CHEM 232 ANALYTICAL CHEMISTRY LAB II

Laboratory Manual

Department of Chemistry
İZMİR INSTITUTE OF TECHNOLOGY
Urla / İZMİR

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CHEM 232 ANALYTICAL CHEMISTRY LABORATORY II

This manual has been prepared for the CHEM 232 Analytical Chemistry Laboratory and includes the experiments, which are related to the topics covered in the CHEM 202 Analytical Chemistry II course. The main purpose of this laboratory is to provide the students an appreciation for the potential applications and limitations of analytical methods of analysis. It is also aimed to provide the students an opportunity to develop their abilities in the laboratory skills required for accurate and precise chemical analyses. Therefore, it is expected that with an acceptable degree of proficiency the students will grasp and apply the principles of analytical chemistry to obtain reliable results in the laboratory experiments.

COURSE POLICIES AND INFORMATION

In this laboratory, you will be working as a team with three or four persons in each group. Each project will take two or three weeks depending on the project given to you. During the first lab period your instructor will assign you to a group. Each student in the group must have a Laboratory Notebook and bring it to the laboratory every week. You should keep a good notebook with all the calculations and results, because your instructors will grade your Lab Notebooks at the end of each experiment. You are also expected to write a purpose and procedure for each experiment prior to coming to the laboratory. At the end of each lab period you will have two days to complete your notebook. **THE NOTEBOOK MUST BE COMPLETED AND TURNED INTO THE TEACHING ASSISTANT WITHIN TWO DAYS AFTER COMPLETION OF THE LAB PERIOD.** Also there will be a pre-lab quiz given at the beginning of each lab period. Therefore, you must be prepared for the lab experiment before it begins.

Your overall lab grade will be calculated by taking the sum of all your individual project grades and dividing it by the total number of lab experiments. There will also be a final exam at the end of the semester.

Attendance is required and you are expected to attend all scheduled laboratory sessions. **If you miss more than two-lab sessions without a valid reason you will be automatically dropped from lab**. Should you be sick and can not come to lab, you need to bring a doctor's excuse from **the UNIVERSITY HEALTH CENTER or an official**

report from a government hospital. Also, if you cannot be available for an official reason and you know this ahead of time, you should notify the teaching assistants in advance of the lab period and make sure you obtain the required documentation. Remember that this is group work and if you cannot be there, you must inform the other members of your group. Be on time since your group members will depend on you to start the experiments. Tardiness will be noted by the teaching assistant and can affect your grade.

FORMAT OF THE LABORATORY NOTEBOOK

EACH STUDENT WILL KEEP AND PROPERLY MAINTAIN A SEPARATE LAB NOTEBOOK.

Every page of the lab notebook must be numbered, including the Table of Contents.

All entries must be made with ink. Pencils cannot be used.

Two or three pages at the beginning of the notebook should be labeled as the Table of Contents.

This is the only time you will ever leave pages blank.

(25 points)

1. Before the lab experiment the following must have been written in your lab notebook

BEFORE THE LAB EXPERIMENT (8 points)

A. Title of the experiment and purpose of the experiment (2-3 sentences)

B. Introduction (Background information about the experiment. Do not forget to write the references used.)

C. Any information related to safety, dangerous chemicals, etc. (You learn this from the procedure, from MSDS sheets, and from the internet.) (approximately half a page).

D. Write a summary of the lab procedure as you understand it and do not copy from the lab manuals (maximum 0.5 to 1 page).

2. During the lab experiment, write the following in your lab notebook (5 points):

E. Information given to you by the TAs at the beginning of the lab

F. Step by step, write everything EXACTLY while you are actually doing the experiment. Make note of all observations. Someone should understand after 100 years EXACTLY what you did and he or she must be able to repeat the experiment exactly as YOU did it so that they can see why the experiment worked or did not work. Proper use during lab time.

Example: ("I weighed 0.5432 g NaCl and added this to 100 mL of the test solution in a 400-mL volume beaker. This solution was heated until boiling. I noticed that some of the boiling solution evaporated and some spilled from the beaker. For a brief moment the solutions turned green and then clear again. The entire experiment took 1 hour.")

Record all raw data and results IN YOUR NOTEBOOK at the same time as you take the data.

THIS DATA AND INFORMATION CANNOT BE WRITTEN LATER.

G. All problems and mistakes should be properly noted, marked properly and signed. ALL BLANK SPACES MUST BE MARKED AND SIGNED PROPERLY. All pages must be signed and witnessed only at the end of the lab period.

3. **Towards the end of the lab experiment, the following must be in your lab notebook (4 points):**

   H. Problems encountered, proposed solutions for problems.

   I. Sources of error, estimates or precision.

   J. Another student in your group or your TA must look briefly at your notes while you explain what you did, he or she must print their name, sign their name and also write the date at the bottom of each page used that day.

4. **After the experiment is finished, include the following (6 points):**

   K. An analysis of the results (calculations),

   L. A brief interpretation of the results,

   M. Ideas for future experimentation to complement this experiment, references.

5. **Also the lab notebook will be graded for legibility (2 pts).**

The names of all students who also directly helped must be included in the lab notebook. Only write the names of those persons from whom you received help.

Sometimes data comes from instrumentation in the form of printouts or electronic copies. These must be handled correctly with the notebook. Original raw results such as spectra, etc. must be stapled in the appropriate location in the notebook. For those experiments where only one copy of results is available, each student must obtain a photocopy of this raw result and staple it in the appropriate location in his or her own notebook. **These spectra must be signed, witnessed, and dated also.**

Finally, at the discretion of the TA or the teacher, notebooks may be graded according to additional criteria specific to each experiment.

Note the following format for citing the lab manual or handout [5], an internet reference [1] a book without an editor [2], a book with an editor [3], and a journal article [4] at the end of your reports.

1. Smith College Lab Report http://www.science.smith.edu/departments/Chem/Courses/labreports.htm **(accessed August 21, 2001).**
2. Skoog, D.A.; West, D.M.; Holler, F.J.; Crouch, S.R. Fundamentals of Analytical Chemistry 8th ed.; Thomson Brooks/Cole: Belmont, CA, **2004**; pp 314-336.
3. Almlof, J.; Gropen, O. Relativistic "Effects in Chemistry." In Reviews in Computational Chemistry; Lipkowitz, K.B.; Boyd, D.B., Eds. VCH: New York, **1996**; Vol. 8 pp. 206-210.
4. Klinger, J. "Influence of Pretreatment on Sodium Powder." Chem Mater. **2005**, 17, 2755-2768.
5. Chemistry 215 Analytical Chemistry Laboratory Manual. **2009**. "Gravimetric Determination of Chloride and Sulfate in Some Inorganic Salts," pp 11-16. Izmir Institute of Technology, Turkey.

FORMAT FOR ORAL PRESENTATIONS

You will be required to give one oral presentation during this semester. In addition to any guidelines given by the teaching assistants you must be aware of the following:

1. Any presentation that is suspected of having been copied from another source (another student, the internet, etc.) will be investigated and graded accordingly. No copying is allowed. A copied presentation will receive a grade of zero points.
2. For EACH slide, any information that is not general information must be properly referenced AT THE BOTTOM OF THAT SLIDE. The referenced source must be written in the proper format and consistent throughout the presentation.
3. The presentation must represent your own attempt to summarize the work of others and you must place references properly for each slide.
4. After presenting the information, you are encouraged to include any ideas of your own. Creativity and originality are encouraged.
5. Slides must be prepared using PowerPoint and your rough draft must be checked prior to presentation by your teaching assistance.
6. At least the following slides must be included:
    a. Title (with your name, address (IYTE Chemistry Depart.), and date)
    b. Background and Importance of the topic
    c. Previous research and findings on/about the topic
    d. Current research and findings on/about the topic
    e. Future goals of research related to the topic
    f. Personal ideas or directions you may have for the research
    g. Conclusions or Summary
    h. Acknowledgements

The presentation should not be over 10 minutes. Two minutes will be allowed for questions.

GRADING SCHEME FOR THE COURSE:

Oral presentation	**10% (individual grade)**
Lab Quizzes	**25 % (individual grade)**
Lab. Notebook	**25 % (individual grade)**
Lab. Final Exam	**30 % (individual grade)**
Participation	**10% (individual grade)**

SAFETY RULES

The chemistry laboratory is not a dangerous place to work as long as all necessary precautions are taken seriously. In the following paragraphs, those important precautions are described. Everyone who works and performs experiments in a laboratory must follow these safety rules at all times. Students who do not obey the safety rules will not be allowed to enter and do any type of work in the laboratory and they will be counted as absent. It is the student's responsibility to read carefully all the safety rules before the first meeting of the lab.

Eye Protection: Because the eyes are particularly susceptible to permanent damage by corrosive chemicals as well as flying objects, safety goggles must be worn at all times in the laboratory. Prescription glasses are not recommended since they do not provide a proper side protection. No sunglasses are allowed in the laboratory. Contact lenses have potential hazard because the chemical vapors dissolve in the liquids covering the eye and concentrate behind the lenses. If you have to wear contact lenses consult with your instructor. If possible try to wear a prescription glasses under your safety goggles. In case of any accident that a chemical splashes near your eyes, immediately wash your eyes with lots of water and inform your instructor. Especially, when heating a test tube do not point it towards anyone. Always assume that you are the only safe worker in the lab. Work defensively. Never assume that everyone else as safe as you are. Be alert for other's mistakes.

Cuts and Burns: Remember you will be working in a chemistry laboratory and many of the equipment you will be using are made of glass and it is breakable. When inserting glass tubing or thermometers into stoppers, lubricate both the tubing and the hole in the stopper with water. Handle tubing with a piece of towel and push it with a twisting motion. Be very careful when using mercury thermometer. It can be broken easily and may result in mercury contamination. Mercury vapor is an extremely toxic.

When you heat a piece of glass it gets hot very quickly and unfortunately hot glass look just like a cold one. Handle glass with tongs. Do not use any cracked or broken glass equipment. It may ruin an experiment and worse, it may cause serious injury. Place any broken glass in the proper waste glass container. Do not throw them into the wastepaper container or regular waste container.

Poisonous Chemicals: All of the chemicals have some degree of health hazard. Never taste any chemicals in the laboratory unless specifically directed to do so. Avoid breathing toxic vapors. When working with volatile chemicals and strong acids and bases use ventilating hoods. If you are asked to smell the odors of a substance do so by wafting a

bit of the vapor toward your nose. Do not stick your nose in and inhale vapor directly from the test tube. Always wash your hands before leaving the laboratory.

Eating and drinking any type of food are prohibited in the laboratory at all times. Smoking is not allowed. Anyone who refuses to do so will be forced to leave the laboratory.

Clothing and Footwear: Everyone must wear a lab coat during the lab and no shorts and sandals are allowed. Students who come to lab without proper clotting and shoes will be asked to go back to change his or her clothing. If they do not come on time they will be counted as an absent. Long hair should be securely tied back to avoid the risk of being set on fire. If large amounts of chemicals are spilled on your body, immediately remove the contaminated clothing and use the safety shower if available. Make sure to inform your instructor about the problem. Do not leave your coats and back packs on the benchs because they may be contaminated. No headphones, Walkmans, mp3 players or cell phones are allowed in the lab because they interfere with your ability to hear what is going on in the Lab. Cell phones must be turned off.

Fire: In case of fire or an accident, inform your instructor at once. Note the location of fire extinguishers and, if available, safety showers and safety blankets as soon as you enter the laboratory so that you may use them if needed. Never perform an unauthorized experiment in the laboratory. Never assume that it is not necessary to inform your instructor for small accidents. Notify him/her no matter how slight it is.

Laboratory Care and Waste Disposal

Remember that the equipment you use in this laboratory will also be used by many other students. Please leave the equipment and all workspaces as you wish to find them. After the end of the each lab, clean off your work area. Wash your glassware. When weighing any material on the balances, do not weigh directly onto the balance pan. Weigh your material on a piece of weighing paper. The balances are very sensitive instruments and should be treated with great care.

If you take more reagents than you need, do not put excess back into the bottle. It may be contaminated. Threat it as waste and dispose of it accordingly. It is most likely that, during any experiment you will perform, you will generate some waste chemicals and solutions to dispose of. Never put them down the sink unless specifically told to do so by your instructor. There will be inorganic, organic, and solid waste containers in the lab. Dispose of your waste in the appropriate container.

Analytical Chemistry II - TIME SCHEDULE OF THE EXPERIMENTS - Spring 2018

Teaching Assistants: Emre Yusuf GÖL, Seçil SEVİM ÜNLÜTÜRK, Seray Ece KESKİN, Ahmet AYTEKİN

March 7 Introduction, safety, items required to enter lab, expectations

March 14 Lab 1 : Determination of Ascorbic Acid in Orange Juice

Drawing (raffle) will be held for your general topic for oral presentation (volumetry, gravimetry or potentiometry).

March 21 Lab 2 : Standardization of Permanganate Solution

March 28 Lab 3: Determination of Calcium in Limestone

April 4 Lab 4: Determination of Hardness in Water Samples with EDTA

******Turn in a summary of your proposal for oral presentation.**

April 11 Lab 5: Potentiometric Titration of Phosphoric Acid

April 18 Lab 6: Determination of Equilibrium Constants for Complex Ions of Silver

April 25 Lab 7: Potentiometric Titration of Chloride and Iodide Mixtures

May 2 Lab 8: The Potentiometric Determination of Solute Species in a Carbonate Mixture

May 9 ******* Oral Presentations *******

May 16 ******* Oral Presentations *******

May 23 Makeup (last possible date - to be used at the discretion of the TAs)

Final Lab Exam will be officially announced and given during the exam week.

Experiment 1. Determination of Ascorbic Acid in Orange Juice

PRINCIPLE:

This method determines the vitamin C concentration in a solution by a redox titration using iodine. Vitamin C, more properly called ascorbic acid, is an essential antioxidant needed by the human body (see additional notes). As the iodine is added during the titration, the ascorbic acid is oxidised to dehydroascorbic acid, while the iodine is reduced to iodide ions.

ascorbic acid + $I_2 \rightarrow 2\ I^-$ + dehydroascorbic acid

Due to this reaction, the iodine formed is immediately reduced to iodide as long as there is any ascorbic acid present. Once all the ascorbic acid has been oxidised, the excess iodine is free to react with the starch indicator, forming the blue-black starch-iodine complex. This is the endpoint of the titration. The method is suitable for use with vitamin C tablets, fresh or packaged fruit juices and solid fruits and vegetables.

PROCEDURE:

1. Pipette a 20 mL aliquot of the sample solution into a 250 mL conical flask and add about 150 mL of distilled water and 1 mL of starch indicator solution.

2. Titrate the sample with 0.005 mol L^{-1} iodine solution. The endpoint of the titration is identified as the first permanent trace of a dark blue-black colour due to the starch-iodine complex.

3. Repeat the titration with further aliquots of sample solution until you obtain concordant results (titres agreeing within 0.1 mL).

Experiment 2. Standardization of Permanganate Solution

Preparation of 0.02 M Potassium Permanganate:

PROCEDURE:

Dissolve about 3.2 g of $KMnO_4$ in 1 L of distilled water. Keep the solution at a gentle boil for about 1 hr. Cover and let stand overnight. Remove MnO_2 by filtration (Note 1) through a fine-porosity filtering crucible (Note 2) or through a Gooch crucible fitted with glass mats. Transfer the solution to a clean glass stoppered bottle; store in the dark when not in use.

Notes

1. Heating and filtering can be omitted if the permanganate solution is standardized and used on the same day.

2. Remove the MnO_2 that collects on the fritted plate with 1 M H_2SO_4 containing a few milliliters of 3% H_2O_2, followed by a rinse with copious quantities of water

Standardization of Potassium Permanganate Solutions

PROCEDURE:

Dry about 1.5 g of primary-standard $Na_2C_2O_4$ at 110°C for at least 1 hr. Cool in a desiccator; weigh (to the nearest 0.1 mg) individual 0.2-g to 0.3-g samples into 400-mL beakers. Dissolve each in about 250 mL of 1 M H_2SO_4. Heat each solution to 80°C to 90°C, and titrate with $KMnO_4$ while stirring with a thermometer. The pink color imparted by one addition should be permitted to disappear before any further titrant is introduced (Notes 1 and 2). Reheat if the temperature drops below 60°C. Take the first persistent (30 s) pink color as the end point (Notes 3 and 4). Determine a blank by titrating an equal volume of the 1 M H_2SO_4. Correct the titration data for the blank, and calculate the concentration of the permanganate solution (Note 5).

Notes

1. Promptly wash any $KMnO_4$ that spatters on the walls of the beaker into the bulk of the liquid with a stream of water.

2. Finely divided MnO_2 will form along with Mn^{2+} if the $KMnO_4$ is added too rapidly, and it will cause the solution to acquire a faint brown discoloration. Precipitate formation is not a serious problem so long as sufficient oxalate remains to reduce the MnO_2 to Mn^{2+}; the titration is simply discontinued until the brown color disappears. The solution must be free of MnO_2 at the end point.

3. The surface of the permanganate solution rather than the bottom of the meniscus can be used to measure titrant volumes. Alternatively, backlighting with a flashlight or a match will permit reading of the meniscus in the conventional manner.

4. A permanganate solution should not be allowed to stand in a buret any longer than

necessary because partial decomposition to MnO_2 may occur. Freshly formed MnO_2 can be removed from a glass surface with 1 M H_2SO_4 containing a small amount of 3% H_2O_2.

5. This procedure yields molarities that are a few tenths of a percent low. For more accurate results, introduce from a buret sufficient permanganate to react with 90% to 95% of the oxalate (about 40 mL of 0.02 M $KMnO_4$ for a 0.3-g sample). Let the solution stand until the permanganate color disappears. Then warm to about 60°C and complete the titration, taking the first permanent pink (30 s) as the end point. Determine a blank by titrating an equal volume of the 1 M H_2SO_4.

Experiment 3. The Determination of Calcium in a Limestone

Discussion

In common with a number of other cations, calcium is conveniently determined by precipitation with oxalate ion. The solid calcium oxalate is filtered, washed free of excess precipitating reagent, and dissolved in dilute acid. The oxalic acid liberated in this step is then titrated with standard permanganate or some other oxidizing reagent. This method is applicable to samples that contain magnesium and the alkali metals. Most other cations must be absent since they either precipitate or coprecipitate as oxalates and cause positive errors in the analysis.

Factors Affecting the Composition of Calcium Oxalate

Precipitates It is essential that the mole ratio between calcium and oxalate be exactly unity in the precipitate and thus in solution at the time of titration. A number of precautions are needed to ensure this condition. For example, the calcium oxalate formed in a neutral or an ammoniacal solution is likely to be contaminated with calcium hydroxide or a basic calcium oxalate, either of which will cause low results. The formation of these compounds is prevented by adding the oxalate to an acidic solution of the sample and slowly forming the desired precipitate by the dropwise addition of ammonia. The coarsely crystalline calcium oxalate that is produced under these conditions is readily filtered. Losses resulting from the solubility of calcium oxalate are negligible above pH 4, provided that washing is limited to freeing the precipitate of excess oxalate. Coprecipitation of sodium oxalate becomes a source of positive error in the determination of calcium whenever the concentration of sodium in the sample exceeds that of calcium. The error from this source can be eliminated by reprecipitation. Magnesium, if present in high concentration, may also be a source of contamination. An excess of oxalate ion helps prevent this interference through the formation of soluble oxalate complexes of magnesium. Prompt filtration of the calcium oxalate can also help prevent interference because of the pronounced tendency of magnesium oxalate to form supersaturated solutions from which precipitate formation occurs only after an hour or more. These measures do not suffice for samples that contain more magnesium than calcium. Here, reprecipitation of the calcium oxalate becomes necessary.

The Composition of Limestones

Limestones are composed principally of calcium carbonate; dolomitic limestones contain large amounts of magnesium carbonate as well. Calcium and magnesium silicates are also present in smaller amounts, along with the carbonates and silicates of iron, aluminum, manganese, titanium, sodium, and other metals. Hydrochloric acid is an effective solvent for most limestones. Only silica, which does not interfere with the analysis, remains undissolved. Some limestones are more readily decomposed after they have been ignited; a few yield only to a carbonate fusion. The

method that follows is remarkably effective for determining calcium in most limestones. Iron and aluminum, in amounts equivalent to that of calcium, do not interfere. Small amounts of manganese and titanium can also be tolerated.

PROCEDURE:

Sample Preparation

Dry the unknown for 1 to 2 hr at 110°C, and cool in a desiccator. If the material is readily decomposed in acid, weigh 3 portions of the sample each 0.25-g to 0.30-g samples (to the nearest 0.1 mg) into 250-mL beakers. Add 10 mL of water to each sample and cover with a watch glass. Add 10 mL of concentrated HCl dropwise, taking care to avoid losses due to spattering as the acid is introduced.

Precipitation of Calcium Oxalate

Dilute each sample solution to about 50 mL, heat to boiling, and add 100 mL of hot 6% (w/v) $(NH_4)_2C_2O_4$ solution. Add 3 to 4 drops of methyl red, and precipitate CaC_2O_4 by slowly adding 6 M NH_3. As the indicator starts to change color, add the NH_3 at a rate of one drop every 3 to 4 s. Continue until the solutions become the intermediate yellow-orange color of the indicator (pH 4.5 to 5.5). Allow the solutions to stand for no more than 30 min (Note) and filter; medium-porosity filtering crucibles or Gooch crucibles with glass mats are satisfactory. Wash the precipitates with several 10-mL portions of cold water. Rinse the outside of the crucibles to remove residual $(NH_4)_2C_2O_4$, and return the precipitate to the beakers in which the CaC_2O_4 was formed. Precipitation will occur as the following reaction:

$$Ca^{2+}_{(aq)} + C_2O_4^{2-}{}_{(aq)} + H_2O_{(l)} \rightarrow CaC_2O_4.H_2O_{(s)}$$

Titration

Add 100 mL of water and 50 mL of 3 M H_2SO_4 to each of the beakers containing the precipitated calcium oxalate. Heat to 80°C to 90°C, and titrate with 0.02 M permanganate. The temperature should be greater than 60°C throughout the titration; reheat if necessary. Report the percentage of CaO in the unknown. Redox titration results this reaction:

$$5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$$

Note

The period of standing can be longer if the unknown contains no Mg^{2+}.

Experiment 4. **Determination of Hardness in Water Samples with EDTA**

PRINCIPLE:

Water hardness, due to Ca^{2+} and Mg^{2+}, is expressed as mg/l $CaCO_3$ (ppm). The total of Ca^{2+} and Mg^{2+} is titrated with standard EDTA using ErioChrome Black T indicator. A standard EDTA solution is prepared from dried $Na_2H_2Y.2H_2O$. If the sample does not contain magnesium, Mg-EDTA is added to titration flask to provide a sharp end point with the ErioChrome Black T, since calcium does not form a sufficiently strong chelate with the indicator to give a sharp end point.

Equations

Titration:

$$Ca^{2+} + H_2Y^{2-} \longrightarrow CaY^{2-} + 2H^+$$

$$Ca^{2+} + MgY^{2-} \longrightarrow CaY^{2-} + Mg^{2+}$$

End Point:

$$Mg^{2+} + Hln^{2-} \longrightarrow Mgln^- + H^+$$

$$Mgln^- + H_2Y^{2-} \longrightarrow MgY^{2-} + Hln^{2-} + H^+$$

(red) (colorless) (colorless) (blue)

The free acid parent of indicator is H_3In, and that of the titrant EDTA is H_4Y.

SOLUTIONS AND CHEMICALS REQUIRED:

1. ErioChrome Black T indicator

2. To prepare:

a) NH_3-NH_4^+ buffer solution, pH 10. Dissolve 3.2 g NH_4Cl in water, add 29 ml conc. NH_3, and dilute to about 50 ml. The buffer solution is best stored for a long period of time in a polyethylene bottle to prevent leaching of metal ions from glass.

b) Standard 500 ml of 0.01 M EDTA solution. Dry about 3g reagent-grade $Na_2H_2Y.2H_2O$ in a weighing bottle at 80^0C 2 hr. Cool in desiccator and weigh necessary amount of $Na_2H_2Y.2H_2O$.

PROCEDURE:

a) Standardization of 0.01 M EDTA

Pipet 10 mL standard 0.010 M Ca^{+2} solution into a clean 250 ml Erlenmeyer flask. Add 3 mL of NH_3-NH_4^+ buffer solution and dilute with distilled water. Then add small amounts of ErioChrome Black T. Titrate Ca^{+2} solution with 0.01 M EDTA until color changes from wine red through purple to a pure blue. Titrate at least three samples of standard Ca^{+2} solution with EDTA. Calculate the concentrations of EDTA.

b) Determination of Hardness in Tap Water

Obtain a water sample from your instructor. Add with a pipette or a burette a 50 ml aliquot of the sample to 250 ml Erlenmeyer flask, add 2 ml buffer solution, and small amounts of ErioChrome Black T. (Avoid adding too much indicator, and the buffer solution should be added before the indicator, so that small amounts of iron present will not react with indicator.). Titrate with 0.01 M EDTA until color changes from wine red through purple to a pure blue. The reaction (color change) is slow at the end point, and titrant must be added slowly and the solution stirred thoroughly in the vicinity of the end point.

CALCULATIONS:

Calculate and report the hardness of the water as ppm $CaCO_3$ for each portion analyzed.

Experiment 5. Potentiometric Titration of Phosphoric Acid

PRINCIPLE:

In this experiment, a solution containing phosphoric acid H_3PO_4, will be titrated with standardized NaOH solution. Measuring the pH of the solution after each addition of titrant will monitor the titration. Analysis of the resulting titration curve will permit calculation of the exact molarity of the phosphoric acid solution. The first and second acid dissociation equilibrium constants for phosphoric acid will also be determined.

Phosphoric acid is a weak polyprotic acid that can dissociate stepwise as shown in equations (1), (2), and (3). ($H_3PO_4 \equiv H_3A$)

$$H_3A + H_2O \leftrightarrow H_2A^- + H_30^+ \quad \ldots\ldots\ldots\ldots\ldots\ldots(1) \quad K_{a1}$$

$$H_2A^- + H_2O \leftrightarrow HA^{2-} + H_30^+ \quad \ldots\ldots\ldots\ldots\ldots\ldots(2) \quad K_{a2}$$

$$HA^{2-} + H_2O \leftrightarrow A^{3-} + H_30^+ \quad \ldots\ldots\ldots\ldots\ldots\ldots(3) \quad K_{a3}$$

As the acid is titrated with strong base, the pH changes in a characteristic way giving rise to a 2 step titration curve (do not observe third ionization constant (K_{a3}) on the titration curve). The rate of change of H^+ ion concentration increases until it reaches a maximum rate at the equivalence point.

SOLUTIONS AND CHEMICALS REQUIRED:

1. 250 mL of 0.1 M H_3PO_4 and 250 mL of 0.1 M NaOH,
2. Standard buffer solutions at pH 4,7,10, for pH meter.

PROCEDURE:

1. Calibrate the pH meter with standard buffer solutions.
2. Transfer 10 mL of 0.1 M H_3PO_4into a 250 mL beaker and then add 90 mL of pure water.
3. Immerse the electrodes into solution after making sure the stirrer cannot hit the electrodes. Measure pH of the solution and then titrate with sodium hydroxide solution with 0.5 mL intervals but 0.1 mL intervals around the expected end points. Continue titrating until the pH is about 11.
4. Plot the pH against the volume of the reagent.

Find the values of K_{a1}, K_{a2} from the graph.

Experiment 6. Determination of Equilibrium Constants for Complex Ions of Silver

PRINCIPLE:

The determination of the equilibrium constants often involve a titration, followed by graphical analysis. A more direct approach for determining such values utilizes a concentration cell and the Nernst equation. The experiment requires only simple equipment and in expensive chemicals, and excellent results can be obtained in a relatively short time.

This method can be extended to include equilibria involving a host of metal ligand complexes, as well as the determination of Ksp values for relatively insoluble salts.

The formation of a metal complex in an aqueous solution can be written as:

$$M^{x+}(aq) + nL^{y-}(aq) \rightarrow ML_n^{(x+)+n(y-)}(aq)$$

where the overall formation constant is

$$K_{form} = [ML_n^{(x+)+n(y-)}(aq)] / [M^{x+}(aq)] [L^{y-}(aq)]^n$$

In the specific example described below, where $x = 1$ and $y = 0$, these equations can be abbreviated as

$$Ag^+ + 2\ NH_3 \rightarrow Ag(NH_3)_2^+$$

and

$$K_{form} = [Ag(NH_3)_2^+] / [Ag^+] [NH_3]^2$$

Knowledge of the three equilibrium concentrations clearly yields K_{form}

Several assumptions are made while doing this experiment:

1. The coordination number of metal ion and the formula of the complex are known.

2. The reaction reaches equilibrium quickly,

3. All activity coefficients are assumed to be 1.00 and junction potentials are negligible;

4. Excess amount of the ligand is added to the metal ion; thus, its concentration is decreased in complex formation; but it can be neglected.

5. The overall formation constant, K_{form}, has a relatively large value, so the equilibrium concentration of $Ag(NH_3)_2^+$ ion is practically the same as the concentration of initial Ag^+ ion.

6. Concentrations of intermediate species (those containing both water and the new ligand in the coordination sphere) are negligibly small.

Because the ligand is in large excess, the equilibrium concentration of the newly formed complex can be calculated by dividing millimoles of Ag^+ to the final volume. The concentration of the remaining free ligand can then be determined from the balanced chemical equation.

The low equilibrium concentration of the aquated metal ion is the only missing datum to determine K_{form}, and it can be obtained using a concentration cell and the Nernst equation. The emf

(voltage) of a cell depends on the concentrations (or activities) of each species involved in the cell reaction. The Nernst equation relates the concentrations in a cell to the cell's emf:

$E = E^0 - [RT / nF] \ln Q$

where E is the emf difference between the electrodes in a cell; E^0 is the standard reduction potential for the cell in volts; R is the gas constant (8.314 J mol^{-1} K^{-1}); T is the temperature; F is Faraday's constant, which is 9.6437 x 10^{-4} J V^{-1} mol^{-1}; n is the number of moles of electrons transferred through the external circuit by molar amounts indicated in the balanced equation; and Q is the reaction quotient. At 25 °C, this reduces to

$E = E^0 - [(0.0591)/n] \log Q$

In this experiment, the cell used is a concentration cell; that is, the two half cells are constructed of the same materials but differ in concentration. Using silver electrodes and Ag^+ ion, the half-reactions are

oxidation (anode): $Ag^0 \rightarrow Ag^+(dil) + e^-$

reduction (cathode): $Ag^+(conc) + e^- \rightarrow Ag^0$

overall: $Ag^+(conc) \rightarrow Ag^+(dil)$

Since $E^0 = 0$ for such a cell, the Nernst equation reduces to

$E_{cell} = - (0.0591\ V) \log \{[Ag^+(dil)] / [Ag^+(conc)]\}$ …… (Eq. 1)

Students check the validity of this equation by using known concentrations in both half-cells and comparing the observed and calculated voltages. Then the equation is used to calculate $[Ag^+(dil)]$ when this dilute solution at the anode contains an equilibrium mixture of silver ion, ligand, and complex ion. This concentration, $[Ag^+(dil)]$, is the missing piece of information needed to calculate K_{form} in the experiment.

PROCEDURE:

A voltmeter that reads in millivolts with a precision of ± 1 mV is adjusted to read zero using the zero, calibration, or standardization knob. Several types of salt bridges can be used to conduct the internal circuit of the voltaic cell. A simple one that works adequately is a strip of porous paper soaked in 1 M KNO_3 (aq). This moistened paper is handled with forceps. Its two ends are dipped into small beakers containing the reference solution and the one to be tested. A short piece of silver wire is placed in each beaker and connected via the plastic-covered electrode clips to the voltmeter. To check the validity of the Nernst equation, several readings are observed and recorded by each student:

1. About 20 mL of 0.010 M $AgNO_3$ is placed in one of two small (50-mL) beakers and one of the silver wires is immersed in the solution. A similar volume of the same 0.010 M $AgNO_3$ solution is added to the other beaker containing its electrode and the salt bridge; then the measured voltage is

recorded. (The electrodes should not be in contact with the paper salt bridge.) In accord with equation 1, students find that the voltmeter reads nearly zero.

2. The solution in one of the beakers is poured into waste and a new half-cell is prepared. 5.0 mL portion of $AgNO_3$ is transferred to a 150 mL beaker and then diluted to 50 mL with distilled water. The Ag wire and salt bridge are reassembled as above and an additional reading is made, which should be about 59 mV. Students are asked to define the cathode and anode and to rationalize the electrode polarities with those of the voltmeter.

3. One additional dilution is made, and the voltage is measured as described. The result is compared with the calculated value**.**

The K_{form} for the diammine silver (I) complex is determined by adding a large but known excess of ammonia to a known amount of aqueous $AgNO_3$. This is done as follows. The reference half-cell is left undisturbed. Into a clean, dry a 50 mL beaker is added 15.0 mL of 0.100 M aqueous ammonia and 15.0 mL of 0.010 M $AgNO_3$. The salt bridge is reassembled and the voltage generated is measured by immersing Ag wire connected to voltmeter. Then concentration of the $Ag^+(aq)$ ion remaining in the beaker is determined from the Nernst equation. The millimoles of the complex formed and the free ammonia remaining, along with the final volume of the solution, yield the molarities of these two species at equilibrium.

Students are asked to repeat the above procedure with different volumes of the Ag^+ and NH_3 solutions and obtain a second value of this formation constant.

Experiment 7. Potentiometric Titration of Chloride and Iodide Mixtures

PRINCIPLE:

The mixture is titrated with a standard solution of silver nitrate, and the potentiometric end points are indicated with a standard silver-wire electrode – glass electrode pair using a pH-meter for potential measurements. Because the pH during the titration remains essentially constant, the glass electrode's potential remains constant, and this electrode serves as the reference electrode. Thus, this eliminates the necessity of preparing a chloride-free salt bridge for the reference electrode. AgI (Ksp= $1x10^{-16}$) precipitates first since it is less soluble than AgCl (Ksp = $1x10^{-10}$). The AgCl starts precipitating near the equivalence point of iodide titration (when $[Ag^+][Cl^-] = 1x10^{-10}$ $[Ag^+]$ at the iodide equivalence point is $(1x\ 10^{-8})^{1/2} = 1x10^{-8}$ M). The potential increment of the iodide titration curve will level off at the point when the chloride starts precipitating, that is, near the iodide equivalence point inflection. This will be followed by the typical S-shaped chloride potentiometric end point. The error in determining the iodide end point is small if it is taken at the point at which the potential levels off.

$$I^- + Ag^+ \rightarrow AgI$$

$$Cl^- + Ag^+ \rightarrow AgCl$$

SOLUTIONS AND CHEMICALS REQUIRED:

1. 0.1 M standard $AgNO_3$: Dry the primary standard $AgNO_3$ for 1-2 hours at 110-120^{0}C (no longer). Store in a dessicator until it is ready for weighing. Obtain and dry your unknown at 120^{o}C for 1-2 hours. Store in dessicator until it is ready for weighing.

PROCEDURE:

Obtain your unknowns from the instructor and dilute to approximately 150 mL and then put a magnetic stirring bar, and place the beaker on a magnetic stirrer. Immerse the electrodes in the solution, taking care that they do not hit the magnetic stirrer. Connect the silver electrode to the reference terminal of the pH/ion meter and glass electrode to its usual terminal. Stir the solution and titrate the sample with the standard $AgNO_3$. Take "pH" readings (actually pX) at 0.5 mL increments until a significant increase is observed and then add 0.1 mL increments. After the first end point is reached, add 0.5 mL increments until the second end point is approached and then 0.1 mL increments. Plot the potential versus volume of $AgNO_3$ and determine the end point for the iodide and the chloride. Use these values to estimate the end point for the other two samples and

repeat the above procedure for these samples. Titrant may be added rapidly up to within 2 or 3 mL of the end point. Be sure to rinse the electrodes between titrations.

CALCULATIONS:

Calculate and report the percent iodide (from the volume required to reach end the first point) and chloride (from the volume required to go from the first end point to the second end point) in your unknown for each portion analyzed.

Experiment 8. The Potentiometric Determination of Solute$_4$ Species in a Carbonate Mixture

PRINCIPLE:

A combination glass/reference electrode (SCE or Ag/AgCl) system can be used to locate end points in neutralization titrations. As a preliminary step to the titrations, the electrode system is standardized against a buffer of known pH.

The unknown is issued as an aqueous solution prepared from one or perhaps two adjacent members of the following series: Na_2CO_3, $NaHCO_3$ and NaOH. The object is to determine which of these components were used to prepare the unknown as well as the weight percent of each solute.

PROCEDURE:

Obtain the unknown from your instructor. Pipette 5 mL of unknown into 250 mL erlenmeyer flask, dilute to 50 mL with distilled water and determine its pH. Titrate with a 50 mL aliquot with 0.1000 M hydrochloric acid solution. Use the resulting titration curves to select indicator(s) suitable for end-point detection, and perform duplicate titrations with these.

CALCULATIONS:

Identify the solute species in the unknown, and report the *mass/volume* percentage of each.