_4$ on the electrodes. Do not skip this step! Write the reaction that occurs in your lab notebook.
2. Pour approximately 75 mL of 6 *M* H_2SO_4 into a 200 mL beaker and place a paper towel in the beaker with the acid.
3. Place the lead electrodes into the beaker, and use the alligator clips to connect them to the power supply as in the “Charging” diagram in Figure 18.1.
4. Use your voltmeter to adjust the charging voltage to approximately 3 volts.
5. Charge for 1 minute and measure the voltage with the voltmeter. After the voltage has been measured, briefly discharge the battery by touching the leads together for a moment.

FIGURE 18.1



6. Charge the battery in 30 second intervals and check the burn-time with the small light bulb provided. That is, charge for 30 s then time the discharge with the bulb, then charge for 1 minute and time the discharge with the bulb. Repeat this until you complete a charge cycle of 5 minutes of charging time.

> **NOTE:** Be sure to disconnect the power supply before attaching the light bulb!

7. Make a graph of run-time vs. charge time. Is this a linear relationship?
8. Now, choose a variable to investigate. Design an experiment to investigate this variable and how it affects the run-time of the battery.

Corrosion Procedure

Anodic and cathodic sites. Place 100 mL of 6 *M* hydrochloric acid in a 250 mL beaker. Obtain and clean with sandpaper, if necessary, a zinc strip, a copper strip, and an iron strip or nail. Immerse the copper strip in the acid and record your observations. Immerse the zinc strip in the acid and record your observations. Immerse the copper and zinc strips in the acid simultaneously; touch them against each other and record your observations when they are in contact and when they are separated. Repeat these steps with copper and iron, and with iron and zinc.

Protection by oxide film. Fill a 10-cm test tube half full with 6 *M* hydrochloric acid and a second, labeled test tube half full with 6 *M* potassium hydroxide solution. Add to each test tube a small strip of aluminum foil. Heat each test tube carefully by immersing it in a 50 °C water bath. Record your observations before and after heating. Fill a third, labeled 10 mL test tube half full with 0.1 *M* mercury(II) chloride solution. Add a small strip of aluminum foil: the aluminum metal reduces Hg^{2+} to Hg which amalgamates (alloys with) the aluminum. Write the net ionic equation for this reduction in the "Data" section on page 150. After 5 minutes decant the solution into a specially marked receptacle: do not pour it down the drain, since mercuric compounds are poisonous and since the solution can be reused. Rinse the amalgamated aluminum foil with water.

Place an unamalgamated aluminum foil strip in a fourth test tube. Fill the third and fourth test tubes with water and place both in a water bath. Bring the water bath to a boil and record what happens to both pieces of aluminum foil.

Data

1. Lead storage battery
2. Observations (reaction of metal, production of gas, and so on; be specific or make a drawing):
   a. Copper strip in hydrochloric acid.;
   b. Zinc strip in hydrochloric acid.;
   c. Copper and zinc strips in hydrochloric acid: t in contact and in contact.
   d. Iron strip in hydrochloric acid:
   e. Iron and copper strips in hydrochloric acid: not in contact, and in contact.
   f. Iron and zinc strips in hydrochloric acid: not in contact, and in contact.
3. Observations on Al foil in 6 *M* HCI solution and in 6*M* KOH solution:
   a. Net ionic reaction for the reduction of Hg^{2+} by Al
4. Observations on Al foil in boiling water.
   a. Amalgamated
   b. Unamalgamated

Data Interpretation

Electrolytic Cell Data

1. What is the voltage of the Pb cell after steps 1-5 in the procedure, “Electrolytic Cell Procedure” on page 148 has been completed?

2. Does the run-time vs. charge time graph appear to be linear? How did you assess the linearity?

3. Briefly describe the variable that you investigated and how it affected burn time.

4. During discharge of a lead storage cell, does [H_2SO_4] increase or decrease? How can the density (or specific gravity) of the solution indicate the state of discharge of the cell?

5. If Na_2SO_4 were used instead of H_2SO_4 could the cell function? What if HNO_3 were substituted for H_2SO_4? Why? (Hint: Consult a solubility table.)

Corrosion

1. Make a drawing of the electrochemical cell set up for each of the following when in contact in hydrochloric acid solution. Show half-reactions. electrode processes, electrode names and current flow outside the solution.
    a. Copper and zinc cell.
    b. Iron and copper cell.
    c. Iron and zinc cell.
2. Suppose that the iron in a bridge girder has inclusions of zinc or copper, or that it is in contact with zinc or copper objects.
    a. Do zinc and copper form anodic or cathodic sites?
    b. Do they hinder or accelerate corrosion of the iron?

3. Answer the following for aluminum:
   a. Write a net ionic reaction for aluminum in 6 *M* HCl solution and also for aluminum in 6 *M* KOH solution.

   b. Also, write reactions for Al_2O_3, in both of these solutions. Remember that aluminum is protected from corrosion by a thin film of Al_2O_3; explain your observations in terms of the relative solubility rates of Al_2O_3 in a 6 *M* HCI versus a 6 *M* KOH solution.

   c. Write the reaction between aluminum and water. (Remember that aluminum hydroxide is insoluble.)

   d. What effect does amalgamation have on the resistance of aluminum to corrosion?

   e. Is aluminum amalgam a corrosion-resistant alloy?

   f. Mercury does not react with aluminum oxide: why does amalgamation affect the corrosion rate of aluminum?

EXPERIMENT 19 *Ligand Substitution*

Background

In this experiment several transition metal complexes will be prepared and the influences on the spectroscopic absorption of different ligands will observed. Metal complexes will be drawn and the different types of isomers explored.

Chemical species like H_2O, NH_3, or Cl^- that have non-bonding electron pairs can form **coordinate covalent bonds** with transition metal cations by sharing an electron pair with the metal. The species that donates the electron pair is called a **ligand** and the resulting compound is called a **complex**. For example, the nitrogen atom in ammonia contains a non-bonding electron pair that can be shared with a transition metal cation such as Ag^+. In this case, the resulting complex is $[Ag(NH_3)_2]^+$, diamminesilver(I) ion. Transition metal cations form complexes very readily with neutral molecules like H_2O and NH_3, and with anions like Cl^- and CN^-. Consider the transition metal complex ion tetraamminedichlorocobalt(III), $[Co(NH_3)_4C1_2]^+$ in aqueous solution. It is made from one Co^{3+} cation, 4 ammonia molecules, and 2 Cl^- anions. The net charge of the complex ion is the sum of the charges on all of the components: (+3 –1 –1) = +1.

The behavior of complex ions is based on their structure; there is a transition metal cation at the center, surrounded by several ionic or neutral chemical groups, the ligands. Transition metal cations, formed by losing electrons from their valence electron shell *s* and *d* orbitals, can share electron-pairs with other chemical species that have non-bonding electron pairs available to donate, forming a coordination bond between the metal cation electron acceptor and the ligand electron donor. Ligands that group around the central cation all have at least one pair of non-bonding electrons that coordinate with unfilled valence orbitals of the cation, to form the complex. Due to the charge on the central cation, coordination bonding frequently is mostly ionic, so that the number of ligands that can coordinate with the cation is determined more by the charge and size of the cation than by the number of valence orbitals.

The number of coordinate bonds that the cation forms is called its **coordination number**, and can vary from 2 to at least 12. The most common coordination numbers are 4 and 6. Only very large, multiply-charged cations form complexes with coordination numbers greater than eight.

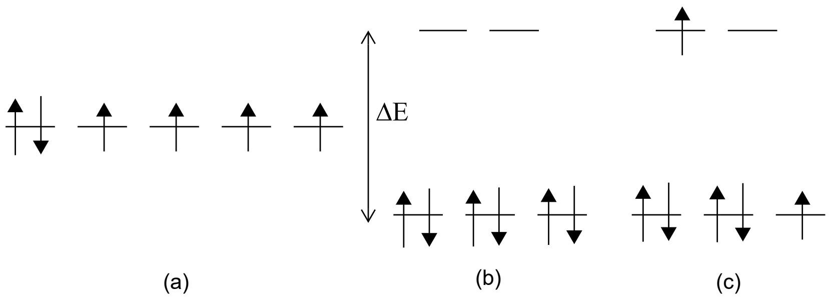
In tetraamminedichlorocobalt(III) ion, $[Co(NH_3)_4C1_2]^+$, which has 4 NH_3 and 2 Cl^- ligands, the coordination number for Co^{3+} is six. Each NH_3 group has one non-bonding electron pair and each

Cl^- ion has four non-bonding pairs available for coordination. The resulting complex ion has an octahedral symmetry, slightly distorted because the NH_3 and Cl ligands are not equivalent with respect to their sizes and electronegativities.

The complex ion hexaamminecobalt(III) ion, $[Co(NH_3)_6]^{3+}$, where all 6 ligands are completely equivalent, would form a perfect octahedron. As a "rule of thumb" the coordination number often turns out to be 2 times the charge on the cation.

The nature of the cation-ligand bond has a very strong influence on the absorption spectrum of the complex ion, and spectroscopy is an important tool for studying the bonding properties of coordination complexes. The presence of the ligands around the central cation removes the energy degeneracy of the cation *d* orbitals. With six ligands in octahedral symmetry, (the geometry of the complexes studied in this experiment) two of the *d* orbitals are raised to a higher energy than the other three (see Figure 19.1 for the splitting diagram). By absorbing light energy, an electron can move from a lower to an upper energy level. (a) in Figure 19.1 represents the uncomplexed Co^{3+}, (b) is the ground state of complexed Co^{3+}, ion and (c) is the excited state of the complexed Co^{3+} ion.

FIGURE 19.1



The energy difference between the lower and upper levels is related to the wavelength of light absorbed, as expressed by the equation:

$$\Delta E = \frac{hc}{\lambda} \qquad \textbf{(EQ 19.1)}$$

ΔE = energy difference between lower and upper levels h = Planck's constant, c = speed of light, and λ = wavelength of light absorbed in meters

Notice that, since both terms in the numerator of Equation 19.1 are constants, to make ΔE larger, λ must be made smaller. In other words, when ΔE is large, the wavelength of light absorbed is short, and when ΔE is small, a longer wavelength of light is absorbed. The nature of the ligand determines the separation of the energy levels and the magnitude of ΔE.

A listing of ligands, in order of how large an energy level splitting they produce, is called a spectrochemical series. Equation 19.2 gives a spectrochemical series for some common ligands arranged in order of decreasing ΔE:

$$CN^- > NO_2^- > NCS^- > NH_3 > H_2O > C_2O_4^{2-} > OH^- > F^- > Cl^- > Br^- > I^- \qquad \textbf{(EQ 19.2)}$$

The color of an aqueous solution of a complex ion is determined by which wavelengths of light are absorbed to excite the *d* electrons. The color observed depends on what wavelengths remain after part of the light has been absorbed. The color that we see is the color of the light that is transmitted through the sample, not the color of the light absorbed by the sample. In Table 19.1 on page 157, the energies absorbed and colors observed are compared for several complex ions of Co^{3+}. A compound that does not absorb at all in the visible wavelength region will appear to be transparent and colorless; one that absorbs fairly uniformly at all visible wavelengths will be gray or black.

TABLE 19.1

Complex Ion Name	Complex Ion	Color of Solution	Color Absorbed from Incident Light	Wavelength of maximum Absorbance (nm)
hexaamminecobalt(III)	$[Co(NH_3)_6]^{3+}$	yellow	violet	430
pentaammineisothiocyanatocobalt(III)	$[Co(NH_3)_5(NCS)]^{2+}$	orange	blue	470
pentaammineaquacobalt(III)	$[Co(NH_3)_5(H_2O)]^{3+}$	red	blue-green	500
pentaamminechlorocobalt(III)	$[Co(NH_3)_5Cl]^{2+}$	purple	yellow-green	530
trans-tetraamminedichlorocobalt(III)	*trans*-$[Co(NH_3)_4Cl_2]^{+}$	green	red	680

By measuring how the absorbance spectrum of a complex ion depends on the ligands that are bonded to the central metal cation, we learn about the energy separation between the *d* orbitals in the metal's valence shell and determine the order of ligands in a spectrochemical series. From Table 19.1 on page 157 we see that the wavelength of maximum absorbance for hexaamminecobalt(III) ion, $[Co(NH_3)_6]^{3+}$, is 430 nm. Therefore the ΔE for the energy splitting of the *d* orbitals is given in Equation 19.3

$$\Delta E = \frac{hc}{\lambda} = \frac{(6.626\times10^{-34}\,\mathrm{J\ s})(3.00\times10^{8}\,\mathrm{m/s})}{430\times10^{-9}\,\mathrm{m}} = 4.62\times10^{-19}\,\mathrm{J} \qquad \textbf{(EQ 19.3)}$$

In Part A, the ligands around an octahedrally complexed Ni^{2+} cation are changed from H_2O to NH_3 and the effect on the absorption spectrum is measured with a spectrophotometer. In Part B, an octahedrally complexed Co^{2+} cation is oxidized to $Co^{3\,+}$, its ligands are changed from H_2O to NO_2, and the effect on the spectrum is measured.

You are to do only one of these parts. Your instructor will tell you whether to do Part A or Part B.

In Part C, you use molecular models to study the geometry and isomers of several complex ions.

Procedure

Part A

1. Be certain that the spectrophotometer is turned on so it is warmed up for your measurements.
2. Place 50 mL of concentrated NH_3 solution into a small Erlenmeyer flask or bottle and cool it in an ice bath.
3. On weighing paper, weigh about 6 g of hexaaquanickel(II) chloride, $[Ni(H_2O)_6]Cl_2$. Transfer to a 50 mL beaker and dissolve it in 10 mL H_2O, warming and stirring as needed. If the solution is not clear, centrifuge it rapidly while it is still warm. Then, cool the solution to room temperature.

4. Transfer 1 mL of the clear solution to a clean graduated cylinder and dilute it to 10 mL with distilled water. Save the concentrated portion for Step 8.
5. Using the diluted portion, rinse a spectrophotometer cell twice with small portions of the solution. Then, fill the cell with the diluted portion of the nickel chloride solution. To remove bubbles on the cell walls, press a piece of parafilm over the top of the cell with your finger to seal it, and slowly invert and rotate the cell to bring all the bubbles to the liquid surface.
6. Insert the sample cell into the spectrometer and measure its absorption spectrum. If using the Spec20, scan over the entire wavelength range, measuring at 20 nm intervals. Record the measured absorbance values on the Data Sheet.

Be sure to reset (zero and 100%) your spectrophotometer after each frequency change if using a Spec20.

7. Repeat the scanning procedure with a distilled water blank. Rinse the cell 2 or 3 times with distilled water before measuring. Record the measured absorbance values on the Data Sheet.
8. In a hood, add 12 mL of chilled, concentrated NH_3 solution to the 9 mL of concentrated nickel(II) chloride solution remaining from Step 4, while stirring. Cool the mixture by placing the beaker on ice. Crystals of hexaamminenickel(II) chloride, $[Ni(NH_3)_6]C1_2$, should form within about 15 minutes. Add more NH_3 if crystallization does not occur.
9. Vacuum filter the crystals. If the filtered crystals are clumped together, spread them out on the filter with a spatula. With suction on, wash the crystals twice, using 2 mL of cold concentrated NH_3 solution each time.
10. Now, wash the crystals 3 times, using 2 mL portions of acetone each time, to remove water. Keep the suction on to draw air through the filter until the crystals are dry.
11. Weigh your product and record the mass in your notebook.
12. Dissolve the hexaamminenickel(II) chloride, $[Ni(NH_3)_6]C1_2$, crystals in 9 mL 6 *M* NH_3 and repeat steps 4-6 to measure the absorption spectrum of the solution. It is not necessary to run another water blank.

NOTE: Dilute with concentrated NH_3 rather than water!

Part B

1. On weighing paper, weigh about 5 g of hexaaquacobalt(II) nitrate, $[Co(H_2O)_6](NO_3)_2$ and record the mass. Transfer the sample to a 100 mL beaker and dissolve it in 15 mL H_2O.
2. Remove 1 mL, of the solution, dilute it to 10 mL with distilled water and measure its absorbance spectrum as in steps 5-6 of Part A.
3. Repeat the scanning procedure with a distilled water blank. Rinse the cell 2 or 3 times with distilled water before measuring. Record the measured absorbance values on the Data sheet.
4. Dissolve 15 g sodium nitrite, $NaNO_2$, into the remaining 14 mL of concentrated cobalt nitrate solution, warming and stirring as needed until dissolved.
5. Cool the solution to 50 °C in a cold water bath.
6. In a hood, add to the solution drop by drop 5 mL of 50% acetic acid solution, while stirring continuously but gently. You want to dissolve the reactants without unnecessary agitation.
7. Transfer the solution to a large test tube (25 × 200 mm). Pour it slowly down the side of the test tube to avoid agitation. The reaction rate in the cool un-agitated solution is very slow.

8. Connect the test tube to an aspirator as in the set-up on the instructor's bench, and turn on the aspirator. Be sure the long tube in the trapping bottle is under the water surface. Air bubbles rising through the reaction solution mixes and warms the reactants. Draw air through the reactants for about 30 minutes. The reaction that occurs is:

$$2\ NO_{2\ (g)} + 2\ H_3O^+_{\ (aq)} \rightarrow 3\ H_2O_{\ (l)} + NO_{\ (g)} + NO_2^{\ +}{}_{(g)} \qquad \textbf{(EQ 19.4)}$$

One product of this reaction is the corrosive gas nitrogen dioxide, NO_2. Nitrogen dioxide is very soluble in water and dissolves in the water trap bottle. If any NO_2 escapes the water trap, it is entrained and dissolved in the aspirator flow and carried down the drain.

When NO_2 dissolves in cold water, a dilute mixture of nitrous and nitric acids is produced by the reaction:

$$2\ NO_{2\ (g)} + 3\ H_2O_{\ (l)} \rightarrow 2\ H_3O^+_{\ (aq)} + NO_{2\ (g)} + NO_3^{\ -}{}_{(aq)} \qquad \textbf{(EQ 19.5)}$$

This solution can safely be disposed of by pouring it down the sink drain.

9. When the reaction in the test tube is complete, pour the solution through an ordinary filter without suction into a beaker. Cool the beaker in an ice bath.While the beaker is in the ice bath, add dropwise to the cold filtered solution (Use a buret or graduated cylinder) 25 mL ethyl alcohol, C_2H_5OH, while stirring continuously. A crystalline precipitate of sodium hexanitrocobaltate(III), $Na_3[Co(NO_2)_6]$, should form.

10. Filter out the crystals with suction. Wash the crystals with 3 small portions of ethanol. Continue to draw air through the filter until the ethanol has evaporated. Then transfer the crystals to an evaporating dish or watch glass and dry in an oven at about 115 °C for 15 min.

11. Weigh the crystals and record their mass in your notebook. Calculate and record the percent yield.

12. Dissolve about 1 g of your crystal product in 100 mL of distilled water. Fill a clean spectrometer cell with this solution and measure its absorbance spectrum as in steps 5-6 of Part A. It is not necessary to run another water blank.

Part C

Models of the following complexes are to be constructed by you from atom models in which the sphere representing the central metal cation has holes arranged in an octahedral configuration. Make all sketches in "Part C: Isomers Sheet" on page 161.

Data Treatment

Part A

1. Plot the absorbance for each of the complexes (aqua and ammine).
2. Determine the wavelength of maximum absorbance for each complex and calculate ΔE.
3. Discuss the differences in the colors, wavelength, ΔE and how this relates to the electron configuration in each complex and to whether NH_3 or H_2O is the ligand.
4. Calculate the theoretical yield of the NH_3 complex.
5. Calculate the percent yield of the NH_3 complex.

Part B

1. Plot the absorbance for each of the complexes (aqua and nitro).
2. Determine the wavelength of maximum absorbance for each complex and calculate ΔE.
3. Discuss the differences in the colors, wavelength, ΔE and how this relates to the electron configuration in each complex and to whether NO_2^- or H_2O is the ligand.
4. Calculate the theoretical yield of the NO_2^- complex.
5. Calculate the percent yield of the NO_2^- complex.

Part C

1. Discuss, briefly, the geometry of each complex for which you built a model.

Part C: Isomers Sheet

1. How many isomers are possible for $[Co(NH_3)_4C1_2]^+$? Use a single sphere to represent NH_3. Make a sketch of each isomer and name each isomer. Be sure to identify the type of isomer.

2. $Pt(NH_3)_2C1_2$: this is a square planar complex. Show that two isomers are possible, sketch their structures, and name each isomer. Be sure to identify the type of isomer.

3. Draw the structures and name each isomer of $[Co(NCS)(NH_3)_5]^{2+}$ and $[Co(SCN)(NH_3)_5]^{2+}$. Be sure to identify the type of isomer.

4. Draw the structures and name each isomer of $[Fe(CO)_3Cl_3]$. Be sure to identify the type of isomer.

5. Sketch all the possible isomers (geometric and optical) of diamminediaquadibromochromium(III), $[Cr(NH_3)_2(H_2O)_2Br_2]^+$. Label them as enantiomers (stereoisomers) and/or diastereoisomers.

6. $Pt(NH_3)ClBrI$: this is a hypothetical square planar complex. Show that three isomers are possible and sketch their structures.

Post Lab Questions

1. Balance the half reaction for the oxidation of hexaaquacobalt(II), $[Co(H_2O)_6]^{2+}$, to hexanitrocobaltate(III), $[Co(NO_2)_6]^{3-}$ and insert the correct number of electrons on the proper side:

$$[Co(H_2O)_6]^{2+}{}_{(aq)} + \quad NO_2^-{}_{(aq)} \rightarrow \quad [Co(NO_2)_6]^{3-}{}_{(aq)} + \quad H_2O_{(l)} \qquad \textbf{(EQ 19.6)}$$

2. Balance the half reaction for the reduction of nitrite, NO_2^-, to nitrogen monoxide, NO:

$$NO_2^-{}_{(aq)} + \quad H_3O^+{}_{(aq)} \rightarrow \quad NO_{(g)} + \quad H_2O_{(l)} \qquad \textbf{(EQ 19.7)}$$

3. Write the balanced equation for the overall redox reaction
   - **a.** in ionic form.
   - **b.** in molecular form. Hint: Use hexaaquacobalt(II) nitrate, $[Co(H_2O)_6](NO_3)_2$, $NaNO_2$, $HC_2H_3O_2$ on the reactants side when balancing the molecular equation.

4. Use the molecular equation from 3 above to calculate the mass of $NaNO_2$ needed to react with 5 g of hexaaquacobalt(II) nitrate, $[Co(H_2O)_6](NO_3)_2$.

5. Calculate the mass of sodium hexanitrocobaltate(III), $Na_3Co(NO_2)_6$ that can be produced from 5 g of hexaaquacobalt(II) nitrate, $[Co(H_2O)_6](NO_3)_2$.

EXPERIMENT 20

First-Order Radioactive Decay

Background

Unstable atomic isotopes undergo first-order decay from parent to **daughter isotopes**. The equation for first order decay is given by:

$$\frac{[\Delta \mathrm{A}]}{\Delta t} = -k[\mathrm{A}] \qquad \textbf{(EQ 20.1)}$$

Solving this differential equation yields the integrated rate law:

$$[\mathrm{A}] = [\mathrm{A}]_0 e^{-kt} \qquad \textbf{(EQ 20.2)}$$

A graph of [A] versus time should exponentially decay to zero. A statistical fit of the curve to an exponential function will allow one to determine the rate constant, k.

Alternately, one can produce a straight line plot by taking the natural log of the equation above, producing a new equation:

$$\ln[\mathrm{A}] = \ln[\mathrm{A}]_0 - kt \qquad \textbf{(EQ 20.3)}$$

In this case, one can see that a plot of the natural log of concentration versus time will produce a straight line, with slope $-k$ and y-intercept $[\mathrm{A}]_0$.

In general, when unstable isotopes decay radioactively, they will give off one of a number of common particles such as an alpha particle, a beta particle, a positron or a neutron. These particles carry off the excess nuclear binding energy produced when a less stable isotope produces a more stable isotope. Occasionally, some of the excess energy is carried off in the form of a high energy photon, called a gamma ray.

There are a number of devices used to measure the rate of radioisotope decay such as a scintillation counter or a Geiger counter. In this case, the kinetics of radioactive decay can be followed by plotting the number of decay events versus time. For obvious reasons, there are significant safety concerns for such experiments, especially in the undergraduate labs. These experiments require a significant amount of radiative shielding using such heavy metals as lead. For this reason, you will be modeling first order nuclear decay using a very simple physical model.

The Experiment

You will be given a container of approximately 100 of some sort of simple object such as paper clips or pins. Your job is to choose a reasonable value of k from Equation 20.2 above which will allow you to place your objects on a balance at a rate which will mimic first order decay. One possible approach would be to choose what you feel is an appropriate half-life and proceed from there. The data you collect will be mass readings on a balance versus time. You will need to choose a value for k which is sufficiently small so that you can keep up with adding the objects to the balance, but one which is not so small that it takes you hours to collect a single data run. Your job then, should you decide to accept it, is to create your own data table which will allow you to decide at what rate to put the items on a balance so as to produce as close to perfect first-order decay as possible.

After creating a table or whatever means you choose to tell you the timing for adding the objects to the balance, you can begin your experiment. At least one of your group should be assigned to simply record mass versus time at regular intervals. This person or persons needs to ignore whatever the others are doing to add the objects to the balance. You are required to take at least ten data points for a successful run. More than ten data points may be helpful. You may take mass readings every five seconds, every five minutes or anything in between. It is your choice.

After collecting mass versus time data in your lab book, make a graph of your data using the Vernier graphing software. You should enter your data into the program. After making a graph of your data, you will find the best exponential fit to the data. The group which produces the graph with the smallest “Mean Square Error” will get bonus credit for the lab. Feel free to repeat the experiment as many times as you like, perfecting your technique to see if you can beat the other teams.

May the best IMF special force group win!

Results

You will be submitting a group write-up. The group should submit just one copy of data from your lab note books. Please submit all data collected, including runs you did not choose as your best value. Also, I need to see the tables you used to help you choose when to add the objects to the balance. In addition, you must submit both a plot of your data alone and a plot of your data which has been fit to an exponential decay. The Vernier program should automatically calculate and display the “Mean Square Error.” Lastly, answer the questions. Be sure the names of everyone in your group is included on the write-up.

Post Lab Questions

1. According to your graph, at what time would you have had 0.010 staples (or whatever object you used) left to put on the balance?

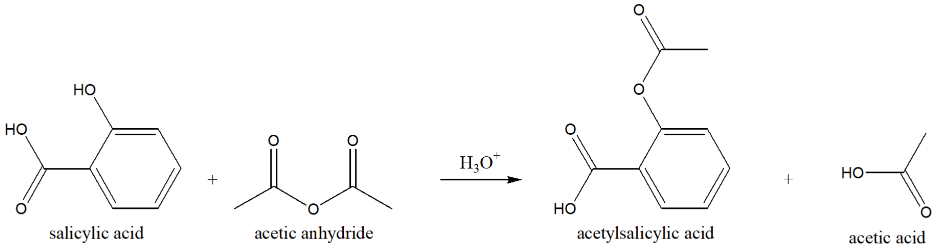
2. According to your graph and the equation produced, how many staples (or other object) were in your sample one hour before you actually started putting them on the balance?

EXPERIMENT 21 *Synthesis of Aspirin*

Background

Aspirin will be synthesized from salicylic acid, the product will be purified by recrystallization, and the percent yield determined. If your instructor directs, you will compare the melting points of the products from the first and second crystallizations with the handbook value to estimate purity.

Without question, aspirin is one of the most generally useful medicinal agents ever discovered. Annual consumption in the United States alone is several million kilograms. Since 1899, when the German scientist Dreser introduced it as a mild analgesic and antipyretic, aspirin has become the layman's first line of defense against minor discomforts such as colds and headaches. It also is used extensively in the treatment of arthritis and rheumatism and for reducing fever accompanying infections. Regular aspirin treatments may reduce the chances for heart attack.We will use the reaction of salicylic acid with acetic anhydride to make aspirin (Equation 21.1).



(EQ 21.1)

To improve the purity of your sample you will recrystallize it and assess the purity of your product by measuring its melting point and comparing it to the accepted value in the *CRC*. The percent yield can be calculated according to the example below:

EXAMPLE 21.1

Aspirin was prepared using 3.02 g of salicylic acid and an excess of acetic anhydride, according to Equation 21.1. After the second recrystallization, the dry product was found to weigh 2.72 g. What is the mass percent yield of aspirin?

First we need to calculate the theoretical yield of aspirin.

$$3.02\text{ g sal. acid} \times \frac{1\text{ mol sal. acid}}{138\text{ g acid}} \times \frac{1\text{ mol aspirin}}{1\text{ mol sal. acid}} \times \frac{180\text{ g aspirin}}{1\text{ mol aspirin}} = 3.94\text{ g aspirirn} \quad \textbf{(EQ 21.2)}$$

Now we can calculate the % yield:

$$\%\text{ yield} = \frac{2.72\text{ g}}{3.94\text{g}} \times 100\% = 69.0\% \quad \textbf{(EQ 21.3)}$$

Procedure

Preparation of Aspirin

1. Weigh accurately about 2.1 g of salicylic acid and record the mass.Transfer the sample to a large dry test tube.
2. In the hood, carefully add 5 mL, each of acetic anhydride and glacial acetic acid to the tube. Stir the mixture with a glass rod until nearly all the solid dissolves. Then add 3–4 drops of 6 *M* sulfuric acid (to catalyze the reaction). Add the reactants very slowly and carefully to avoid a rapid reaction that might cause spattering. The first few drops of acid can cause a sudden eruption from the test tube. Gently swirl the flask.
3. Heat in a 45–50 ºC water bath, with continuous stirring, until the salicylic acid dissolves. Then continue to heat for another 5 minutes. It is important that all the solid dissolves if you are to get a good yield of aspirin. Additional stirring near the end of the heating period may be necessary.
4. While the reactants are heating, set up a Büchner funnel suction filtering apparatus, with an aspirator trap between the filter and the sink aspirator. Be sure to clamp the filter flask for support.
5. After heating is complete and all the solid has dissolved, the solution must be cooled to crystallize the aspirin before filtering. Let the flask stand to cool to room temperature.
6. When the precipitate has formed, stir in 30.0 mL of cold DI water and break up the lumps of solid.
7. Cool in ice until the crystallization is complete.
8. Filter the product through the Büchner funnel. Wash twice to remove unwanted impurities from the crystals. Use two 10 mL portions of ice-cold distilled water as follows:
    a. Open the pinch clamp to turn off the suction.
    b. Add 10 mL of distilled ice water to the funnel, covering the filtrate.
    c. Stir the solid gently with a glass rod wash the solid thoroughly but not dislodge or tear the filter paper.
    d. Reconnect the pinch clamp to turn on the suction and suck to dryness.
    e. Repeat for a second washing.

9. After the second washing, when the filtrate has been sucked as dry as possible, place the damp filter paper containing the filtrate on top of a dry piece of filter paper for support and to aid further drying. Place the double layer of filter papers with precipitate on a watch glass to air dry.

Recrystallization

1. Prepare a water bath, using a 600 mL beaker about 1/3 full of water on a hotplate. Be certain there are no open flames in the laboratory.
2. Set aside about 1-2 mg of your first product. You will not recrystallize this portion but will compare its color and crystal forms with your recrystallized product. If your instructor directs, you also will compare its melting point with that of your recrystallized product.
3. Dissolve the remaining aspirin crystals in 95% *boiling* ethanol using a **minimum amount of solvent to dissolve** in a 100 mL beaker
4. Add twice this amount of warm (60 ºC) DI water while the ethanol is still boiling.
5. Let cool, then place the beaker in ice.
6. Collect the crystals by suction filtration, washing them twice with 10 mL, portions of ice-cold distilled water as in Steps 7-8 in “Preparation of Aspirin” on page 170.
7. Continue to draw air through the sample to remove excess water and speed drying. Speed up the drying process by breaking up the caked filtrate and spreading it out on the paper.
8. After the second washing, when the filtrate has been sucked as dry as possible, place the damp filter paper containing the filtrate on top of a dry piece of filter paper for support and to aid further drying. Place the double layer of filter papers with precipitate on a watch glass to air dry for about 5 minutes.
9. Dry your product in an electric oven at 75 °C for about 30 minutes. Then transfer the dry sample to a tared weighing bottle. If preferred, the product may be air dried on the filter assembly by suction in about 20 minutes. Also dry and weigh the small portion of our first crude product that you set aside earlier. Record the masses.
10. In your notebook, compare the colors and crystal forms of the products obtained in “Preparation of Aspirin” on page 170 and “Recrystallization” on page 171.
11. Calculate the theoretical and percent yields of aspirin, knowing that salicylic acid was the limiting reactant.

The Melting Point

The melting point of a pure crystalline substance is a characteristic property of the substance and usually is quite sharp, meaning that it becomes completely liquid over a narrow temperature range. Impurities cause defects in the crystal lattice and usually lowering the melting point by some amount that depends on the quantity and nature of the impurities. Impurities also broaden the temperature range over which melting occurs. A measured melting point that occurs over a narrow temperature range and agrees closely with the handbook value is a good indicator of a pure product.

Your instructor will demonstrate the use of the melting point apparatus. Because the melting point of aspirin is higher than the boiling point of water, you must use a liquid such as mineral oil in the heating bath.

1. Measure the melting points of your first crude product and your recrystallized product. Record the temperature where melting is complete and the temperature range over which melting occurs.

Purity

If you have enough time you may want to test the purity of your sample. To test the purity of your sample is to use iron(III) chloride to detect the presence of unreacted salicylic acid. If your sample contains salicylic acid it will turn a blue-purple color, otherwise there will be no change.

1. Use a pea sized amount of your crystallized and recrystallized product and test the purity. It may also be a good idea to test pure salicylic acid so that you may observe a positive result.

EXPERIMENT 22

Chemical Equilibrium using Vernier

Background

The purpose of this lab is to experimentally determine the equilibrium constant, K_c, for the formation of the ion $FeSCN^{2+}$, according to the equation:

$$\underset{\text{iron(III) ion}}{Fe^{3+}_{(aq)}} + \underset{\text{thiocyanate ion}}{SCN^{-}_{(aq)}} \rightleftharpoons \underset{\text{thiocyanatoiron(III) ion}}{[FeSCN]^{2+}_{(aq)}} \qquad K_c = \frac{[FeSCN^{2+}]_{eq}}{[Fe^{3+}]_{eq}[SCN^{-}]_{eq}} \tag{EQ 22.1}$$

when Fe^{3+} and SCN^{-} are combined, equilibrium is established between these two ions and the complex ion, $FeSCN^{2+}$.

In order to calculate the equilibrium constant K_c, you must know the concentrations of all ions at equilibrium: $[Fe^{3+}]_{eq}$, $[SCN^{-}]_{eq}$, and $[FeSCN^{2+}]_{eq}$. You will prepare four equilibrium systems containing different concentrations of these ions. The equilibrium concentrations of these ions will be experimentally determined. These values will be substituted into the equilibrium expression for this reaction to see if the determined K_c is indeed constant.

The Vernier Spectrophotometer, *SpectroVis*, and the LabQuest data acquisition system will be used to determine the $[FeSCN^{2+}]_{eq}$. The $FeSCN^{2+}$ ion produces a reddish colored solution. Because the red solution absorbs blue light well, the *SpectroVis* will determine the appropriate wavelength based on the absorption spectrum of the solution. The light that strikes the detector when the absorbing speices is present is copmared with the light that strikes the detector when it is absent. The ratio is converted inot a valued called, absorbance. By comparing the absorbance of each equilibrium system, A_{eq}, to absorbance of a *standard* solution, A_{std}, you can determine $[FeSCN^{2+}]_{eq.}$ The standard solution has a known $[FeSCN^{2+}]$.

To prepare the standard solution, a very large concentration of Fe^{3+} ion will be added to a small concentration of SCN^{-} ion, $[SCN^{-}]_i$. The $[Fe^{3+}]$ in the standard solution is 100 times larger than the $[Fe^{3+}]$ in the equilibrium mixtures. Recall Le Chatelier's principle tells us this high concentration of Fe^{3+} forces the reaction far to the right, thus using nearly 100% of the SCN^{-} ions. According to the balanced equation above, for every one mole of SCN^{-} reacted, one mole of $FeSCN^{2+}$ is produced. Hence, $[FeSCN^{2+}]_{std}$ is assumed to be equal to $[SCN^{-}]_i$.

Spectrophotometry

An instrument that measures the relative intensity that is associated with the wavelength of radiation from a sample is called a spectrophotometer. Spectroscopic measurements generally use a light source, dispersive device (like a mirror, prism, or diffraction grating), and a detector to analyze the absorption or emission spectrum of a sample. Absorption spectra are often defined by their percent transmittance, %T:

$$\%T = 100\left(\frac{I}{I_0}\right) \tag{EQ 22.2}$$

where I = light transmitted by the solution, and I_o = light incident upon the solution. Rearranging Equation 22.2 and taking the log of both sides yields Equation 22.3:

$$\log\left(\frac{100}{\%T}\right) = -\log\left(\frac{I}{I_0}\right) \tag{EQ 22.3}$$

Spectrophotometers can measure absorbance over a range of wavelengths. A plot of absorbance vs. wavelength is know as an absorbance spectrum. Absorbance, A, is another way to describe spectra. So, absorbance can be defined as:

$$A = \log\left(\frac{100}{\%T}\right) \tag{EQ 22.4}$$

The amount of visible light a sample absorbs in aqueous solution is in direct proportion to the concentration of the solute according to **Beer's Law** Equation 22.4:

$$A = -\log\left(\frac{I}{I_0}\right) = \varepsilon bc \tag{EQ 22.5}$$

where A = absorbance, ε = the extinction coefficient (or molar absorptivity), b = the length of the light path, usually one centimeter, and c = the molar concentration of solute. The extinction coefficient is a constant for a particular substance at a particular wavelength.

Beer's Law tells us absorbance is directly related to concentration. We can use Beer's law to calculate the extinction coefficient of a solution at a specific wavelength.

EXAMPLE 22.1 Calculate the extinction coefficient given the following data that was collected at a wavelength of 456.1 nm and a temperature of 25.7 °C:

TABLE 22.2

Solution	0.100 M $Fe(NO_3)_3$ (mL)	0.00150 M KSCN (mL)	H_2O (mL)	Abs
Standard solution	9.00	1.00	0.00	0.777

To determine the extinction coefficient, first calculate the dilution concentrations:

$$\frac{9.00\text{ mL }Fe(NO_3)_3}{10.00\text{ mL soln}} \times \frac{0.100\text{ mmol }Fe(NO_3)_3}{1\text{ mL }Fe(NO_3)_3} \times \frac{1\text{ mmol }Fe^{3+}}{1\text{ mmol }Fe(NO_3)_3} = 0.0900\text{ M }Fe^{3+} \tag{EQ 22.6}$$

$$\frac{1.00\text{ mL KSCN}}{10.00\text{ mL soln}} \times \frac{0.00150\text{ mmol KSCN}}{1\text{ mL KSCN}} \times \frac{1\text{ mmol }SCN^-}{1\text{ mmol KSCN}} = 1.50 \times 10^{-4}\text{ M }SCN^- \tag{EQ 22.7}$$

Next, complete an ICE table. Looking at the initial concentrations of iron(III) and thiocyanate ions below, we can see that the concentration of Fe^{3+} of 0.0900 M is much larger than the concentration of SCN^- of 1.50×10^{-4}. We assume that the equilibrium is shifted completely to the right, so the maximum about of reactant gets used up. From the balanced chemical equation, Equation 22.1, we can see that thiocyanate is the limiting reagent.

	$Fe^{3+}_{(aq)}$	+	$SCN^{-}_{(aq)}$	$\rightarrow$	$[FeSCN]^{2+}_{(aq)}$
I	$0.0900\ M$		$1.50 \times 10^{-4}\ M$		0 M
Δ	$-x$		$-x$		$+x$
	$0.0900\ \text{M} - x \approx$		$1.50 \times 10^{-4}\ \text{M} - \text{x} \approx$		$x = 1.50 \times 10^{-4}\ \text{M}$
	$0.0900\ \text{M} - 1.50 \times 10^{-4}\ \text{M} \approx$		$1.50 \times 10^{-4}\ \text{M} - 1.50 \times 10^{-4}\ \text{M} =$		
E	0.0900 M		0 M		

Finally, calculate the extinction coefficient by rearranging Equation 22.4 and plugging in data:

$$\varepsilon = \frac{A}{bc} = \frac{0.777}{(1\ \text{cm})(1.50 \times 10^{-4}\ \text{M [FeSCN]}^{2+})} = 5180\frac{1}{M\ cm} \qquad \textbf{(EQ 22.8)}$$

EXAMPLE 22.3 The following data was collected under the same conditions as the standard solution. Calculate the equilibrium constant, $K_{c.}$

TABLE 22.4

Test Tube Number	0.00150 M $Fe(NO_3)_3$ (mL)	0.00150 M KSCN (mL)	H_2O (mL)	Abs
1	2.50	1.00	1.50	0.136
2	2.50	1.50	1.00	0.204
3	2.50	2.00	0.50	0.253
4	2.50	2.50	0.00	0.333

To calculate the equilibrium constant, K_c, for test tube number 1 first calculate the initial diluted concentrations of the reactants, as shown above, and start an equilibrium ICE table:

	$Fe^{3+}_{(aq)}$	+	$SCN^{-}_{(aq)}$	$\rightleftharpoons$	$[FeSCN]^{2+}_{(aq)}$
I	$7.50 \times 10^{-4}\ M$		$3.00 \times 10^{-4}\ M$		0 M
Δ	$-x$		$-x$		$+x$
E	$7.50 \times 10^{-4}\ \text{M} - x \approx$		$3.00 \times 10^{-4}\ \text{M} - \text{x} \approx$		x

To find the value of x, use Beer's law, the extinction coefficient you determined from the standard solution, and the measured absorbance value:

$$c = \frac{A}{b\varepsilon} = \frac{0.136}{(1\ \text{cm})\left(5180\frac{1}{M\ cm}\right)} = 2.63 \times 10^{-5}\ \text{M [FeSCN]}^{2+}_{eq} \qquad \textbf{(EQ 22.9)}$$

Now complete the ICE table:

	$Fe^{3+}_{(aq)}$	+	$SCN^{-}_{(aq)}$	$\rightleftharpoons$	$[FeSCN]^{2+}_{(aq)}$
I	$7.50 \times 10^{-4}\ M$		$3.00 \times 10^{-4}\ M$		0 M
Δ	$-x$		$-x$		$+x$
	$7.50 \times 10^{-4}\ \mathrm{M} - x =$		$3.00 \times 10^{-4}\ \mathrm{M} - \mathrm{x} =$		
	$7.50 \times 10^{-4}\ \mathrm{M} - 2.63\times 10^{-5}\ \mathrm{M} =$		$3.00 \times 10^{-4}\ \mathrm{M} - 2.63\times 10^{-5}\ \mathrm{M} =$		
E	$7.24 \times 10^{-4}\ \mathrm{M}$		$2.74 \times 10^{-4}\ \mathrm{M}$		$x = 2.63\times 10^{-5}\ \mathrm{M}$

Notice that using a lower concentration of reactants allows an equilibrium to be established where the reactant is not completely used up. There is a significant amount of reactant that remains when the reaction has concluded. Therefore, the equilibrium constant, K_c, can be calculated:

$$K_c = \frac{[\mathrm{FeSCN}^{2+}]_{eq}}{[\mathrm{Fe}^{3+}]_{eq}[\mathrm{SCN}^{-}]_{eq}} = \frac{(2.63 \times 10^{-5})}{(7.24 \times 10^{-4})(2.74 \times 10^{-4})} = 133 \qquad \textbf{(EQ 22.10)}$$

The same calculation should be completed for each trial then an average and standard deviation can be determined. The average equilibrium constant is found to be 133 with a standard deviation of 4.5. All four trials fall within one standard deviation. So, the data is precise. To determine if our data is accurate the actual equilibrium constant needs to be found (by you).

Procedure

TABLE 22.5 **Materials**

Equipment		Reagents
Vernier LabQuest	5 test tubes (1 large)	0.0020 M KSCN
SpectroVis	5 stoppers	0.200 M $Fe(NO_3)_3$ (in 1 M HNO_3)
Thermometer or probe	5 plastic cuvettes	0.0020 M $Fe(NO_3)_3$ (in 1 M HNO_3)
	Chem-wipes	DI H_2O

Caution: *$Fe(NO_3)_3$ solutions in this experiment are prepared in 1.0 M HNO_3 and should be handled with care.*

Label four small test tubes 1-4. Dispense each reagent from the appropriate buret into corresponding test tube. Stopper the test tubes and mix each solution thoroughly. Measure and record the temperature of one solution to use as the temperature for the equilibrium constant, K_c. Volumes of reagent added to each test tube are summarized below:

TABLE 22.6

Test Tube Number	0.0020 M $Fe(NO_3)_3$ (mL)	0.0020 M KSCN (mL)	H_2O (mL)
1	5.00	2.00	3.00
2	5.00	3.00	2.00
3	5.00	4.00	1.00
4	5.00	5.00	0.00

Prepare a standard solution of $FeSCN^{2+}$ by dispensing 18.00 mL of 0.200 M $Fe(NO_3)_3$ into a large test tube (test tube 5). Add 2.00 mL of 0.0020 M KSCN into the same test tube, stopper and mix thoroughly.

Prepare a *blank* by filling a cuvette ¾ full with DI water. To correctly use cuvettes, remember to wipe the outside of the cuvette with a chem-wipe. Handle cuvettes only by the top edge of the ribbed sides. Dislodge any bubbles by gently tapping the cuvette on a hard surface. Always position the cuvette so the light passes through the clear sides.

Using the *SpectroVis*

Choose Calibrate. After the spectrophotometer has warmed up, place the blank cuvette into the cuvette slot. Follow the instructions in the dialogue box to complete the calibration, and then click OK.

Collecting Data with LabQuest

Measurement vs. Wavelength (Generate a Spectrum)

1. Rinse a cuvette twice with approximately 1 mL amounts of solution from test tube 1. Fill a cuvette about ¾ full with the solution from test tube 1, wipe the sides with a chem-wipe, and place it in the spectrophotometer.

2. Start the data collection by tapping the green Start button in the lower left corner of the screen. Tap the red Stop button to end the data collection. Record the wavelength of max absorbance and the corresponding absorbance or test tube 1 on Run 1.
3. Select wavelength. **Note:** The wavelength of maximum absorbance (λ_{max}) is should be automatically selected, however sometimes you need to set it manually. This λ_{max} will be used for subsequent data collection.
4. Tap on the file cabinet icon in the upper right portion of the screen to advance to the next Run.
5. You are now ready to collect absorbance data for the four equilibrium systems and the standard solution.
6. Save your file using the extension “qmbl”. Name the file something you will remember.

Data Interpretation

1. Calculate the initial concentration of Fe^{3+}. This will be initial concentration of Fe^{3+}, $[Fe^{3+}]_i$, for all four equilibrium systems.
2. Calculate the initial concentration of SCN^- for each equilibrium system. This will be $[SCN^-]_i$ for each trial.
3. Calculate the concentration of $[FeSCN^{2+}]_{std}$.
4. Calculate the extinction coefficient.
5. Calculate $[FeSCN^{2+}]_{eq}$ using the extinction coefficient and absorbance.
6. Calculate the concentrations of $[Fe^{3+}]_{eq}$ and $[SCN^-]_{eq}$ for trials 1-4 and use the law of mass action to determine K_c of each trial.
7. Determine an average K_c, standard deviation, and percent error.

TABLE 22.7

	Trial 1	Trial 2	Trial 3	Trial 4
Wavelength (nm)				
Absorbance				
Absorbance of standard				
Extinction Coefficient				
$[Fe^{3+}]_i$				
$[SCN^-]_i$				
$[FeSCN^{2+}]_{eq}$				
$[Fe^{3+}]_{eq}$				
$[SCN^-]_{eq}$				
Temperature				
K_c				
Average of K_c values		±	at	°C
Actual K_c value				
Percent error K_c				

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