Chemistry 3

Volumetric Chemical Analysis

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NOTICE

TABLE OF CONTENTS

I. Chemistry 3, Volumetric Chemical Analysis

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II. Prerequisite Courses or Knowledge

Module 1
Introduction to Chemistry – Atomic Structure and Chemical Reactions.

Specific knowledge necessary

- Molecules and Compounds
- Calculating composition in percentage.
- Use the idea of the mole to carry out stoichiometric calculations involving quantitative relations in chemical reactions.
- Writing of balanced equations of acid-base reaction
- Methods of writing balanced equations.

Modules 2
Introduction to General Chemistry - Chemical Kinetics, Thermodynamics and Chemistry of Solutions.

Specific knowledge necessary:

- Distinction between reversible and irreversible reactions.
- Calculating equilibrium constants and concentrations.
- Differentiate between units of concentration and their use in appropriate calculations.

III. Time

120 hours (20 more)

Unit	Topic	Approximate no. of Hours
Unit I	Sampling and Statistical analysis of data	25 Hours
Unit II	Fundamentals of volumetric chemical analysis, Chemical equilibrium and Acid-Base Reactions & Titrations	50 Hours
Unit III	Redox Reactions and Titrations	25 Hours
Unit IV	Complex Equilibria and Complexometric Titrations	20 Hours

IV. Material

In order to successfully complete the learning activities in this module you will require Internet-connectivity to enable you to access and /or use:

CD-ROMs and Internet-based:-

Computer aided instruction (CAI);

Multimedia delivery (including video conferencing);

e-Library and data base utilization;

Integrated learning environment; and

Recommended textbooks and reference materials (including web-based learning material)

V. Module Rationale

Chemists generally use standardized symbols and equations for recording their measurements and observations. Most of the data that we obtain in the subject of chemistry may be qualitative or quantitative or both qualitative and quantitative. This module will be concerned with the tools and techniques of quantitative chemical analysis. In quantitative measurements and analyses, there is always some degree of uncertainity associated with the various measurements made. Knowing how to determine this uncertainty is just as important as knowing the final result of the analysis. This is because having data that is so uncertain as to be useless is no better than having no data at all. A unit of this module will deal with the ways of minimizing any uncertainty in quantitative measurements. Other analytical techniques and the principles which underpin them to be studied in this module include titration. Titration is based on the measurement of concentrations of substances, which affords the chemist the opportunity to undertake quantitative study of reactants and products in a chemical reaction. This study is known as stoichiometry of a reaction.

VI. Content

6.1 Overview

This module covers introductory topics that are fundamental to ***analytical chemistry***; the branch of chemistry that deals with qualitative and quantitative aspects of chemical analysis. In this module, we shall examine the quantitative aspects of reactions in aqueous solution. These quantitative dimensions are sometimes referred to as solution stoichiometry. The focus will be on volumetric chemical analysis and specifically titration, which is one of the techniques for studying solution stoichiometry. Through titration, the quantitative studies of acid-base neutralization reactions will be covered. In addition, a review of the basic concepts of chemical equilibria and specifically, acid-base equilibria will also be treated. As a prelude to all the topics mentioned, the concept of reliability in quantitative measurements such as *sampling procedures*, *uncertainty* as well as *statistical treatment* and *presentation* of experimental results will be discussed.

6.2 Outline

Unit I: Sampling and Statistical analysis of data (25 Hours)

- Proper sampling strategies
- Statistical Treatment of Data
- Statistical Parameters
- Statistical Tests
- Propagation of Errors in Calculations

Unit II: Fundamentals of volumetric chemical analysis, Chemical equilibrium and Acid-Base Reactions & Titrations (50 Hours)

- Introduction to Chemical Equilibria: Types of Equilibria
- Bronsted Definition of Acids and Bases
- Monoprotic Acid-Base Equilibria
- Distinctinction between Strong Acids and Strong Bases
- Distinctinction between Weak Acids and Weak Bases
- Volumetric Analysis and Titration Principles
- Monoprotic Acid-Base Titration
- Polyprotic acid-base equilibria and titrations

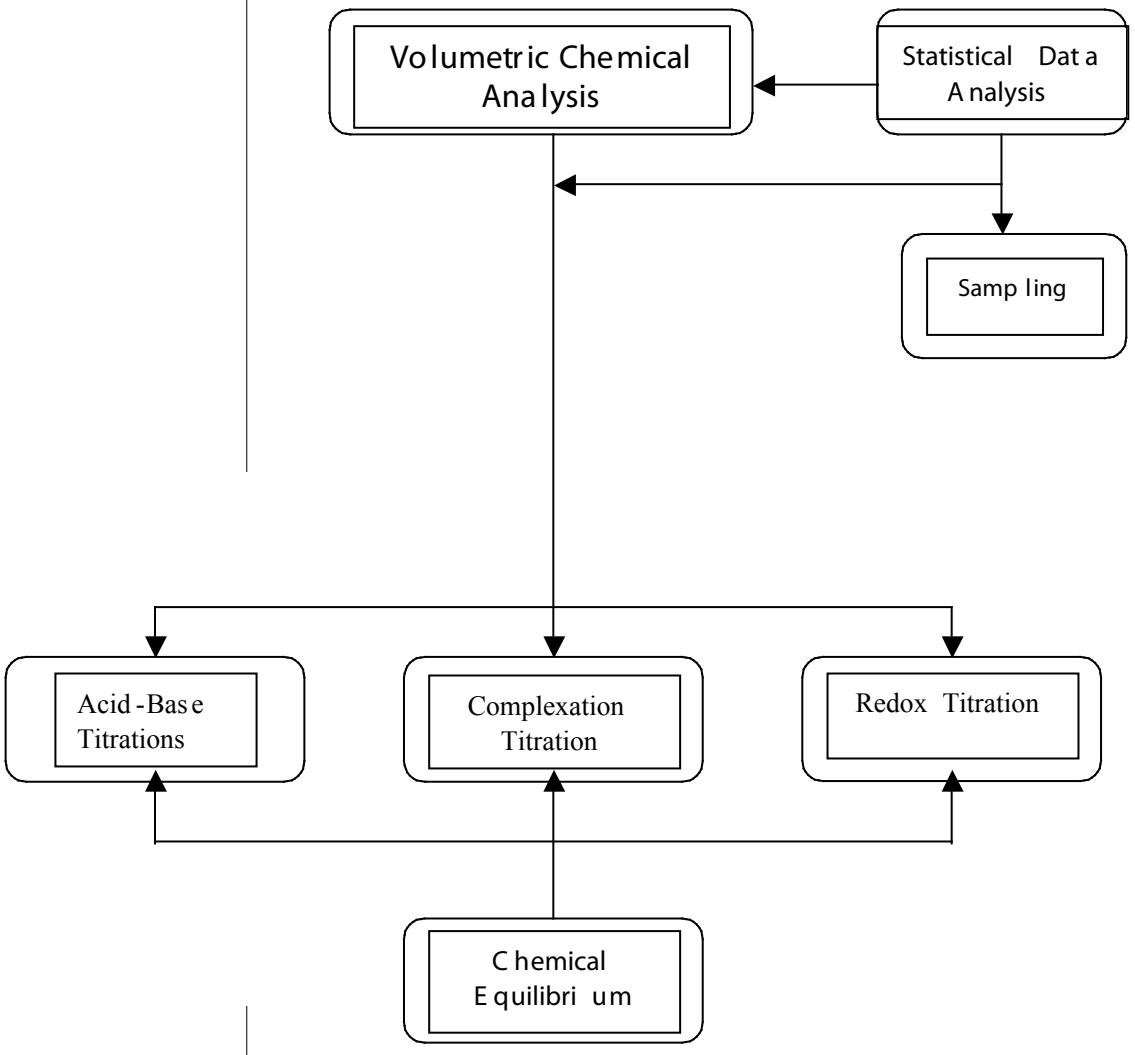
Unit III: Redox Reactions and Titrations (25 Hours)

- Definition of Redox Reactions
- Recognition of Redox Equations
- Definition of Oxidizing and Reducing Agents (with examples)
- Identification of Oxidizing and Reducing agents
- Assigning Oxidation numbers (Rules) with examples
- Balancing Oxidation/Reduction Equations
- Oxidation/Reduction Titrations

Unit IV: Complex Equilibria and Complexometric Titrations (20 Hours)

- Concepts and terminologies in Complex equilibria
- Stepwise Equilibrium Reactions and Applications
- Complexometric Titrations and related calculations (See Module 11 adobe file)

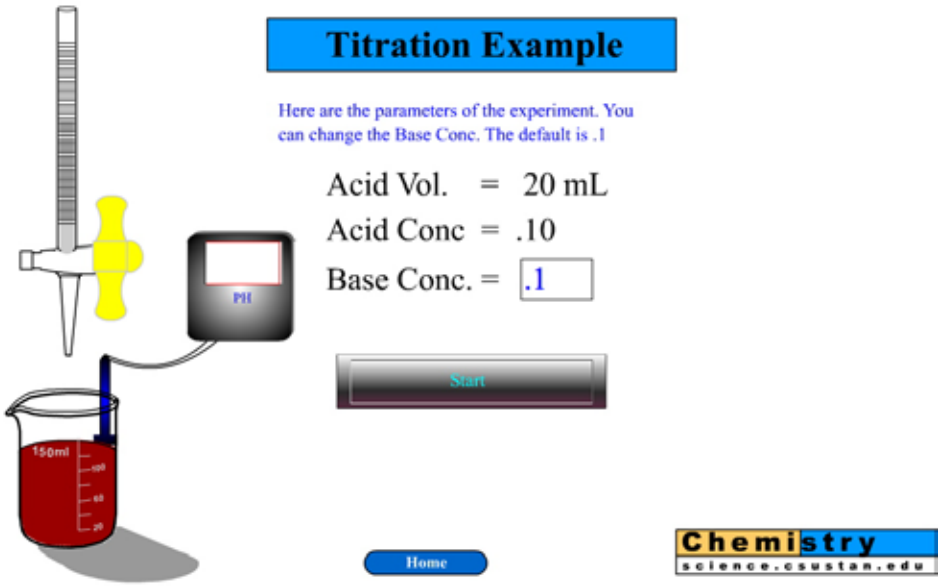
6.3 Graphic Organizer



VII. General Objective(s)

The overall objective of this course is to introduce the student to the fundamental concepts of analytical chemistry with particular emphasis on volumetric chemical analysis. The module is designed to familiarise the learner with the principles that underpin chemical reactivity of different types of chemical reactions. The theories, concepts of volumetric analysis and measurements of data as they apply to analytical chemistry are examined. Special emphasis is placed on the application of basic principles of chemical equilibria to acid-base reactions, precipitation reactions, oxidation-reduction (electron –transfer) reactions, and complex ion reactions. We will look in more detail at the quantitative aspects of acid-base titrations.

The figure below shows a pH meter used to monitor an acid-base titration



VIII. Specific Learning Objectives (Instructional Objectives)

Unit I: Sampling and Statistical Analysis of data

At the end of this unit the student should be able to:

- Define and use the concept of sampling in quantitative chemical analysis.
- Define and distinguish the various types of errors encountered in quantitative experimental measurements.
- Explain the difference between between *accuracy* and *precision*.
- Perform basic statistical analysis of experimental data involving descriptive statistics.

UNIT II: Fundamentals of volumetric chemical analysis, Acid-Base Reactions & Titrations

At the end of this unit the student should be able to:

- Identify acids and bases using the Bronsted-Lowry and Lewis concepts of acids and bases.
- Use acid-base theories to distinguish between strong and weak acid/base.
- Use the concept of diprotic and polyprotic acid equilibria to do related calculations.
- Explain the basic concepts of acid-base equilibria and carry out associated calculations.
- Apply the general principles of chemical equilibrium to precipitation, acid-base, complexation, reactions and titrations.
- Define and apply the principles and steps involved in acid-base equilibria and solubility equilibria
- Evaluate the pH in the course of acid-base titrations.

Unit III: Redox reactions and titrations

At the end of the unit the student should be able to:

- Define and describe the concept of redox reactions, with examples.
- Write balanced net ionic reactions for Oxidation/Reduction equations.
- Carry out Redox-type titration experiments and associated calculations.

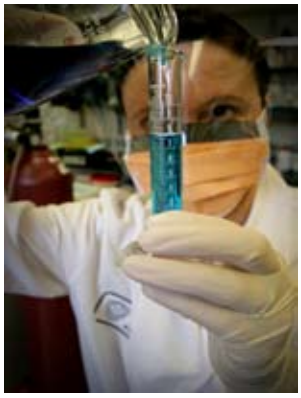
Unit IV: Complex-ion equilibria and complexometric titrations

At the end of the unit the student will be able to:

- Define and understand the use of terminologies relevant in complex ion equilibria.
- Describe and explain the fundamental principles of complex equilibria and stepwise equilibrium reactions.
- Apply the principles of chemical equilibria to complexometric titrations.
- Carry out complexometric titrations and related calculations.

Unit Number	Learning Objective(s)
UNIT I: Sampling and Statistical Analysis of data	- Explain the notion of ***Sampling*** as an integral part of Analytical Methods of Analysis. - Identify and describe the sources of sampling error. - Have a knowledge of some important basic principles of error analysis. - Identify and discuss the various types and sources of experimental errors. - Explain and use the concept of significant figures. - Define and distinguish between absolute vs. relative error; random vs. systematic error; - Describe the relationship between error and probability. - Apply simple statistics and error analysis to determine the reliability of analytical chemical procedures. - Clearly and correctly report measurements and the uncertainties in them.

UNIT II: Fundamentals of Volumetric Chemical Analysis, Acid/Base Equilibria & Titrations	- Perform stoichiometry & titration calculations. - Use equilibrium constants for acid base reactions. - Distinguish between equivalence and end point, blank and back titrations. - Have a working knowledge of end point detection and its significance. - Explain weak acid/base dissociations. - Explain and sketch precisely the titration curves (pH profiles) of different types of acid-base reactions. - Explain the concept of diprotic acid/ base neutralizations. - Identify some common acid-base indicators and be able to specify which ones to use for various titrations.
UNIT III: Redox Reactions and Titrations	- Define Oxidation/Reduction Reactions, Oxidation and Reduction, Oxidation numbers. - Define Oxidizing and Reducing agents with Examples. - Assign oxidation numbers based on the Rules of assignment. - Know the steps needed to balance Oxidation/Reduction reactions in acidic and basic solutions. - Carry out oxidation/Reduction titration experiments and related calculations.
UNIT IV: Complex-ion equilibria and complexometric titrations	- Understand the concept of stepwise Equilibrium processes. - Define and discuss Polyprotic acid equilibria and titrations. - Understand the concept of Complexo metric Titrations and their applications.



IX. Pre-assessment

Title of Pre-assessment

Review of Concepts of chemistry on measurements, chemical reactions and stoichiometry

Rationale

The fields of science and technology rely very much on measurements of physical and chemical properties of materials for these are central in defining the nature of substances or quantifying them. Some of the concepts involved in measurements such as mass, volume, concentration you would have come across in the earlier modules. There are others you will be meeting for the first time in this module, that have to do with determining the identity of a substance based on quantitative analysis. The set of pre-assessment questions below are meant to help you assess your level of mastery of the concepts on measurements that are most often used by chemists to determine a specific chemical property. Some questions which will be new to you have been included. Such questions are meant to give you some idea as to what to expect in this module that deals with various aspects of volumetric analysis.

Questions

For each of the following test items, select the option that you think is the correct one.

1. Each response below lists an ion by name and by chemical formula. Also, each ion is classified as monatomic or polyatomic and as a cation or anion. Which particular option is incorrect?

   A. carbonate, CO_3^{2-}, polyatomic anion.
   B. ammonium, NH_4^+, polyatomic cation.
   C. magnesium, Mg^{2+}, monatomic cation.
   D. hydroxide, OH-, monatomic anion.
   E. sulfite, SO_3^{2-}, polyatomic anion.

2. Equal number of moles of different compounds

   A. May or may not have the same number of atoms
   B. Have the same number of molecules
   C. Have equal weights
   D. Have the same number of atom
   E. A & B

3. What do you understand by the term "molecular mass of a molecule"?

   A. The summation of atomic masses, in grams, of all the atoms in the molecule.
   B. The mass, in grams of the molecule.
   C. The gram molecular weight of a substance.
   D. The mass, in grams of a substance.
   E. The mass, in grams of the heaviest atom of the molecule

4. Calculate the molecular mass of NaCl?

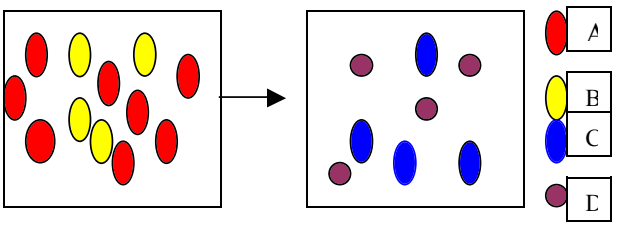
   A. 58
   B. 23
   C. 35
   D. 28
   E. 51

5. All of the substances listed below are fertilizers that contribute nitrogen to the soil. Which of these is the richest source of nitrogen on a mass perentage basis?

   A. Urea, $(NH_2)_2CO$
   B. Ammonium nitrate, NH_4NO_3
   C. Guanidine, $HNC(NH_2)_2$
   D. Ammonia, NH_3
   E. Potassium nitrate, KNO_3

6. What do 2.4 moles of CO and CO_2 have in common?

   A. same mass
   B. contain the same mass of carbon and oxygen
   C. contain the same mass of oxygen
   D. contain the same number of molecules
   E. contain the same number of total atoms



7. Which of the following equations best represents the reaction shown in the diagram above? This can be answered by simple elimination.

   A. $8A + 4B \rightarrow C + D$
   B. $4A + 8B \rightarrow 4C + 4D$
   C. $2A + B \rightarrow C + D$
   D. $4A + 2B \rightarrow 4C + 4D$
   E. $2A + 4B \rightarrow C + D$

8. Which of the following can be used to measure a more accurate volume of a liquid?

   A. Beaker
   B. Graduated cylinder
   C. Burrette
   D. Bottle
   E. All

9. How can one prepare 750 mL solution of 0.5 M H_2SO_4, from 2.5 M H_2SO_4 stock solution?

   A. by mixing 250 mL of the stock solution with 500 mL of water
   B. by mixing 150 mL of the stock solution with 600 mL of water
   C. by mixing 600 mL of the stock solution with 150 mL of water
   D. by mixing 375 mL of the stock solution with 375 mL of water
   E. none

10. If the concentration of H^+ ions in an aqueous solution is 2.5×10^{-4} then,

   A. its pH is less than 7
   B. the solution is acidic
   C. its pOH is greater than 7
   D. its OH^- concentration is less than the concentration of OH^- in neutral solution
   E. All

11. What do you understand by the term "Quantitative analysis"?

   A. Involves determining the individual constituents of a given sample.
   B. Involves the determination of the relative or absolute amount of an analyte in a given sample
   C. Involves the addition of measured volume of a known concentration of reagent into a solution of the substance to be determined (analyte).

D. Involves determining the level of purity of an analyte.
E. Involves determining the quality of a sample.

12. Which of the following statements does not appropriately describe a stage in a titration process?

A. Before equivalence point is reached, the volume of a reagent added to the analyte does not make the reaction complete (when there is excess of analyte).
B. At equivalence point the reagent added is the amount that is chemically equivalent to the amount of substance being determined (analyte).
C. After equivalence point, the amount of reagent added is higher than the amount of substance being determined.
D. After equivalence point, the amount of reagent added cannot be higher than the amount of substance being determined.
E. At the beginning of a titration, the number of moles of the reagent added is always less than that of the analyte present (when there is excess analyte).

13. Which of the following is correct about titration of a polyprotic weak acid such as orthophosphoric acid (H_3PO_4) with a strong base such as NaOH?

A. H_3PO_4 titration curve has only one equivalence point.
B. H_3PO_4 titration curve has only two equivalence points.
C. H_3PO_4 titration curve has only three equivalence points.
D. H_3PO_4 titration curve does not have any equivalence point.
E. H_3PO_4 titration curve has only seven equivalence points.

14. Which of the following reactions is not a redox reaction?

A. $H_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2HCl$
B. $CuSO_4 + Zn \rightarrow ZnSO_4 + Cu$
C. $2NaI + Cl_2 \rightarrow 2NaCl + I_2$
D. $C + O_2 \rightarrow CO_2$
E. None

Answer questions 15 to 18 based on the following chemical equation:

$CuSO_4 + Zn \rightarrow ZnSO_4 + Cu$

15. Which of the following is a reducing agent if the reaction is a redox reaction?

A. $CuSO_4$
B. Zn
C. $ZnSO_4$
D. Cu
E. the reaction is not a redox reaction

16. Which of the following species gained electrons?

A. $CuSO_4$
B. Zn
C. $ZnSO_4$
D. Cu
E. None

17. What is the number of electrons gained per mole of the oxidizing agent?

A. 1 mole
B. 2 moles
C. 3 moles
D. 4 moles
E. 0 moles

18. What is the number of electrons lost per mole of the reducing agent?

A. 1 mole
B. 2 moles
C. 3 moles
D. 4 moles
E. 0 moles

19. Which one of the following is a redox reaction?

A. $H^+ (aq) + OH^- (aq) \rightarrow H_2O (l)$
B. $2\ KBr (aq) + Pb(NO_3)_2 (aq) \rightarrow 2\ KNO_3 (aq) + PbBr_2 (s)$
C. $CaBr_2 (aq) + H_2SO_4 (aq) \rightarrow CaSO_4 (s) + 2\ HBr (g)$
D. $2\ Al (s) + 3\ H_2SO_4 (aq) \rightarrow Al_2(SO_4)_3 (aq) + 3H_2 (g)$
E. $CO_3^{2-} (aq) + HSO_4^- (aq) \rightarrow HCO_3^- (aq) + SO_4^{2-} (aq)$

20. In the reaction, $Zn(s) + 2HCl (aq) \rightarrow ZnCl_2 (aq) + H_2 (g)$, what is the oxidation number of H_2?

A. +1
B. -1
C. 0
D. +2
E. -2

Title of Pre-assessment : _____

Answers Key

1. D
2. D
3. A
4. A
5. D
6. D
7. C
8. C
9. B
10. E
11. B
12. D
13. C
14. E
15. B
16. A
17. B
18. B
19. D
20. C

X. Key Concepts (Glossary)

Accuracy: this is the closeness of a result to the *correct* answer.

Acid: A substance that yields hydrogen ions (H^+) when dissolved in water.

Base: A substance that yields hydroxide ions (OH^-) when dissolved in water.

Base ionization constant (K_b): The equilibrium constant for the base ionization.

Bronsted acid: A substance that is able to donate a proton.

Bronsted base: A substance that is capable of accepting a proton.

Chemical equation: An equation that uses chemical symbols to show what happens during a chemical reaction.

Chemical equilibrium: A state in which the rates of the forward and reverse reactions are equal.

Chemical reaction: A process in which a substance (or substances) is changed into one or more new substances.

Complex ion: An ion containing a central metal cation bonded to one or more molecules or ions.

Common ion effect: The shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substances.

Determinate errors: these are mistakes, which are often referred to as "bias". In theory, these could be eliminated by careful technique.

Diprotic acid: Each unit of the acid yields two hydrogen ions upon ionization.

End point: The pH at which the indicator changes colour.

Equilibrium constant (K_{eq}): A number equal to the ratio of the equilibrium concentrations of products to the equilibrium concentrations of reactants, each raised to the power of its stoichiometric coefficient.

Equivalence point: The point at which the acid has completely reacted with or been neutralized by the base.

Homogeneous sample: sample is the same throughout.

Hydronium ion: The hydrated proton, H_3O^+.

Indeterminate errors: these are errors caused by the need to make estimates in the last figure of a measurement, by noise present in instruments, etc. Such errors can be reduced, but never entirely eliminated.

Law of mass action: For a reversible reaction at equilibrium and at a constant temperature, a certain ratio of reactant and product concentrations has a constant value, K_{eq} (the equilibrium constant).

Lewis acid: A substance that can accept a pair of electrons.

Lewis base: A substance that can donate a pair of electrons.

Monoprotic acid: Each unit of the acid yields one hydrogen ion upon ionization.

Neutralization reaction: A reaction between an acid and a base.

Oxidation reaction: The half-reaction that involves the loss of electrons.

Oxidation-reduction reaction: A reaction that involves the transfer of electron(s) or the change in the oxidation state of reactants.

Oxidizing agent: A substance that can accept electrons from another substance or increase the oxidation numbers in another substance.

pH: The negative logarithm of the hydrogen ion concentration.

Precision: the reproducibility of a data set; a measure of the ability to obtain the same number (not necessarily the correct number) in every trial.

Redox reaction: A reaction in which there is either a transfer of electrons or a change in the oxidation numbers of the substances taking part in the reaction.

Reducing agent: A substance that can donate electrons to another substance or decrease the oxidation numbers in another substance.

Representative sample: a sample whose content is the same overall as the material from which it is taken from.

Sampling: this is used to describe the process involved in finding a reasonable amount of material that is representative of the whole..

Significant figures: The number of meaningful digits in a measured or calculated quantity.

Solution: A homogeneous mixture of two or more substances.

Standard solution: A solution of accurately known concentration.

Stoichiometrry: The quantitative study of reactants and products in a chemical reaction

XI. Compulsory Readings

Reading #1

Complete reference: See PDF file named "Acid-Base-Equilibria and Titrations"

Abstract : This is a 48 page book entitled "A Chem 1 Reference Text by Stephen K. Lower of Simon Fraser University"; an Openware Source material. The text provides a comprehensive coverage of the topic of Acid-Base Equilibrium and calculations.

Rationale: This book provides good cover of quantitative treatment of acid-base equilibria and gives an in depth discussion of acid-base titrations. It also looks at acid-base neutralizing capacity and provides graphical treatment of acid-base problems.

Reading #2

Complete reference: See document "Introduction to acid-base chemistry"

Abstract: This is a 19 page book entitled "A Chem 1 Reference Text by Stephen K. Lower of Simon Fraser University"; an Openware Source material. The text provides a comprehensive coverage of the topic of Introduction to Acid-Base Chemistry.

Rationale: The book makes good treatment of the concepts of acids and bases and emphasizes mainly on the qualitative aspects, definitions and the fundamental ideas associated with acids and bases.

Reading #3

Complete reference : See document "Material and Matters"

Abstract : This is a 30 page book entitled "Matter and Measure: A Chem 1 Reference Text by Stephen K. Lower of Simon Fraser University"; an Openware Source material. The text covers the following topics: Units and dimensions; The meaning of measure: accuracy and precission; Significant figures and rounding off; and Assessing reliability of measurements: simple statistics. A web Version of the document can be accessed via: http://www.stu.ca/person/lower/TUTORIALS/matmeas/.

Rationale: Other than the first Chapter that deals with "Units and Dimensions", the rest of the chapters provide useful material for the understanding of "UNIT 1: Sampling and Statistical Analysis of Data" of this module. The chapters provide comprehensive coverage of Error in measured values; accuracy and precision;

ways of dealing with scatter (mean, standard deviation, etc); systematic error; absolute versus relative uncertainty; significant figures and rules for rounding off; dispersion of the mean; assessing reliability of measurements through statistics; confidence intervals; using statistical tests to make decisions; etc. The chapters emphasize mainly on the qualitative aspects, definitions and the fundamental ideas associated with experimental measurements of data and treatment.

Additional Compulsory Readings (Specific To Learning Activities)

Learning Activity #1

Measurements and significant figures (Reading #4)
Units and dimensions (Reading #5)
Significant figures (Reading #6)
Significant figures and rounding off (Reading #7)
Measurements (Reading #8)

Learning Activity #2

Chemical equilibria (Reading #9)
Introduction to acid-base chemistry (Reading #10)
Acid-Base equilibria and Calculations (Reading #11)
Acid-base equilibria of aquatic environment (Reading #12)
A reference text with file with sub-sections containing sample problems dealing with acids and bases, chemical equilibrium, quantitative calculations in acids and bases (Reading #13).
Acid Base (Reading #14)
Bronsted-Lowry Acid-Base Reactions (Reading #15)
Chemistry Chapter 16 Complex Ions (Reading #16)
Chemistry Chapter 16 Hydrolysis of Bases (Reading #17)
Chemistry Chapter 16 Titrations (Reading #18)
Chemistry Chapter 16 Hydrolysis of Acids (Reading #19)
Chemistry Chapter 16 Autoionization of Water (Reading #20)
Addition of Strong Base to a weak Acid (Reading #21)
pH curves (titration curves) (Reading #22)
Titration of a Weak Acid with a Strong Base (Reading #23)

Learning Activity #3

A text that contains vital information on the Nernst Equation, the significance of the equation and analytical applications in quantitative analysis of metal ions in solution (Reading #24)

A text on “Redox Equilibria in Natural Waters” (Reading #25)

A text with sub-sections containing sample problems dealing with chemical equilibrium, oxidation-reduction reactions (Reading #13)

Balancing Redox Equations by Using Half-reactionsBalancing Redox Equations (Reading # 26)

Oxidation NumbersRules for Oxidation Numbers (Reading #27)

Reactions in Aqueous solutions (Reading #28)

Balance redox (Reading #29)

Learning Activity #4

Complex Formation (Reading #30)

Ethlyne diamine tetraacetic acid (Reading #31, Reading #32)

XII. Compulsory Resources

Resource #1

Complete reference: See **ChemLab-Techniques-Titration.PDF obtained from the site: https://www.dartmouth.edu/~chemlab/techniques/titration.html.**

Abstract : The accuracy of results obtained from a titration exercise is as good as the diligence with which a titration process is carried out. The still pictures or photographs provided here not only show the various apparatus needed to carry out a successful titration but also the best practices, stages and precautions necessary during a titration experiment. These photos begin right from the stage of preparing a buret for the delivery of a stream of a titrant to within a couple of mL of expected endpoint; preparation of a solution to be analysed in an Erlenmeyer flask or beaker; addition of an appropriate indicator; necessary precautions to be taken as one approaches an endpoint (if an indicator is used); through reading of the final volume of the buret. At each stage, cautions to be taken are highlighted. In addition, illustrations showing the use of the alternative procedure of titrating with a pH meter is also included.

Rationale: This is a must-see set of illustrations of the process of titration as they clearly show step-by-step procedures and associated precautions necessary for a successful titration exercise. Among the precautions highlighted in the form of captions to each photo include buret conditioning which amounts to checking of air bubbles and leaks before proceeding, calculating of expected endpoint volume, rinsing of flask sides and buret tip to ensure that all titrant is mixed in the flask, adding of partial drops of titrant, etc.

Resource #2

Complete reference: See **ChemLab-Glassware-Burets.htm**

Abstract : The photo illustrations are a step-by-step sequence of events necessary for the maintenance of the integrity and proper working of a buret which is the primary apparatus in a titration exercise. Through these clear illustrations, you will learn alternative ways of how to properly fill a buret; the need and how to remove an air bubble so as to prevent or minimize error in volume readings; how to check for leaks in the buret; how to take more accurate volume readings; how to deliver solution using the buret; and how to use a wash bottle to rinse the buret tip and sides of the titration flask using a wash bottle.

Rationale: For all practical purposes, the laboratory is supposed to support and illustrate chemical concepts studied or read among other things. Along with concepts and chemistry covered in sections of this module, these photo illustrations show how a buret; a major component of the apparatus for a titration exercise works. For anyone keen on correctly carrying out a titration exercise, the photo illustrations are therefore, a must-see. The photo illustrations feature clear description of the events at every stage: from filling the buret to controlled delivery of titrant solution. With these colourful illustrations, you will learn how to avoid making errors that would otherwise put the integrity of your titration exercise in jeopardy. This is significant considering the fact that, aside from the Erlenmeyer flask, the buret is a major significant component of a titration appartus.

Resource #3

Complete reference: See **DVAction Digital Video to Assist Chemistry Teachers and Instructors Online.htm**

Abstract : DvAction is a digital video to assist chemistry teachers and instructors online from Northwestern University. It is a digital video narrative showing how to perform a common strong acid-strong base titration of hydrochloric acid and sodium hydroxide using a buret. The site: http://qt.nulmedia.northwestern.edu/dvaction/movies/ progressive/euc-NU020-026.mov has around 80 images and or videos illustrating various chemical techniques and you are encouraged to visit the webpage and select or browse an appropriate item that is also relevant to this module. The browsing options include by title, equipment, chemicals, or microscale.

Rationale: For anyone taking a course in volumetric chemical analysis, in which titration is key, this video narratve is a must see. The digital video presentation is a colourful step-by-step illustration of the entire process of carrying out an acid-base titration: right from setting up the apparatus and doing the actual titration process to determining the endpoint following the use of an appropriate indicator. The video narrative which is done in a very clear and pleasant voice also points out the necessary precautions needed to be taken at every stage of the titration process and shows tips of carrying out a successful titration exercise. In addition to assisting chemistry teachers and laboratory instructors online, it is a useful resource for learners wishing to see first hand how a titration experiment is effectively carried out.

XIII. Useful Links

Useful Link #1

Title : A Chem1 General Chemistry Virtual Textbook on Matter and Measure.

URL : http://www.Chem1.com/acad/webtext/matmeasure/index.html

Description: This is an online General Chemstry Virtual Textbook on "**Matter and Measure**" existing in the form of a set of HTML files that users can download. It gives access to material that constitute a major chunk of the topic under UNIT 1 of this module that deals with "**Sampling and Statistical Analysis of Data**". Through this website, one is able to access material under five (5) different subtopic headings, namely: Units; Measurement error; Significant Figures; Reliability; and Simple Statistics. Each of these subtopics is accessble via, http://www.chem1.com/acad/webtext/matmeasure/mm1.html; http://www.chem1.com/acad/webtext/matmeasure/mm2.html; http://www.chem1.com/acad/webtext/matmeasure/mm3.html; http://www.chem1.com/acad/webtext/matmeasure/mm4.html; and http://www.chem1.com/acad/webtext/matmeasure/mm5.html; respectively.

Rationale*:* This is a useful link as it provides basically ALL the material that constitute UNIT 1 of this module. Each HTML file of the various subtopics outlined above is quite comprehensive in content with very good coloured illustrations that makes reading the material enjoyable. The subtopic on **Measurement Error** is titled "The meaning of Measure: Dealing with error and uncertainty in measured values"; that on significant Figures is titled "The measure of Matter: Significant figures and rounding off"; The subtopics have worked out sample problems, where necessary, for better understanding and corresponding exercises to test ones understanding of the concept(s) learned. In addition, each website has a "What you should be able to do" section which guides the learner in what is expected of him or her at the end of each subtopic.

Useful Link #2

Title: Chemistry: The Science in Context

URL: http://www.wwnorton.com/chemistry/concepts/ch16.htm

Description: This is an 18-chapter online text material for chemistry entitled "Chemistry: The Science in Context". Each Chapter comes as a separate HTML file accessible via the site Homepage. Each Chapter is grouped into four main categories, namely: Overview, Tutorials, Key Equations, Crossword, and Quizes. The Key chapter that is quite relavant to this Module is **Chapter 16: Equilibrium in the Aqueous Phase and Acid Rain.** One is also encouraged to look at the rest of the chapters via their respective site addresses for other supportive material for this Module. For instance, Chapters 4 and 5 provide some material on Stoichiometry; a useful topic when carrying out calculations related to titrations. It is therefore the responsibility of the student to sift through the various HTML files of the various chapters for relevant additional material that will supplement the compulsory reading material outlined elsewhere in this module besides chapter 16.

Rationale: This is a useful digital/electronic textbook relevant to the subject matter provided in the outline of this module. Students wishing to acquire knowledge on the concepts of volumetric chemical analysis –specifically titrations as well as chemical equilibria in aqueous solutions, Hydrolysis of acids and bases (strong, weak, polyprotic), Complex ions, Bronsted-Lowry Acid-Base reactions, and Autoionization of water will find Chapter 16 of this online book useful. It is organized in a very interesting way that provides Key Equations and Concepts that are relevant to the topic of Equilibrium in aqueous phases. It has sample problems on each subtopic with corresponding exercises, tutorials and quizes.

Useful Link #3

Title: Acids and Bases : Chemistry Online

URL : http://www.teachmetuition.co.uk/Chemistry/Acids_and_Bases/acids_and_bases.h

Description: This Website part of Chemistry Online, provided by Teach-me Service gives access to notes on material that constitute a major chunk of this module. The contents specifically are acids and bases; including basic definitions; strong and weak acids; principles of pH; the ionic product of water; calculating the pH of weak acids; calculating the dissociation constant (K_a) of weak acids; acid-base titration curves; selection of indicators (litmus, methyl orange, phenolphthalein), and buffers.

Rationale: This is a useful link as it provides material that constitute a major part of this module. In addition, the link offers both worked out examples on acids and bases and sample questions on how to calculate pH of either an acidic or basic solution and should provide good practice for the learner.

Useful Link #4

Title : Ions and Equilibrium; Acids and Bases : Chapter 16 : Foundations to Chemistry

URL : http://www.chem.ox.ac.uk/vrchemistry/chapter16/pag01.htm

Description: This Website avails notes on strong and weak acids and bases, calculations with equilibrium constants, dissociation constants and the dissociation of water, the pH scale, neutralisation, concepts of acids and bases, acids with several dissociating protons, buffers and pH control, acid-base indicators and the measurement of pH, solubility equilibria and acid-base catalysis. These notes are part of an online pre-University chemistry course, and form part of 'Virtual Chemistry' from the Department of Chemistry, University of Oxford. They are based on an extract from the book 'Chemistry, Matter and the Universe' by Richard E Dickerson and Irving Geis, used with permission. The plug-ins Shockwave (for Flash and Director) and CHIME are required to view the multimedia animations and 3D molecules.

Rationale: This resource contains useful information on various aspects of "Ions and Equilibria: Acids and Bases". Among the important coverage include; the meaning of acids and bases; differences between strong acid and weak acids; acid-base indicators; solubility equilibria; strong acids and bases; polyprotic acids; neutralization reactions; and the pH scale. In addition, the resource contains many sample questions on the various aspects of acids and bases as well as calculations with equilibrium constants.

Useful Link #5

Title : Redox Titration Experiment

URL : http://www.chem.iastate.edu/group/Greenbowe/sections/projectfolder/flashfil.

Description: This is an interactive animation that allows the user to participate in redox titration experiments (potassium manganate/iron (II), potassium dichromate/tin (II), and iodine with disulphur trioxide). The aim of the experiments is to calculate the molarity of the reducing agents, from equations and data supplied. The animation is supplied by Thomas J Greenbowe of Iowa State University Chemical Education Research Group. Macromedia Flash is required to view the simulation.

Rationale: This is a useful interactive animation resource that helps the learner to participate in three redox titration experiments. It affords the learner the opportunity to calculate the molarity of the reducing agent for each of the three experiments during a redox titration exercise.

Useful Link #6

Title : Equilibrium : Acids and Bases

URL: http://www2.ucdsb.on.ca/tiss/stretton/CHEM2/acidx.htm

Description: This website created by Tom Stretton of the Thousand Island Secondary School provides university preparation chemistry notes. The notes cover; Arrhenius/Bronsted-Lowry definitions of acids and bases; weak acids; the pH scale; the pOH scale; equilibrium in Bronsted acid-bases; ion concentrations; weak bases; solution containing ions which do not hydrolyse appreciably, buffer solutions; pH of a buffered solution; calculating the pH of a buffered solution; volumetric analysis; standard solutions; percentage purity of a sample; titration curves; titration of a weak acid by a strong base; titration of a weak base by a strong acid; polyprotic acids; and calculating [H] and $[A^{2-}]$ for a weak diprotic acid.

Rationale: This resource comprises 28 html documents covering various aspects of acid-base solution chemistry. The clear step-by-step presentation of material makes the learning and understanding of the concepts enjoyable. Some html files contain "follow-up" problems at the end of the lecture notes, hence should prove useful to the learner. There is a single html file that contains only acid-base unit review questions for practice by the learner.

Useful Link #7

Title: Acid-Base Theory : Quantitative Analysis

URL : http://chemistry.olivet.edu/classes/chem301/pdf/Acid%20BaseTheory.PDF

Description: This resource comprises lecture notes from a course in quantitative analysis offered by the Division of Chemistry at Olivet Nazarene University. This lecture covers acid-base theory, including Arrhenius, Lewis and Bronsted definitions, pH, water ionisation, ionisation of weak acids and bases, hydrolysis, titration curves, and related areas. The document is in PDF format, requiring Adobe Acrobat Reader software to view.

Rationale: This pdf file is a useful resource for learners wishing to get a better understanding of how to apply the various concepts and theories of acids and bases in solving practical problems such as carrying out titration curve calculations. It provides excellent step-by-step clear illustrations on how to carry out titration curve calculations; gives useful tips/approaches on how to calculate pH during a titration exercise; and provides sample questions dealing with calculations of pHs of various acid-base combinations.

Useful Link #8

Title: Chemical Reactions : Acids and Bases

URL : http://dwb.unl.edu/Teacher/NSF/C12/C12.html

Screen capture :

Description: This site is one of the online graduate chemistry courses for high school teachers supported by the National Science Foundation (NSF), USA. It provides detailed information about acids and bases. Topics covered include acid-base theory; acid anhydrides; base anhydrides; concentration; dissociation of strong acids and bases; buffers; neutralisation; titrations; indicators, etc. The resource also includes: the relationship between acids and bases and science and mathematics; simulations; practical activities; applications of acid-base chemistry (practical, industrial, environmental); the history of acids and bases; safety; common misconceptions; practical demonstrations; and experiments. There are quizzes after the explanation of each concept.

Rationale: This is a must-read set of notes as it covers a significant portion of this module. In addition to the fundamental principles governing acid and base reactions, the notes provide useful general information on some important applications of acids and bases in real life. The website also provides useful links to a simple calculator program to generate a titration curve for any reacting acid species with a strong base. It also provides microscale titration activities involving a strong acid and a strong base, and a weak acid and a strong base for illustration purposes.

Useful Link #9

Title : Chemical Principles : the Quest for Insight : Second Edition

URL : http://www.whfreeman.com/chemicalprinciples/

Description: This website is a book companion site for 'Chemical Principles: a Quest for Insight', second edition (published by W H Freeman). This site has been developed to serve as an additional free resource for students and instructors using the textbook. It includes chapter outlines, living graphs, animations, videos, molecular visualisations, simulations, exercises and links to related websites. The topics are: atoms (the quantum world), chemical bonds, molecular shape and structure, the properties of gases, liquids and solids, thermodynamics (first, second and third laws), physical equilibria, chemical equilibria, acids and bases, aqueous equilibria, electrochemistry, chemical kinetics, the elements (the first four and last four main groups), the d-block elements (metals in transition), nuclear chemistry, and organic chemistry (the hydrocarbons and functional groups). Many resources require Macromedia Shockwave Player (version 8.5 or above), Macromedia Flash Player (version 6.0 or above), Apple QuickTime (5.0 or above), and Adobe Acrobat (version 6 or above) plug-ins.

Rationale: This Web site is designed to help the learner review key concepts from the textbook; "*Chemical Principles 2e, the Quest for Insight by Peter Atkins and Loretta Jones*" through interactive exercises and learning tools. Resources are organized by chapter of the textbook and by content type. The chapters relevant to this module are Chapter 9 -Chemical equilibria; Chapter 10 – Acids and Bases; and Chapter 11 –Aqueous equilibria. These relevant chapters should therefore be selected to access the corresponding resources.

Useful Link #10

Title : Acids and Bases : an Introduction

URL : http://www.visionlearning.com/library/module_viewer.php?mid=58

Description: Visionlearning's guide to acids and bases draws together a mix of documents written in-house with news and articles culled from elsewhere on the Web. The front page provides a brief overview of acids, bases, pH and neutralisation, while there are links to articles about chemists associated with the field (Arrhenius, Bronsted), virtual experiments, and media stories about acids and bases. Links to other Web-based chemistry resources both within the field and covering more general topics are also provided. The site is also available in Spanish.

Rationale: Provides an easy to read introductory text on the historical perspectives of acids/bases and is written in a very simple and interesting manner; giving a good discussion on the various theories that exist on acids/bases. Provides useful links to excellent and comprehensive set of tutorials detailing acid/base chemistry, including practice tests.

XIV. Learning Activities

Learning activity # 1

Title of Learning Activity :Sampling and Statistical Analysis of data

Specific Learning Objectives:

- Describe and explain the importance of the concept of "*sampling*" in analytical methods of analysis.
- Describe and discuss the sources and types of sampling error and uncertainty in measurement.
- Acquire the techniques for handling numbers associated with measurements: scientific notation and *significant figures*.
- Explain the concept of data rejection (or elimination) and comparison of measurements.
- Apply simple statistics and error analysis to determine the reliability of analytical chemical measurements and data.

Summary of the learning activity

This activity comprises two fairly distinct study topics: *Sampling* and *Statistical analysis of data*. Under "*Sampling*", you will be introduced to the concept and challenges of *sampling* as a means to acquiring a representative laboratory sample from the original bulk specimen. At the end of the subtopic on "*sampling*", you will not only appreciate that a sampling method adopted by an analyst is an integral part of any analytical methods, but will also discover that it is usually the most challenging part of an analysis process. Another very important stage in any analytical method of analysis is *evaluation of results*, where statistical tests (i.e., quantities that describe a distribution of, say, experimentally measured data) are always carried out to determine confidence in our acquired data. In the latter part of this activity, you will be introduced to the challenges encountered by an analytical chemist when determining the uncertainity associated with every measurement during a chemical analysis process, in a bid to determine the most probable result. You will be introduced to ways of describing and reducing, if necessary, this uncertainity in measurements through statistical techniques.

Key Concepts

Accuracy: refers to how closely the measured value of a quantity corresponds to its "true" value.

Determinate errors: these are mistakes, which are often referred to as "bias". In theory, these could be eliminated by careful technique.

Error analysis: study of uncertainties in physical measurements.

Indeterminate errors: these are errors caused by the need to make estimates in the last figure of a measurement, by noise present in instruments, etc. Such errors can be reduced, but never entirely eliminated.

Mean (m): defined mathematically as the sum of the values, divided by the number of measurements.

Median: is the central point in a data set. Half of all the values in a set will lie above the median, half will lie below the median. If the set contains an odd number of datum points, the median will be the central point of that set. If the set contains an even number of points, the median will be the average of the two central points. In populations where errors are evenly distributed about the mean, the mean and median will have the same value.

Precision: expresses the degree of reproducibility, or agreement between repeated measurements.

Range: is sometimes referred to as the *spread* and is simply the difference between the largest and the smallest values in a data set.

Random Error: error that varies from one measurement to another in an unpredictable manner in a set of measurements.

Sample: a substance or portion of a substance about which analytical information is sought.

***Sampling*:** operations involved in procuring a reasonable amount of material that is representative of the whole bulk specimen. This is usually the most challenging part of chemical analysis.

Sampling error: error due to sampling process(es).

Significant figures: the minimum number of digits that one can use to represent a value without loss of accuracy. It is basically the number of digits that one is certain about.

Standard deviation (s): this is one measure of how closely the individual results or measurements agree with each other. It is a statistically useful description of the scatter of the values determined in a series of runs.

Variance (s^2): this is simply the square of the standard deviation. It is another method of describing precision and is often referred to as the *coefficient of variation.*

Introduction to the activity

A typical analytical method of analysis comprises seven important stages, namely; *plan of analysis* (involves determination of sample to be analysed, analyte, and level of accuracy needed); *sampling*; *sample preparation* (involves sample dissolution, workup, reaction, etc); *isolation of analyte* (e.g., separation, purification, etc); *measurement of analyte*; standardization of method (instrumental methods need to be standardized inorder to get reliable results); and evaluation of results (statistical tests to establish most probable data). Of these stages, *sampling* is often the most challenging for any analytical chemist: the ability to acquire a laboratory sample that is representative of the bulk specimen for analysis. Therefore, *sampling* is an integral and a significant part of any chemical analysis and requires special attention. Furthermore, we know that analytical work in general, results in the generation of numerical data and that operations such as weighing, diluting, etc, are common to almost every analytical procedure. The results of such operations, together with instrumental outputs, are often combined mathematically to obtain a result or a series of results. How these results are reported is important in determining their significance. It is important that analytical results be reported in a clear, unbiased manner that is truly reflective of the very operations that go into the result. Data need to be reported with the proper number of significant digits and rounded off correctly. In short, at the end of, say a chemical analysis procedure, the analyst is often confronted with the issue of reliability of the measurement or data acquired, hence the significance of the stage of *evaluation of results*, where statistical tests are done to determine confidence limits in acquired data.

In this present activity, procedures and the quantities that describe a distribution of data will be covered and the sources of possible error in experimental measurements will be explored.

Sampling errors

Biased or nonrepresentative sampling and contamination of samples during or after their collection are two sources of sampling error that can lead to significant errors. Now, while selecting an appropriate method helps ensure that an analysis is accurate, it does not guarantee, however, that the result of the analysis will be sufficient to solve the problem under investigation or that a proposed answer will be correct. These latter concerns are addressed by carefully collecting the samples to be analyzed. Hence the import of studying “proper sampling strategies”. It is important to note that the final result in the determination of say, the copper content in an ore sample would typically be a number(s) which indicates the concentration(s) of a compound(s) in the sample.

Uncertainty in measurements

However, there is always some uncertainity associated with each operation or measurement in an analysis and thus there is always some uncertainity in the final result. Knowing the uncertainty is as important as knowning the final result. Having data that are so uncertain as to be useless is no better than having no data at all. Thus, there is a need to determine some way of describing and reducing, if necessary, this uncertainty. Hence the importance of the study of the subtopic of *Statistics*, which assists us in determining the most probable result and provides us the quantities that best describe a distribution of data. This subtopic of *Staistics* will form a significant part of this learning activity.

List of other compulsory readings

Material and Matters (Reading #3)
Measurements and significant figures (Reading #4)
Units and dimensions (Reading #5)
Significant figures (Reading #6)
Significant figures and rounding off (Reading #7)
Measurements (Reading #8)

List of relevant resources

List of relevant useful links

http://www.chem1.com/acad/webtext/matmeasure/mm1.html
Deals with Units of measurements.
http://www.chem1.com/acad/webtext/matmeasure/mm2.html
Deals with measurement error.
http://www.chem1.com/acad/webtext/matmeasure/mm3.html
Deals with significant figures.
http://www.chem1.com/acad/webtext/matmeasure/mm4.html
Deals with testing reliability of data or measurements.
http://www.chem1.com/acad/webtext/matmeasure/mm5.html
Covers useful material on simple statistics.

Detailed description of the actvity

Studying a problem through the use of statistical data analysis often involves four basic steps, namely; (a) defining the problem, (b) collecting the data (c) analyzing the data, and (d) reporting the results. In order to obtain accurate data about a problem, an exact definition of the problem must be made. Otherwise, it would be extremely difficult to gather data without a clear definition of the problem. On collection of data, one must start with an emphasis on the importance of defining the ***population***, *the set of all elements of interest in a study*, about which we seek to make inferences. Here, all the requirements of ***sampling***, *the operations involved in getting a reasonableamount of material that is representative of the whole population,* and experimental design must be met. ***Sampling*** is usually the most difficult step in the entire analytical process of chemical analysis, particularly where large quantities of samples (*a sample is the subset of the population*) to be analysed are concerned. Proper sampling methods should ensure that the sample obtained for analysis is **representative** of the material to be analyzed and that the sample that is analyzed in the laboratory is **homogeneous**. The more representative and homogeneous the samples are, the smaller will be the part of the analysis error that is due to the sampling step. Note that, an analysis cannot be more precise than the least precise operation.

The main idea of statistical inference is to take a random finite sample from a population (since it is not practically feasible to test the entire population) and then use the information from the sample to make inferences about particular population characteristics or attributes such as mean (*measure of central tendency*), the standard deviation (*measure of spread*), or the proportion of items in the population that have a certain characteristic. A sample is therefore the only realistic way to obtain data due to the time and cost contraints. It also saves effort. Furthermore, a sample can, in some cases, provide as much or more accuracy than a corresponding study that would otherwise attempt to investigate the entire population (careful collection of data from a sample will often provide better information than a less careful study that attempts to look at everything). Note that data can be either ***qualitative***, *labels or names used to identify an attribute of each element of the population*, or ***quantitative***, numeric values that indicate how much or how many a particular element exists in the entire population.

Statistical analysis of data: *Assessing the reliability of measurements through simple statistics*

In these modern times, the public is continuously bombarded with data on all sorts of information. These come in various forms such as public opinion polls, government information, and even statements from politicians. Quite often, the public is wonders about the "truth" or reliability of such information, particularly in instances where numbers are given. Much of such information often takes advantage of the average person's inability to make informed judgement on the reliability of the data or information being given.

In science however, data is collected and measurements are made in order to get closer to the "truth" being sought. The reliability of such data or measurements must then be quantitatively assessed before disseminating the information to the stakeholders. Typical activities in a chemistry laboratory involve measurement of quantities that can assume a continuous range of values (e.g. Masses, volumes, etc). These measurements consist of two parts: the reported value itself (never an exactly known number) and the uncertainty associated with the measurement. All such measurements are subject to *error* which contributes to the uncertainty of the result. Our main concern here is with the kinds of errors that are inherent in any act of measuring (not outright mistakes such as incorrect use of an instrument or failure to read a scale properly; although such gross errors do sometimes occur and could yield quite unexpected results).

Experimental Error and Data Analysis

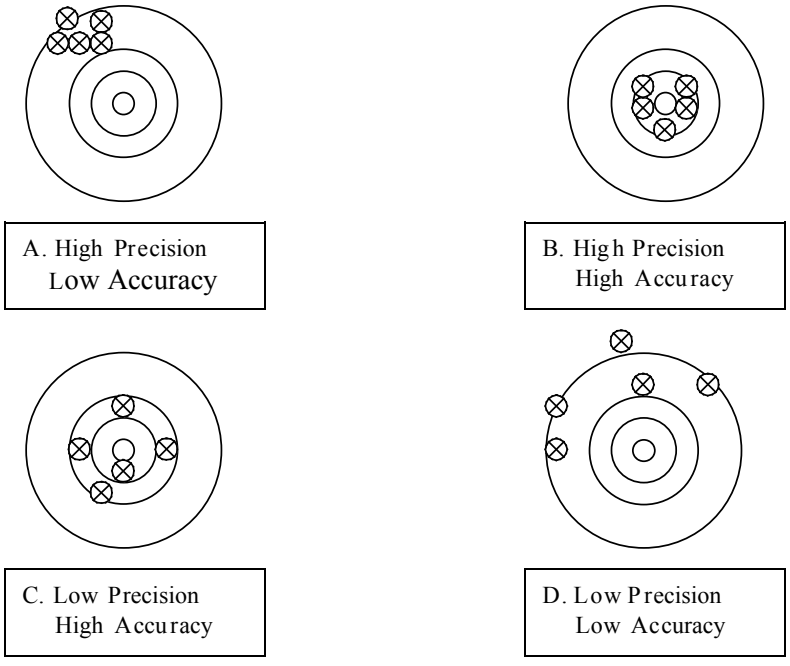
Theory:

Any measurement of a physical quantity always involves some uncertainty or experimental error. This means that if we measure some quantity and then repeat the measurement, we will most certainly obtain a different value the second time around. The question then is: Is it possible to know the true value of a physical quantity? The answer to this question is that we cannot. However, with greater care during measurements and with the application of more experimental methods, we can reduce the errors and, thereby gain better confidence that the measurements are closer to the true value. Thus, one should not only report a result of a measurement but also give some indication of the uncertainty of the experimental data.

Experimental error measured by its *accuracy* and *precision*, is defined as the difference between a measurement and the true value or the difference between two measured values. These two terms have often been used synonymously, but in experimental measurements there is an important distinction between them.

Accuracy measures how close the measured value is to the true value or accepted value. In other words, how correct the measurement is. Quite often however, the true or accepted value of a physical quantity may not be known, in which case it is sometimes impossible to determine the accuracy of a measurement.

Precision refers to the degree of agreement among repeated measurements or how closely two or more measurements agree with each other. The term is sometimes referred to as repeatability or reproducibility. Infact, a measurement that is highly reproducible tends to give values which are very close to each other. The concepts of precision and accuracy are demonstrated by the series of targets shown in the figure below. If the centre of the target is the "true value", then A is very precise (reproducible) but not accurate; target B demonstrates both precision and accuracy (and this is the goal in a laboratory); average of target C's scores give an accurate result but the precision is poor; and target D is neithet precise nor accurate.



It is important to note that no matter how keenly planned and executed, all experiments have some degree of error or uncertainty. Thus, one should learn how to identify, correct, or evaluate sources of error in an experiment and how to express the accuracy and precision of measurements when collecting data or reporting results.

Types of experimental errors

Three general types of errors are encountered in a typical laboratory experiment measurements: random or statistical errors, systematic errors, and gross errors.

Random (or indeterminate) errors arises due to some uncontrollable fluctuations in variables that affect experimental measurements and therefore has no specific cause. These errors cannot be positively identified and do not have a definite measurable value; instead, they fluctuate in a random manner. These errors affect the precision of a measurement and are sometimes referred to as two-sided errors because in the absence of other types of errors, repeated measurements yield results that fluctuate above and below the true value. With sufficiently large number of experimental measurements, an evenly distributed data scattered around an average value or mean is achieved. Thus, precision of measurements subject to random errors can be improved by repeated measurements. Random errors can be easily detected and can be reduced by repeating the measurement or by refining the measurement method or technique.

Systematic (or determinate) errors are instrumental, methodology-based, or individual mistakes that lead to "skewed" data, that is consistently deviated in one direction from the true value. These type of errors arises due to some specific cause and does not lead to scattering of results around the actual value. Systematic errors can be identified and eliminated with careful inspection of the experimental methods, or cross-calibration of instruments.

A ***determinate error*** can be further categorized into two: ***constant determinate error*** *and* ***proportional determinate error***.

Constant determinate error (e_{cd}**)** gives the same amount of error independent of the concentration of the substance being analyzed, whereas **proportional determinate error (**e_{pd}**)** depends directly on the concentration of the substance being analyzed (i.e., $\boldsymbol{e_{pd}} = K\,C$), where K is a constant and C is the concentration of the analyte.

Therefore, the total ***determinate error (*** $\boldsymbol{E_{td}}$***)*** will be the sum of the proportional and constant determinate errors, i.e.,

$$\boldsymbol{E_{td}} = \boldsymbol{e_{cd}} + \boldsymbol{e_{pd}}$$

Gross errors are caused by an experimenter's carelessness or equipment failure. As a result, one gets measurements, ***outliers***, that are quite different from the other sets of similar measurements (i.e., the outliers are so far above or below the true value that they are usually discarded when assessing data. The "***Q-test***" (discussed later) is a systematic way to determine if a data point should be discarded or not.

Example: Classify each of the following as determinate or random error:

(a) Error arising due to the incomplete precipitation of an analyte in a gravimetric analysis.

(b) Error arising due to delayed colour formation by an indicator in an acid-base titration.

Solution:

(a) Incomplete precipitation of an analyte in gravimetric analysis results in a determinate error. The mass of the precipitate will be consistently less than the actual mass of the precipitate.

(b) Delayed color formation by an indicator in an acid-base titration also introduces a ***determinate*** error. Since excess titrant is added after the equivalence point, the calculated concentration of the titrand will be consistently higher than the value obtained by using an indicator which changes color exactly at the equivalence point is used.

Exercise 1: An analyst determines the concentration of potassium in five replicates of a standard water sample with an accepted value for its potassium concentration of 15 ppm by Flame Atomic Emission Spectrophotometry technique. The results he obtained in each of the five analyses in ppm were: 14.8, 15.12, 15.31, 14.95 and 15.03. Classify the error in the analysis described above for the determination of potassium in the standard water sample as determinate or random.

Exercise 2: Classify each of the errors described below as '***constant determinate error***' or '***proportional determinate error***

a) The error introduced when a balance that is not calibrated is used for weighing samples?

b) The error introduced when preparing the same volumes of solutions magnesium ions having different concentrations from a $MgCl_2$ salt that contains 0.5 g Ca^{2+} impurity per 1.0 mol (95 g) of $MgCl_2$?

Expressing and Calculating Experimental Error and Uncertainty

An analyst reporting results of an experiment is often required to include ***accuracy*** and ***precision*** of the experimental measurements in the report to provide some credence to the data. There are various ways of describing the degree of accuracy or presision of data and the common ways are provided below, with examples or illustrations.

Significant Figures: Except in situations where numbers or quantities under investigation are integers (for example counting the number of boys in a class) it is

often impossible to get or obtain the exact value of the quantity under investigation. It is precisely for this reason that it is important to indicate the margin of error in a measurement by clearly indicating the number of *significant figures, which are really the meanigful digits in a measurement or calculated quantity.*

When significant figures are used usually the last is understood to be uncertain.

For example, the average of the experimental values 51.60, 51.46, 51.55, and 51.61 is 51.555. The corresponding standard deviation of the sum is ± 0.069. It is clear from the above that the number in the second decimal place of the experimental values is subject to uncertainty. This implies that all the numbers in succeeding decimal places are without meaning, and we are therefore forced to round the average value accordingly. We must however, consider the question of taking 51.55 or 51.56, given that 51.555 is equally spaced between them. As a guide, when rounding a 5, always round to the nearest even number so that any tendency to round in a set direction is eliminated, since there is an equal likelihood that the nearest even number will be the higher or the lower in any given situation. Thus, we can report the above results as 51.56 ± 0.07.

It is the most general way to show "how well" a number or measurement is known. The proper usage of significant figures becomes even more important in today's world, where spreadsheets, hand-held calculators, and instrumental digital readout systems are capable of generating numbers to almost any degree of apparent precision, which may be much different than the actual precision associated with a measurement.

Illustration:

A measurement of volume using a graduated measuring cylinder with 1-mL graduation markings will be reported with a precision of ± 0.1 mL, while a measurement of length using a meter-rule with 1-mm graduations will be reported with a precision of ± 0.1 mm. The treatment for digital instruments is however different owing to their increased level of accuracy. Infact, most manufacturers report precision of measurements made by digital instruments with a precision of ± 1/2 of the smallest unit measurable by the instrument. For instance, a digital multimeter reads 1.384 volts; the precision of the multimeter measurement is ± 1/2 of 0.001 volts or ± 0.0005 volts. Thus, the significant numbers depend on the quality of the instrument and the fineness of its measuring scale.

To express results with the correct number of significant figures or digits, a few simple rules exist that will ensure that the final result should never contain any more significant figures than the least precise data used to calculate it.

Rules for Significant Figures

We must always be careful in scientific/chemistry work to write the proper number of significant figures. The following rules should help to determine how many significant figures a number has.

- All non-zero digits are significant. Thus 789 km has three significant figures; 1.234kg has four significant figs and so on
- Zeros between non-zero digits are significant. Thus 101 years contains three significant figures, 10,501m contains five significant figures and so on.
- The most significant digit in a reported result is the left-most non-zero digit: 359.742 (3 is the most significant digit). (How does this help to determine the number of significant figures in a measurement? I would rather include this:
- Zeros to the left of the first non-zero digit are not significant. Their purpose is to indicate the placement of the decimal point. For examplle, 0.008L contains one significant figure, 0.000423g contains three significant figures and so on.
- If a number is greater than 1 then all the zeros to the right of the decimal point count as significant figures. Thus 22.0mg has three significant figures; 40.065 has five significant figures. If a number is less than1, then only the zeros that are at the end of the number and the zeros that are between nonzero digits are significant. For example, 0.090 g has two significant figures, 0.1006 m has four significant figures, and so on.
- For numbers without decimal points, the trailing zeros (i.e. zeros after the last nonzero digit) may or may not be significant. Thus 500cm may have one significant figure (the digit 5), two significant figures (50) or three significant figures (500). It is not possible to know hich is correct without more information. By using scientific notation we avoid such ambiguity. We can therefore express the number 400 as 4×10^2 for one significant figure or 4.00×10^{-2} for three significant figures.
- If there is a decimal point, the least significant digit in a reported result is the right-most digit (whether zero or not): 359.742 (2 is the least significant digit). If there is no decimal point present, the right-most non-zero digit is the least significant digit.
- The number of digits between and including the most and least significant digit is the number of significant digits in the result: 359.742 (there are six significant digits).

Exercise 1: Determine the number of significant figures in the following measurements: (a) 478m (b) 12.01g (c) 0.043kg (d) 7000mL (e) 6.023×10^{23}

Note that, the proper number of digits used to express the result of an arithmetic operation (such as addition, subtraction, multiplication, and division) can be obtained by remembering the principle stated above: *that numerical results are reported with a precision near that of the least precise numerical measurement used to generate the number*.

Illustration:

For Addition and subtraction

The general guideline when adding or subtracting numerical values is that the answer should have decimal places equal to that of the component with the least number of decimal places. Thus, 21.1 + 2.037 + 6.13 = 29.267 = 29.3, since component 21.1 has the least number of decimal places.

For Multiplication and Division

The general guideline is that the answer has the same number of significant figures as the number with the fewest significant figures: Thus

$$\frac{56 \times 0.003462 \times 43.72}{1.684} = 4.975740998 = 5.0,$$

since one of the measurements (i.e., 56) has only two significant figures.

Exercise 1: To how many significant figures ought the result of the sum of the values 3.2, 0.030, and 6.31 be reported and what is the calculated uncertainty?

Exercise 2: To how many significant figures ought the result of the operation

$\frac{\left(28.5 \times 27\right)}{352.3}$ be reported and what is the calculated uncertainty?

Percent Error (% Error): This is sometimes referred to as ***fractional difference***, and measures the accuracy of a measurement by the difference between a measured value or experimental value ***E*** and a ***true*** or accepted value ***A***. Therefore

$$\textit{\% Error} = \left(\frac{\left|E - A\right|}{A}\right) \times 100\%$$

Percent Difference (% Difference): This measures precision of two measurements by the difference between the measured experimental values ***E1*** and ***E2*** expressed as a fraction of the average of the two values. Thus

$$\textit{\% Difference} = \left(\frac{|E1 - E2|}{\frac{E1 + E2}{2}} \right) \times 100\%$$

Mean and Standard Deviation

Ordinarily, a single measurement of a quantity is not considered scientifically sufficient to convey any meaningful information about the quality of the measurement. One may need to take repeated measurements to establish how consistent the measurements are. When a measurement is repeated several times, we often see the measured values grouped or scattered around some central value. This grouping can be described with two numbers: a single representative number called the ***mean***, which measures the central value, and the ***standard deviation***, which describes the spread or deviation of the measured values about the ***mean***.

The ***mean*** ($\bar{x}$) is the sum of the individual measurements (x_i) of some quantity divided by the number of measurements (N). The mean is calculated by the formula:

$$\bar{x} = \frac{1}{N}\sum_{i=1}^{N} x_i = \frac{1}{N}\left(x_1 + x_2 + x_3 + ... + x_{N-1} + x_N \right)$$

where $\bar{x}$ is the i^{th} measured value of $\boldsymbol{x}$.

The ***standard deviation*** of the measured values, represented by the symbol, σ_x is determined using the formula:

$$\sigma_x = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left(x_i - \bar{x} \right)^2}$$

The standard deviation is sometimes referred to as the ***mean square deviation***. Note that, the larger the standard deviation, the more widely spread that data is about the mean.

The simplest and most frequently asked question is: "What is the typical value that best represents experimental measurements, and how reliable is it?"

Consider a set of *N (=7)* measurements of a given property (e.g., mass) arranged in increasing order (i.e., x1, x2, x3, x4, x5, x6 and x7). Several useful and uncomplicated methods are available for finding the most probable value and its confidence interval, and for comparing such results as seen above. However, when the number of measurements available ***N*** are few, the ***median*** is often more appropriate than the ***mean***. In addition to the ***standard deviation***, the ***range*** is also used to describe the scatter in a set of measurements or observations. The ***range*** is simply the difference between the largest and the smallest values or observations in a data set. ***Range*** = $x_{max} - x_{min}$, where x_{max} and x_{min} are the largest and smallest observations in a data set, respectively.

The ***median*** is defined as the value that bisects the set of *N* ordered observations, i.e., it is the central point in an ordered data set. If the ***N*** is odd, then (***N*-1**)/2 measurements are smaller than the ***median***, and the next higher value is reported as the median (i.e., the ***median*** is the central point of that set). In our illustration above, the 4th measurement (i.e., x4) would be the ***median***. If the data set contains an even number of points, the ***median*** will be the average of the two central points. If, however, the data set contains an even number of points, the ***median*** will be the average of the two central points.

Example 1: For $N = 6$ and x() = 2, 3, 3, 5, 6, 7; ***median*** = (3+5)/2 = 4; the ***mean*** = (2 + 3 + 3 + 5 + 6 + 7)/6 = 4.33; and the ***range*** = (7 – 2) = 5.

Note: The *median* can thus serve as a check on the calculated mean. In samples where errors are evenly distributed about the mean, the ***mean*** and ***median*** will have the same value. Often ***relative standard deviation*** is more useful in a practical sense than the ***standard deviation*** as it immediately gives one an idea of the level of precision of the data set relative to its individual values.

Relative standard deviation (rel. std. dev.) is defined as the ratio of the standard deviation to the mean. The formula for it evaluation is:

$$\textit{rel. std. dev.} = \sigma_x / \bar{x}$$

The ***standard deviation*** can also be expressed as a percent of the ***mean*** and would then be called the ***percent relative standard deviation*** **(% rel. std. dev.)**.

$$\textit{\% rel. std. dev.} = \textit{rel. std. dev.} \times 100 = (\sigma_x / \bar{x}) \times 100$$

Example 2. Assume that the following values were obtained in the analysis of the weight of iron in 2.0000g portions of an ore sample: 0.3791, 0.3784, 0.3793, 0.3779, and 0.3797 g.

x_i (g)	$(x_i - \bar{x})^2$ $(g)^2$
0.3791	$(0.3791 - 0.37888)^2 = 4.84 \times 10^{-8}$
0.3784	$(0.3784 - 0.37888)^2 = 2.30 \times 10^{-7}$
0.3793	$(0.3793 - 0.37888)^2 = 1.76 \times 10^{-7}$
0.3779	$(0.3779 - 0.37888)^2 = 9.60 \times 10^{-7}$
0.3797	$(0.3797 - 0.37888)^2 = 6.72 \times 10^{-7}$
$\sum x_i = 1.8944$	$\sum \left(x_i - \bar{x} \right)^2 = 2.09 \times 10^{-6}$

The ***mean*** = $\bar{x}$ = 1.8944g / 5 = 0.37888g

The ***standard deviation*** = σ_x = $\{(2.09 \times 10^{-6}\ g^2)/(5-1)\}^{1/2}$ = 0.00072g

The ***variance*** = s^2 = $(2.09 \times 10^{-6}\ g^2)/4 = 5.2 \times 10^{-7}\ g^2$

Rel. std. dev. = s_r = 0.00072g/0.37888g = 0.0019

% Rel. std. dev. = (0.0019) x 100 = 0.19%

To easily see the ***range*** and ***median*** it is convenient to arrange the data in terms of increasing or decreasing values. Thus: 0.3779, 0.3784, 0.3791, 0.3793, and 0.3797 g. Since this data set has an odd number of trials, the ***median*** is simply the middle datum or 3rd datum, 0.3791 g. Note that for a finite data set the ***median*** and ***mean*** are not necessarily identical. The ***range*** is 0.3797 – 0.3779 g or 0.0018.

Example 3. The concentration of arsenic in a standard reference material which contains 2.35 mg/L arsenic was determined in a laboratory by four students (St1, St2, St3, and St4) who carried out replicate analyses. The experimental values as determined and reported by each of student are listed in the table below. Classify the set of results given by the students as: ***accurate***; ***precise***; ***accurate and precise***; and ***neither accurate nor precise.***

Trial No	Concentration of Arsenic (in mg/L)			
	St1	**St2**	**St3**	**St4**
1	2.35	2.54	2.25	2.45
2	2.32	2.52	2.52	2.22
3	2.36	2.51	2.10	2.65
4	2.34	2.52	2.58	2.34
5	2.30	2.53	2.54	2.78
6	2.35	2.52	2.01	2.58
Mean	**2.34**	**2.52**	**2.33**	**2.50**

Solution:

- The set of results as obtained by St1 and St2 (see columns 1 and 2) are close to each other. However, the calculated ***mean*** value of the six trials (the value reported as the most probable value of arsenic concentration in the reference material) as reported by St1 is close to the reported true value of 2.35 mg/L while that of St2 is relatively far from this true value. It can then be concluded that the analytical result reported by ***St1*** is ***both precise and accurate*** while that for St2 is ***precise but not accurate***.
- The set of values from the six trials by students St3 and St4 appear relatively far apart from each other. However, the mean of the analytical results reported by St3 is closer to the true value while that of St4 is not. It can therefore be concluded that the analytical result reported by ***St3*** is ***accurate but not precise***; while that for ***St4*** is ***neither precise nor accurate***.

Reporting the Results of an Experimental Measurement

Results of an experimental measurement by an analyst should always comprise of two parts: The first, is the best estimate of the measurement which is usually reported as the ***mean*** of the measurements. The second, is the variation of the measurements, which is usually reported as the ***standard deviation***, of the measurements. The measured quantity will then be known to have a best estimate equal to the average of the experimental values, and that it lies between ($\bar{x} + \sigma_x$) and ($\bar{x} - \sigma_x$). Thus, any experimental measurement should always then be reported in the form:

$$x = \bar{x} \pm \sigma_x$$

Example 3: Consider the table below which contains 30 measurements of the mass, ***m*** of a sample of some unknown material.

Table showing measured mass in kg of an unknown sample material

1.09	1.14	1.06
1.01	1.03	1.12
1.10	1.17	1.00
1.14	1.09	1.10
1.16	1.09	1.07
1.11	1.15	1.08
1.04	1.06	1.07
1.16	1.12	1.14
1.13	1.08	1.11
1.17	1.20	1.05

For the 30 measurements, the mean mass (in kg) = $\frac{1}{30}(33.04\ \text{kg}) = 1.10\ \text{kg}$

The standard deviation =

$$\sigma_x = \sqrt{\frac{1}{N-1}\sum_{i=1}^{N}\left(x_i - \bar{x}\right)^2} = \sqrt{\frac{1}{30-1}\sum_{i=1}^{30}\left(x_i - 1.10\text{kg}\right)^2} = 0.05\text{kg}$$

The measured mass of the unknown sample is then reported as = 1.10 ± 0.05kg

Statistical Tests

Sometimes a value in a data set appears so far removed from the rest of the values that one suspects that that value (called an ***outlier***) must have been the result of some unknown large error not present in any of the other trials. Statisticians have devised many rejection tests for the detection of non-random errors. We will consider only one of the tests developed to determine whether an outlier could be rejected on statistical rather than arbitrary grounds and it is the ***Q test***. Its details are presented below.

The Q test: Rejecting data.

Note that we can always reject a data point if something is known to be "wrong" with with the data or we may be able to reject outliers if they pass a statistical test that suggests that the probability of getting such a high (or low) value by chance is so slight that there is probably an error in the measurement and that it can be discarded. The statistical test is through the Q test outline below.

The ***Q test*** is a very simple test for the rejection of ***outliers***. In this test one calculates a number called Q_{exp} and compares it with values, termed Q_{crit}, from a table. If $Q_{exp} > Q_{crit}$, then the number can be rejected on statistical grounds. Q_{exp} is calculated as follows:

$$Q_{exp} = \frac{|\text{questionable value - its nearest neighbour}|}{\text{range}}$$

An example will illustrate the use of this test.

Example 4. Suppose that the following data are available: 25.27, 25.32, 25.34, and 25.61. It looks like the largest datum is suspect. Q_{exp} is then calculated.

$Q_{exp} = (25.61 - 25.34)/(25.61\text{-}25.27) = 0.79$

The values of Q_{crit} are then examined in statistical tables. These values depend on the number of trials in the data set, in this case 4. For example, the table below shows the values of Q for rejection of data at the 90% confidence level.

TABLE 4-4 Critical Values for the Rejection Quotient Q^*

	Q_{crit} (Reject if $Q_{exp} > Q_{crit}$)		
Number of Observations	**90% Confidence**	**95% Confidence**	**99% Confidence**
3	0.941	0.970	0.994
4	0.765	0.829	0.926
5	0.642	0.710	0.821
6	0.560	0.625	0.740
7	0.507	0.568	0.680
8	0.468	0.526	0.634
9	0.437	0.493	0.598
10	0.412	0.466	0.568

From: Skoog, West, Holle, "Intro to Analytical Chemsitry," 7th Ed., Thomson Publishing

The values are as follows:

$Q_{crit} = 0.76$ at 90% confidence

$Q_{crit} = 0.85$ at 96% confidence

$Q_{crit} = 0.93$ at 99% confidence

Since $Q_{exp} > Q_{crit}$ at 90% confidence, the value of 25.61 can be rejected with 90% confidence.

What does this mean? It means that in rejecting the datum the experimentalist will be right an average of 9 times out of 10, or that the chances of the point actually being bad are 90%.

Is this the one time out of 10 that the point is good? This is not known! When data are rejected, there is always a risk of rejecting a good point and biasing the results in the process. Since $Q_{exp} < Q_{crit}$ at the 96% and 99% levels, the datum cannot be rejected at these levels. What this says is that if one wants to be right 96 times or more out of 100, one cannot reject the datum. It is up to you to select the level of confidence you wish to use.

Exercise 1: Figure 1 below shows several separate steps involved in a typical total chemical analysis process in a chemical laboratory. Each step of the chemical analysis process has some random error associated with it. It is therefore clear that if a major error is made in any single step of the analysis it is unlikely that the result of the analysis can be correct even if the remaining steps are performed with little error. Discuss and list the possible sources of error an analyst is likely to commit in each of the analytical steps given in figure 1, when determining the concentration of iron in a soil sample spectrophotometrically.

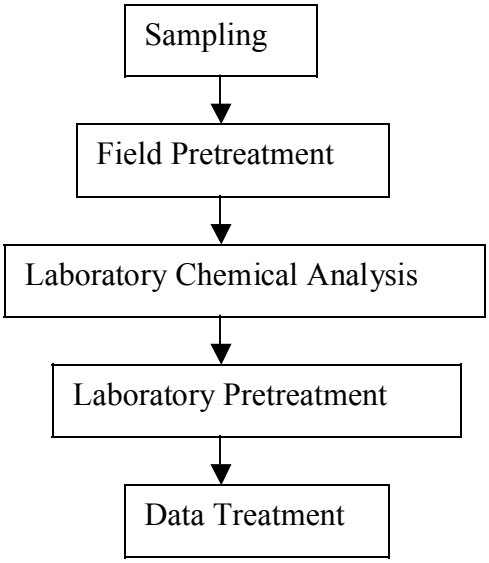


Figure 1. Block diagram of the major steps in a typical total chemical analysis process

Exercise 2: In groups of atleast 2 people, obtain twenty-10 cent coins and determine the weight of each coin separately. Calculate the median, mean, range, standard deviation, relative standard deviation, % relative standard deviation and variance of your measurements.

Exercise 3: Calculate the σ and **s** (a) for each of the first 3, 10, 15 & 20 measurements you carried out in **Exercise 2** to determine the mass of a 10 cents coin. b) compare the difference between the σ and **s** values you obtained in each case and describe your observation on the difference between the two values as the number of replicate analysis increase.

Exercise 4: Using data obtained in **Exercise 2**, determine the percent of your results that fall within the range of one, two, and three standard deviations, i.e., the results within $\mu \pm \sigma$, $\mu \pm 2\sigma$, $\mu \pm 3\sigma$. Based on your findings, can you conclude that the results you obtained in determining the mass of a 10 cents coin (**Exercise 2**) yield a normal distribution curve?

Exercise 5: Refer to your results of **Exercise 3** and (a) calculate the RSD and % RSD for the 3, 10, 15 and 20 measurements (b) compare the values you obtained and give a conclusion on what happens to the RSD and %RSD values as the number of replicate analyses increase.

Exercise 6:

(a) Calculate the variances for the values you obtained in the measurements i) 1 – 5, ii) 6 – 10, iii) 11 – 15, iv) 16 – 20, and v) 1 – 20, in activity 1.
(b) Add the values you found in i, ii, iii, iv and compare the sum with the value you obtained in v.
(c) Calculate the standard deviations for the measurements given in i, ii, iii, iv and v of question a.
(d) Repeat what you did in question 'b' for standard deviation
(e) Based on your findings, give conclusions on the additiveness or non-additiveness of variance and standard deviation.

Problem 7: Compute the mean, median, range, absolute and relative standard deviations for the following set of numbers: 73.8, 73.5, 74.2, 74.1, 73.6, and 73.5.

Problem 8: Calculate the mean and relative standard deviation in ppt of the following data set: 41.29, 41.31, 41.30, 41.29, 41.35, 41.30, 41.28.

Problem 9: A group of students is asked to read a buret and produces the following data set: 31.45, 31.48, 31.46, 31.46, 31.44, 31.47, and 31.46 mL. Calculate the mean and percent relative standard deviation.

Problem 10 : The following data set is available: 17.93, 17.77, 17.47, 17.82, 17.88. Calculate its mean and absolute standard deviation.

Learning activity # 2

Title of Learning Activity : Fundamentals of Volumetric Chemical Analysis, Acid/Base Equilibria & Titrations

Specific Learning Objectives

- Review the concept of chemical equilibria, and in particular ionic equilibria.
- Define and distinguish between acids and bases.
- Distinguish between ***monoprotic*** and ***polyprotic*** acid-base equilibrium.
- Describe and distinguish between weak acid/base dissociations.
- Have a woking knowledge of the fundamentals of volumetric analysis.
- Define and distinguish between ***equivalence*** and ***end point***.
- Use the concept of titration to distinguish between ***blank*** and ***back*** titrations .
- Define ***neutralization reactions*** and explainheir corresponding titration curve structures.
- Define and explain ***standardization***, ***indicators***, and ***primary standards*** and their use
- Use the concept of polyprotic acid equilibria to do related calculations.

Summary of the learning activity

Some of the most important processes in chemical and biological systems are acid-base reactions in aqueous solutions. At the onset of this unit, a review of the topic of acid-base equilibria, together with the properties of acids and bases is undertaken. This is because the concepts of ionic equilibria and reactions are important for a better understanding of the ideas and workings of acid-base ***neutralization titrations***. This unit discusses the basic principles of titrimetric analytical methods, and the use of the equivalence concept in quantitative titration methods. The latter part of this unit will provide you with the opportunity to carry out simple acid-base titration reactions and calculations as well as demonstrations of simulated acid-base titrations.

Key Concepts

Arrhenius Acid: A substance that yields hydrogen ions (H^+) when dissolved in water.

Arrhenius Base: A substance that yields hydroxide ions (OH^-) when dissolved in water.

Bronsted acid : A substance capable of donationg a proton.

Bronsted base: A substance capable of accepting a proton.

Chemical Equilibrium: A state in which the rates of the forward and reverse reactions are equal.

Chemical Reaction: A process in which a substance (or substances) is changed into one or more new substances.

End point: The volume of titrant required for the detection of the equivalence point.

Equilibrium constant: A number equal to the ratio of the equilibrium concentrations of products to the equilibrium concentrations of reactants, each raised to the power of its stoichiometric coefficient.

Equivalence point: The point at which the acid has completely reacted with or been neutralized by the base.

Indicators: Substances that have distinctly different colours in acidic and basic media.

Molar solubility: The number of moles of solute in one litre of a saturated solution (mol/L)

Monoprotic acid: Each unit of the acid yields one hydrogen ion upon ionization.

Neutralization reaction: A reaction between an acid and a base.

Precipitation reaction: A reaction that results in the formation of a precipitate.

Primary Standard: a high purity compound used to prepare the standard solution or to standardize the solution with.

Quantitative analysis: The determination of the amount of substances present in a sample.

Secondary Standard: a second material used as a substitute for a suitable primary standard. This standard solution should always be standardized using a primary standard.

Solubility product, K_{sp}: The equilibrium constant for the reaction in which a solid salt dissolves to give its constituent ions in solution. It expresses the equilibrium between a solid and its ions in solution.

Standardization: The process by which the concentration of a solution is determined.

Standard Solution: A solution of accurately known concentration.

Stoichiometry: The quantitative study of reactants and products in a chemical reaction.

Stoichiometric amounts: The exact molar amounts of reactants and products that appear in the balanced chemical equation.

Strong acids: Strong electrolytes which are assumed to ionize completely in water.

Strong bases: Strong electrolytes which are assumed to ionize completely in water.

Titration: The gradual addition of of a solution of accurately known concentration to another solution of unknown concentration until the chemical reaction between the two solutions is complete.

Volumetric methods of analysis:based on the measurement of the amount of reagent that combines with the analyte. The terms volumetric analysis specifically involves the determination of the volume of the reagent solution needed for a complete reaction.

Volumetric titrimetry: methods that require that a reagent solution of known concentration, *standard solution or titrant*, be used.

Introduction to activity # 2

The thrust of this unit deals primarily with the fundamentals of volumetric methods of analysis. Volumetric method of analysis or sometimes referred to as titrimetric method of analysis is a quantitative method of analysis that is based upon the measurement of volume. These methods are considered important since they are usually rapid, convenient and are often accurate. The concept of pH and the pH scale, the ionization of weak acids and weak bases are introduced and discussed at length. Also, the unit looks at the relationship between acid strength and molecular structure.

List of other compulsory readings

Chemical equilibria (Reading #9)
Introduction to acid-base chemistry (Reading #10)
Acid-Base equilibria and Calculations (Reading #11)
Acid-base equilibria of aquatic environment (Reading #12)

A reference text with file with sub-sections containing sample problems dealing with acids and bases, chemical equilibrium, quantitative calculations in acids and bases (Reading #13).

Acid Base (Reading #14)

Bronsted-Lowry Acid-Base Reactions (Reading #15)

Chemistry Chapter 16 Complex Ions (Reading #16)

Chemistry Chapter 16 Hydrolysis of Bases (Reading #17)

Chemistry Chapter 16 Titrations (Reading #18)

Chemistry Chapter 16 Hydrolysis of Acids (Reading #19)

Chemistry Chapter 16 Autoionization of Water (Reading #20)

Addition of Strong Base to a weak Acid (Reading #21)

pH curves (titration curves) (Reading #22)

Titration of a Weak Acid with a Strong Base (Reading #23)

List of relevant resources

List of relevant useful links :

http://antoine.frostburg.edu/chem/senese/101/acidbase/glossary.shtml

An Online resource for a more comprehensive chemistry glossary of terms for acid and base chemistry with corresponding brief definitions and hyperlinks to related terms.

http://www.wwnorton.com/chemistry/concepts/ch16.htm

An Online resource dealing with “Equilibrium in the Aqueous Phase and Acid Rain”

http://www.wwnorton.com/chemistry/concepts/chapter 16/ch16_7.htm#1

An Online resource dealing with “Volume at the equivalence point”

http://www.wwnorton.com/chemistry/concepts/chapter 16/ch16_7.htm#2

An Online resource dealing with “Sketching the titration curve (Qualitative titration curves)”

http://www.wwnorton.com/chemistry/concepts/chapter 16/ch16_1.htm#1

An Online resource dealing with “Identifying acids and Bases”

http://www.wwnorton.com/chemistry/concepts/chapter 16/ch16_1.htm#2

An Online resource dealing with “Conjugate acids and Bases”

http://www.wwnorton.com/chemistry/concepts/chapter 16/ch16_4.htm#1

An Online resource dealing with “Strong acids”

http://www.wwnorton.com/chemistry/concepts/chapter 16/ch16_4.htm#2

An Online resource dealing with “Strong bases”

http://www.chemguide.co.uk/physical/acideqiamenu.html#top

An Online resource MENU on “ACID-BASE EQUILIBRIA” with very useful links.

Detailed description of the activity

Review of General concepts and Principles of Chemical Equilibria:

The concept of equilibrium is extremely important in chemistry. For example, an industrial chemist who wants to maximize the yield of sulphuric acid, must have a clear understanding of the equilibrium constants for all the steps in the process, starting from the oxidation of sulphur as a reactant and ending with the formation of the final product.

For a "general" reaction at equilibrium, we write:

$$aA + bB \Leftrightarrow cC + dD$$

where the double arrow, $\Leftrightarrow$, is used to indicate that the chemical reaction proceeds in both directions. Dynamic equilibrium is said to occur when the rate of the forward reaction (represented by the chemical reaction, $aA + bB \rightarrow cC + dD$, which implies that *a* moles of substance A reacts with *b* moles of substance B to form *c* moles of C and *d* moles of D) equals the rate of the reverse reaction represented by the chemical reaction $cC + dD \rightarrow aA + bB$, which again implies that *c* moles of substance C reacts with *d* moles of substance D to form *a* moles of A and *b* moles of B).

At equilibrium, when there is no net change in any of the concentrations of the materials involved in that reaction over time,

$$K_{eq} = \frac{[C]^c[D]^d}{[A]^a_{eq}[B]^b_{eq}}$$

where the K_{eq} is the ***equilibrium constant*** and the square brackets, [ ], indicate a concentration of a species relative to the ***standard state*** for that particular phase at equilibrium. The standard state and their standard concentrations are:

[solutes] = mol/L; [gases] = atmospheres (atm) and [pure liquids], [pure solids], and [solivents] = unity.

NOTE: For most calculations required for this module, it is sufficient to remember that the molar concentrations are to be used in the equilibrium expressions.

Types of Equilibria:

There are 4 main types of chemical equilibria that will be discussed in this module:

(i) Solubility Equilibria
(ii) Acid-Base Equilibria
(iii) Oxidation/Reduction Equilibria and
(iv) Complex ion Formation Equilibria

In this unit, our discussions will be limited to solubility and acid-base equilibria. The latter two equilibria types will be dealt with in the subsequent two units of this module.

Solubility Equilibria: In solubility equilibrium, (see equation below) ***a*** moles of the analyte *A* reacts with ***r*** moles of the reagent, *R*, to form an insoluble species, A_aR_r. Recall that the ***standard state*** for a solid solution is unity (i.e., x = 1). The solid precipitate is assumed to be pure, thus has *x* =1. Thus, because of this, the concentration of A_aR_r **(s)** does not appear in the solubility product expression given below.

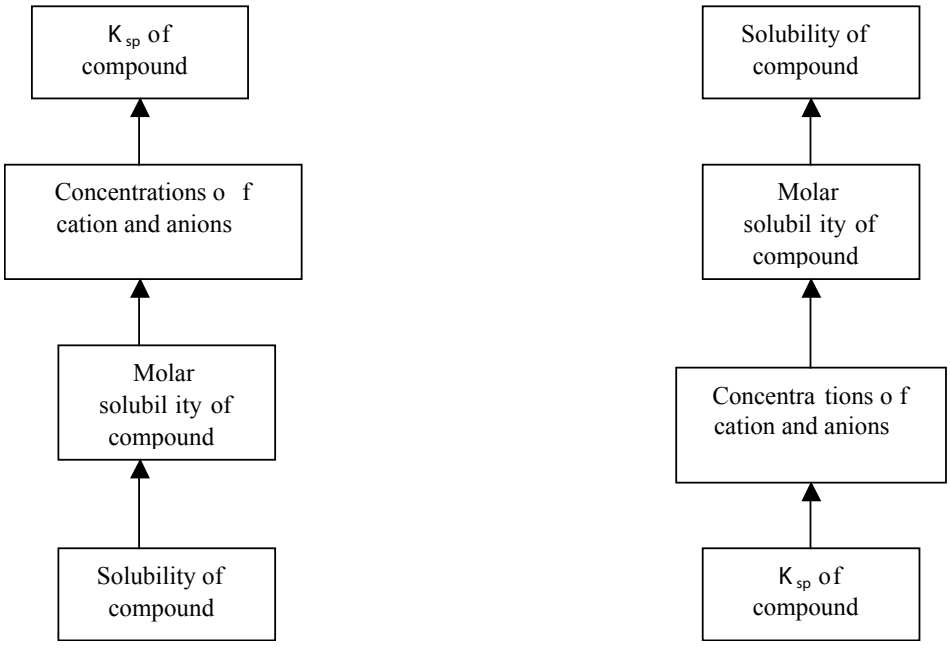
$$aA(aq) + rR(aq) \Leftrightarrow A_aR_x(s)$$

$$K_{sp} = [A]^a[R]^r$$

where K_{sp} is defined as the solubility product constant.

The sequence of steps for (a) calculating K_{sp} from solubility data and (b) calculating solubility from K_{sp} data are given in the figure below:

Here, ***molar solubility***, is *the number of moles of solute in 1 L of a standard solution (mol/L)*, and solubility, which is the number of grams of solute in 1 L of a saturated solution (g/L). Note that both of these expressions refer to the concentration of saturated solutions at some given temperature (usually 25°C).



Example 1. Consider the reaction in which a solid salt of mercury chloride dissolves in water to give its constituent ions in solutions as shown below:

$$Hg_2Cl_2(s) \rightleftharpoons Hg_2^+(aq) + 2Cl^-(aq)$$

If the solubility product, K_{sp} is 1.2 x 10^{-18}, then

$Hg_2Cl_2(s) \rightleftharpoons$	$Hg_2^+(aq)$	$+ 2Cl^-(aq)$
Initail Conc.	**0**	**0**
Final Conc.	**x**	**2x**

where ***x*** equals solubility only if there is little ion-pair formation. Therefore,

$$\boldsymbol{K_{sp}} = 1.2 \times 10^{-18} = [Hg_2^{2+}]\,[Cl^-]^2$$

This implies that: $[Hg_2^{2+}]\,[Cl^-]^2 = 1.2 \times 10^{-18}$. Thus, $(x)\,(2x^-)^2 = 1.2 \times 10^{-18}$

Therefore, the solubility x = 6.7 x 10-7 M.

Since some dissolved Hg_2Cl_2 may not dissociate into free ion, we say that its solubility is at least 6.7×10^{-7} M.

Example 2: The solubility of calcium sulphate ($CaSO_4$) is found to be 0.67 g/L. Calculate the value of K_{sp} for calcium sulphate.

Solution:

Please note that we are given the solubility of $CaSO_4$ and asked to calculate its $\boldsymbol{K_{sp}}$. The sequence of conversion steps, according to the Figure above is:

Solubility of $CaSO_4$	→ Molar Solubility of $CaSO_4$	→ $[Ca^{2+}]$ and $[SO_4^{2-}]$	→ $\boldsymbol{K_{sp}}$ of $CaSO_4$

Now consider the dissociation of $CaSO_4$ in water. Let ***s*** be the molar solubility (in mol/L) of $CaSO_4$.

$$CaSO_4\ (s) \rightleftharpoons [Ca^{2+}]\ (aq) + SO_4^{2-}\ (aq)$$

Initial (M):		0	0
Change (M):	-s	+s	+s
Equilibrium (M):		s	s

The solubility product of $CaSO_4$ is:

$$K_{sp} = [Ca^{2+}]\,[SO_4^{2-}] = S^2$$

First, we calculate the number of moles of $CaSO_4$ dissolved in 1 L of solution.

$$\frac{0.67\text{g } CaSO_4}{1\text{L solution}} \times \frac{1\text{mol } CaSO_4}{136.2\text{ g } CaSO_4} = 4.9\times10^{-3}\text{ mol / L} = s$$

From the solubility equilibrium we see that for every mole of $CaSO_4$ that dissolves, 1 mole of Ca^{2+} and 1 mole of SO_4^{2-} are produced. Thus, at equilibrium

$[Ca^{2+}] = 4.9 \times 10^{-3}$ M and $[SO_4^{2-}] = 4.9 \times 10^{-3}$ M

Now we can calculate K_{sp}:

$$\begin{aligned} K_{sp} &= [Ca^{2+}]\,[SO_4^{2-}] \\ &= (4.9 \times 10^{-3})\,(4.9 \times 10^{-3}) \\ &= 2.4 \times 10^{-5} \end{aligned}$$

Exercise 1: The solubility of lead chromate ($PbCrO_4$) is 4.5 x 10-5 g/L. Calculate the solubility product of this compound.

Acid-Base Equilibria

Theory of Acids and Bases (Arrhenius and Bronsted-Lowry Theories):

According to the Arrhenius Theory of Acids*:* All acids contain H^+ ions and **All** bases contain OH^- ions; and that an acid-base reaction involves the reaction of hydrogen and hydroxide ions to form water. The corresponding equation is as below:

$$H^+ (aq) + OH^- (aq) \rightarrow H_2O (i)$$

Where (***aq***) stands for aqueous phase in which the species exists and ***l***, the liquid phase.

Problems with *Arrhenius Theory* are two-fold:

(i) Theory requires bases to have an OH^- group. However, we know that ammonia (whose structural formula is NH_3) does not contain the OH-group but is nonetheless a base.
(ii) Theory does not consider the role of the solvent water, H_2O.

These shortcomings are overcome by the *Bronsted-Lowry Theory*.

Bronsted-Lowry Theories on acids and bases:

Acid*:* An acid as any substance that can donate a proton to a base.

HA	+	H_2O	$\rightarrow$	A^-	+	H_3O^+
acid		base		conjugate base of HA		conjugate acid of H_2O

Base: A base is any substance that can accept a proton from an acid.

NH_3	+	H_2O	$\rightarrow$	NH_4^+	+	OH^-
base		acid		conjugate acid		conjugate base

We now recognize that NH_3 acts as a base (proton acceptor) because of its role as a hydrogen atom acceptor in the reaction and H_2O acts as an acid (proton donor). Moreover, H_2O is now included as a solvent in our consideration. The ***conjugate acid*** of NH_3 is NH_4^+ while the ***conjugate base*** of water in the reaction is OH^-. NH_4^+/NH_3 are referred to as ***conjugate acid/base pair***.

In these two examples, water has acted as either an acid or a base, hence a unique solvent. This is one of the Hence it is called water is called an ***amphiprotic*** solvent. It undergoes self ionization in a process called (autoprotolysis) as shown below:

$$H_2O + H_2O \leftrightarrow H_3O^+ + OH^-$$

In the study of acid-base reactions, the hydrogen ion concentration is key; its value indicates the acidity or basicity of the solution. In pure water, only 1 water in 10^7 undergoes autoprotolysis. This implies that only a very small fraction of water molecules are ionized, hence the concentration of water, $[H_2O]$, remains virtually unchanged. Therefore, the equilibrium constant for the autoionization of water according to the immediate above equation is

$$\boldsymbol{K}_c = [H_3O^+][OH^-]$$

And because we use H^+ (aq) and H_3O^+ (aq) interchangeably to represent the hydrated proton, the equilibrium constant can also be expressed as

$$\boldsymbol{K}_c = [H^+][OH^-]$$

To indicate that the equilibrium constant refers to the autoionization of water, we replace $\boldsymbol{K}_c$ by $\boldsymbol{K}_w$

$$\boldsymbol{K}_w = [H_3O^+][OH^-] = [H^+][OH^-]$$

Where is the ***ion-product constant***, which is the product of the molar concentrations of H^+ and OH^- ions at a particular temperature.

In pure water at 25°C, the concentrations of H^+ and OH^- ions are equal and found to be $[H^+] = 1.0 \times 10^{-7}$ M and $[OH^-] = 1.0 \times 10^{-7}$ M. From the above equation

$$\boldsymbol{K}_w = (1.0 \times 10^{-7}\ M)\ (1.0 \times 10^{-7}\ M) = 1.0 \times 10^{-14}$$

Note that, whether we have pure water or an aqueous solution of dissolved species, the following relation always holds at 25°C:

$$\boldsymbol{K}_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

Whenever $[H^+] = [OH^-]$, the aqueous solution is said to be neutral. In an acidic solution, there is an excess of H^+ ions and $[H^+] > [OH^-]$. In a basic solution, there is an excess of hydroxide ions, so $[H^+] < [OH^-]$. In practice, we can change the concentration of either H^+ or OH^- ions in solution, but we cannot vary both of them independently. If we adjust the solution so that $[H^+] = 1.0 \times 10^{-6}$ M, the OH^- concentration must change to

$$[OH^-] = \frac{K_w}{[H^+]} = \frac{1.0x10^{-14}}{1.0x10^{-6}} = 1.0x10^{-8}\ M$$

Example: Calculate the concentration of H^+ ions in a certain cleaning solution if the concentration of OH^- ions is 0.0025 M.

Solution:

We are given the concentration of the OH^- ions and asked to calculate $[H^+]$. We also know that $\boldsymbol{K_w} = [H^+][OH^-] = 1.0 \times 10^{-14}$. Hence, by rearranging the equation,

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0x10^{-14}}{0.0025} = 4.0x10^{-12}\ M$$

Exercise 1: Calculate the concentration of OH^- ions in a HCl solution whose hydrogen ion concentration is 1.4×10^{-3} M.

pH as a measure of acidity:

The ***pH*** of a solution is defined as the negative logarithm of the hydrogen ion concentration (in mol/L).

$pH = -\log [H_3O^+]$ or $pH = -\log [H^+]$

Note that because pH is simply a way of expressing hydrogen ion concentration, acidic and basic solutions at 25°C can be distinguished by their pH values, as follows:

Acidic solutions: $[H+] > 1.0 \times 10^{-7}$ M, pH < 7.00

Basic solutions: $[H+] < 1.0 \times 10^{-7}$ M, pH > 7.00

Neutral solutions: $[H+] = 1.0 \times 10^{-7}$ M, pH = 7.00

Note that pH increases as $[H^+]$ decreases.

Now, taking the negative logarithm of both sides of the expression $[H^+][OH^-] = 1.0 \times 10^{-14}$

yields the expression,

$$-\log ([H^+][OH^-]) = -\log (1.0 \times 10^{-14})$$

$$-(\log ([H^+]) + \log ([OH^-]) = -\log (1.0 \times 10^{-14})$$

$$-\log ([H^+]) - \log ([OH^-]) = 14.00$$

From the definitions of pH and pOH we obtain

$$pH + pOH = 14.00$$

This expression provides us with another way of showing the relationship between the H^+ ion concentration and the OH^- ion concentration.

Example: The pH of a rain water sample collected in the Western Province of Kenya on a particular day was found to be 4.82. Calculate the H^+ ion concentration of the rain water.

Solution: We know that $pH = -\log [H^+] = 4.82$

Therefore, $\log [H^+] = -4.82$

This implies that $[H^+] = \text{antilog } (-4.82)$

Therefore, $[H^+] = 10^{-4.82} = 1.5 \times 10^{-5}$ M.

Exercise 1: If the pH of a mixture of orange and passion juice is 3.30, calculate the H^+ ion concentration.

Exercise 2: Calculate the hydrogen ion concentration in mol/L for solutions with the following pH values: (a) 2.42, (b) 11.21, (c) 6.96, (d) 15.00

Base/Acid Ionization Constant:

In the reaction below,

NH_3	+	H_2O	$\rightleftharpoons$	NH_4^+	+	OH^-
base		acid		conjugate acid		conjugate base

we can write the following equilibrium expression, called the base ionization constant, K_b.

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8x10^{-5}$$

Note that water does not explicitly appear in the equilibrium expression because the reaction is taking place in water (water being the solvent). It is important to note that the larger the K_b, the stronger the base. Since NH_3 is a known weak base, there will be a reasonable amount of unreacted NH_3 in solution when equilibrium is established. Hence the low value of its K_b.

Strength of Acids and Bases

Strong acids are assumed to ionize completely in water. Examples of strong acids are hydrochloric acid (HCl), nitric acid (HNO_3), perchloric acid ($HClO_4$) and sulphuric acid (H_2SO_4). Most acids are ***weak acids***, which *ionize only to a limited extent in water*.

Strong bases ionize completely in water. Examples of strong bases are Hydroxides of alkali metals (e.g., NaOH, KOH, etc).

Dissociation of Weak acids and Bases:

Weak Acids:

If ***HA*** is a weak acid, then

$$HA + H_2O \leftrightarrow H_3O^+ + A^-$$

$$K_A = \frac{[H_3O^+][A^-]}{[HA]}$$

Weak Bases:

If ***B*** is a weak base, then

$$B + H_2O \leftrightarrow BH^+ + OH^-$$

$$K_B = \frac{[OH^-][BH^+]}{[B]}$$

Note that water is not included in both expressions because it is a constant.

Example: Determine the pH of a 0.10 M acetic acid solution, if the acid dissociation constant, K_A is 2.24 x 10^{-5}.

Solution:

We need to know that acetic acid is a weak acid which will only ionize to a limited extent. This can be represented by the equilibrium reaction below:

$$HAc + H_2O \rightleftharpoons H_3O^+ + Ac^-$$

where ***HAc*** represents the weak acetic acid.

$$K_A = \frac{[H_3O^+][A^-]}{[HA]} = 2.24x10^{-5}$$

Since both a H_3O^+ and a A^- is produced for each ***HA*** that dissociates:

$$[H_3O^+] = [A^-]$$

Also,

$$[HA] = 0.10\ M - [H_3O^+]$$

Suppose $y = [H_3O^+]$, then

$$K_A = 2.24 \times 10^{-5} = y^2 / (0.10-y)$$

Rearranging yields a quadratic equation of the form: $y^2 + 2.24 \times 10^{-5}\ y - 2.24 \times 10^{-6} = 0$

Note that this quadratic equation can be solved

(using $y = \frac{-b \pm \sqrt{(b^2 - 4ac)}}{2a}$) or the solution can be estimated by assuming that the amount of acid dissociated is insignificant when compared with the undissociated form (***HAc***).

Let us try the exact solution using $y = \frac{-b \pm \sqrt{(b^2 - 4ac)}}{2a}$:

$y = [-2.24 \times 10\text{-}5 + \{(2.24 \times 10^{-5})^2 - (4 \times 2.24 \times 10^{-6})\}^{1/2}]/2$

$y = 0.00149$

Therefore, pH = -log (0.00149) = 2.82

Exercise 1: The K_a for benzoic acid is 6.5 x 10-5. Calculate the pH of a 0.10 M benzoic acid solution.

Exercise 2: The pH of an acid solution is 6.20. Calculate the K_a for the acid. The initial acid concentration is 0.010 M.

Dissociation of Weak bases:

The calculations are essentially the same as for weak acids. The important expression to remember is:

$$pH + pOH = pK_W = 14.00$$

Also, it can be shown that $pK_A + pK_B = 14.00$, where $pK_A = -\log (K_A)$

Note the following:

- If you are starting with an acid, acidic conditions or the conjugate acid of a base, then perform your calculations using K_A.
- If starting with a base, basic conditions or the conjugate base of an acid, then do your calculations using K_B.
- You can readily convert pH to pOH (i.e., pH + pOH = 14.00) and K_A to K_B (i.e., $pK_A + pK_B = 14.00$) values.

Fundamentals of Volumetric Analysis

Volumetric or titrimetric analyses are quantitative analytical techniques which employ a ***titration*** in comparing an unknown with a standard. In a **titration**, a measured and controlled volume of a ***standardized solution***, a *solution containing a known concentration of reactant «A»* from a buret is added incrementally to a sample solution of known volume (measured by a pipete) containing a substance to be determined (*analyte*) of unknown concentration of reactant «B». The titration proceeds until reactant «B» is just consumed (*stoichiometric completion*). This is known as the *equivalence point*. (The titration is complete when sufficient titrant has been added to react with all the analyte.) At this point the number of *equivalents* of «A» added to the unknown equals the number of equivalents of «B» originally present in the unknown.

An ***indicator***, a *substance that have distinctly different colours in acidic and basic media*, is usually added to the reaction flask to signal when and if all the analyte has reacted. The use of indicators enables the end point to be observed. In this, the titrant reacts with a second chemical, the ***indicator***, after completely reacting with the analyte in solution. The indicator undergoes a change that can be detected (like colour). The titrant volume required for the detection of the equivalence point is called the ***end point***. Note that the **end point** and **equivalence point** are seldomly the same. Ideally, we want the ***equivalence point*** and the ***end point*** to be the same. This seldom happens due to the methods used to observe end points. As a result, we get a ***titration error***, *the difference between the end point and the equivalence point*, which leads to ***overtitration***.

The ***end point*** is then the point where sufficient indicator has been converted for detection. The sequence of events can be demonstrated as below:

$$\text{Analyte} + \text{titrant} \xrightarrow[\text{addition}]{\text{stoichiometric}} \text{equivalence point}$$

followed by

$$\text{Indicator} + \text{titrant} \longrightarrow \text{reacted indicator}$$

1^{st} indicator color 1 2^{nd} colour product

Note: The last step does NOT require that all indicator be converted. Infact, it is best if a very small percent need to be reacted to make the colour change visible.

For volumetric methods of analysis to be useful, the reaction must reach 99%+ completion in a short period of time. In almost all cases, a *burette* is used to measure out the *titrant*. When a titrant reacts directly with an analyte (or with

a reaction the product of the analyte and some intermediate compound), the procedure is termed a ***direct titration***. The alternative technique is called a ***back titration***. Here, an intermediate reactant is added in excess of that required to exhaust the analyte, then the exact degree of excess is determined by subsequent titration of the unreacted intermediate with the titrant. Regardless of the type of titration, an ***indicator*** is always used to detect the ***equivalence point***. Most common are the ***internal indicators***, *compounds added to the reacting solutions that undergo an abrupt change in a physical property (usually absorbance or color) at or near the equivalence point*. Sometimes the analyte or titrant will serve this function (auto indicating). ***External indicators***, electrochemical devices such as pH meters, may also be used. Ideally, titrations should be stopped precisely at the ***equivalence point***. However, the ever-present random and systematic error, often results in a titration ***endpoint***, *the point at which a titration is stopped*, that is not quite the same as the ***equivalence point***. Fortunately, the systematic error, or bias may be estimated by conducting a ***blank titration***. In many cases the titrant is not available in a stable form of well-defined composition. If this is true, the titrant must be ***standardized*** (usually by volumetric analysis) against a compound that is available in a stable, highly pure form (i.e., a primary standard).

Note that by accurately measuring the volume of the titrant that is added (using a buret), the amount of the sample can be determined.

For a successful titrimetric analysis, the following need to be true:

- The titrant should either be a standard or should be standardized.
- The reaction should proceed to a stable and well defined equivalence point.
- The equivalence point must be able to be detected.
- The titrant's and sample's volume or mass must be accurately known.
- The reaction must proceed by a definite chemistry. There should be no complicating side reactions.
- The reaction should be nearly complete at the equivalence point. In other words, chemical equilibrium should favour the formation of products.
- The reaction rate should be fast enough to be practical.

Illustration: In the determination of chloride, 50 ml of a 0.1M $AgNO_3$ solution would be required to completely react with 0.005 moles of chloride present in solution.

$Cl^-_{(aq)}$	+	$Ag^+_{(aq)}$	$\xrightarrow{\text{Titration}}$	$AgCl_{(s)}$
Analyte of		titrant ($AgNO_3$)		
unknown		- a standard		
concentration		- known concentration		

Balanced Equation for the reaction: $Ag^+(aq) + Cl^-(aq) \rightarrow AgCl(s)$. Here, 1 mole of Ag^+ ions reacts stoichiometrically with 1 mole of Cl^- ions. Therefore 50 ml (0.05L) of a standard 0.10 M $AgNO_3$ which contains 0.005 moles (= 0.10 moles L^{-1} x 0.050 L) requires an equivalent number of moles of Cl^- ions.

Note: Since the titrant solution must be of known composition and concentration, we ideally would like to start with a ***primary standard material***, *a high purity compound used to prepare the* ***standard solution*** *or to standardize the solution with.* A ***standard solution*** is one whose concentration is known. The concentration of a ***standard solution*** is usually expressed in molarity (mole/liter). The process by which the concentration of a solution is determined is called ***standardization***. Because of the availability of some substances known as ***primary standards***, in many instances the standardization of a solution is not necessary. Primary standard solutions are analytically pure, and by dissolving a known amount of a primary standard in a suitable medium and diluting to a definite volume, a solution of known concentration is readily prepared. Most standard solutions, however, are prepared from materials that are not analytically pure and they have to be standardized against a suitable primary standard.

The following are the desired requirements of a ***primary standard***:

- High purity
- Stable in air and solution: composition should be unaltered in the air at ordinary or moderately hgh temperatures.
- Not hygroscopic.
- Inexpensive
- Large formula weight: equivalence weight ought to be high in order to reduce the effects of small weighing error.
- Readily soluble in the solvent under the given conditions of the analysis.
- On titration, no interfering product(s) should be present.
- The primary standard should be colorless before and after titration to avoid interference with indicators.
- Reacts rapidly and stoichiometrically with the analyte.

The following are also the desired requirements of a ***primary standard solution***:

- Have long term stability in solvent.
- React rapidly with the analyte.
- React completely with analyte.
- Be selective to the analyte.

The most commonly used primary standards are:

A. Acidimetric standards.

Sodium carbonate (Na_2Co_3, equivalent weight 53.00) and Borax ($Na_2B_4O_7.10H_2O$,equivalent weight 63.02)

B. Alkalimetric standards.

Sulphamic acid ($NH_2\ SO_3H$, equivalent weight 97.098),

Potassium hydrogenphthalate ($KHC_8H_2O_4$, equivalent weight 204.22)

Oxalic acid ($H_2C_2O_4.2H_2O$,Equivalent weight 63.02)

This is a second material used As a substitute for a suitable ***primary standard***, a ***secondary standard*** are often used as a second material. However, the ***standard solution*** should always be standardized using a primary standard.

Exercise 1: *Discuss the following analytical terms: Standard solution; Primary standards; Standardized solution; Standardization; End point of titration; Equivalence point of titration; and Titration error*

Summary:

The basic requirements or components of a volumetric method are:

(a) A standard solution (i.e., titrant) of known concentration which reacts with the analyte in a known and repeatable stoichiometry (i.e., acid/base, precipitation, redox, complexation).
(b) A device to measure the mass or volume of sample (e.g., pipet, graduated cylinder, volumetric flask, analytical balance).
(c) A device to measure the volume of the titrant added (i.e., buret).
(d) If the titrant-analyte reaction is not sufficiently specific, a pretreatment to remove interferents.
(e) A means by which the endpoint can be determined. This may be an internal indicator (e.g., phenolphthalein) or an external indicator (e.g., pH meter).

Apparatus for titrimetric analysis:

The most common apparatus used in volumetric determinations are the pipette, buret, measuring cylinder, volumetric and conical (titration) flask. Reliable measurements of volume is often done with the help of a pipet, buret, and a volumetric flask. The conical flask is preferred for titration because it has a good "mouth" that minimizes the loss of the titrant during titration.

Classification of reactions in volumetric (titrimetric) analysis

Any type of chemical reactions in solution should theoretically be used for titrimetric analysis. However, the reactions most often used fall under two main categories:

(a) Those in which no change in oxidation state occurs. These are dependent on combination of ions.

(b) Oxidation-reduction reactions: These involve a change of oxidation state (i.e., the transfer of electrons).

For convenience, however, these two types of reactions are further divided into four main classes:

(i) Neutralization reactions or acidimetry and alkalimetry:
$HA + B \rightleftharpoons HB^+ + A^-$

(ii) Precipitation reactions: $M(aq) + nL(aq) \rightleftharpoons ML_n(s)$

(iii) Oxidation-reduction reactions: $Ox + Red \rightleftharpoons Red' + ox'$

(iv) Complex ion formation reactions: $M(aq) + nL(aq) \rightleftharpoons ML_n(aq)$

In this unit, we shall focus on neutralization reactions. The latter two will be dealt with in the next two units that follow in this module.

General Theory of Titrations

In determining what happens during a titration process, some of the theories of chemical equilibria (previously covered in this unit as well as in an earlier Module entitled General Chemistry) are often used. To fully understand what happens during a titration experiment enables one to set up a titration and choose an indicator wisely.

Consider a hypothetical titration reaction illustrated as follows:

$$T + A \rightarrow P_x + P_y$$

where T is the titrant (considered as the standard), A is the titrand (considered as the unknown analyte whose concentration is desired), and P_x and P_y are products.

Note that the extent of the above hypothetical reaction is determined by the magnitude of the equilibrium constant, $K_{eq} = \dfrac{[P_x][P_y]}{[T][A]}$

Suppose $\mathbf{C_t}$ is the concentration of the titrant which must be known (in the buret) and $\mathbf{C_A}$ is the concentration of the unknown analyte A in the titration flask before any titrant is added. For the purposes of our illustrations here, we shall assume that both $\mathbf{C_t}$ and $\mathbf{C_A}$ are known.

In order to understand what is occuring in a titration flask, we shall consider a single step titration to comprise of four (4) distinct regions described as below:

- **Region 1 –Initial Stage (*i.e., before the addition of any titrant):*** *Here*, a pure solution of analyte, A is placed in a titration flask before any volume of reagent is added. At this point there is no titrant, T introduced in the flask, no products $\mathbf{P_x}$ or $\mathbf{P_y}$ formed yet and [A] in the titration flask is a function of $\mathbf{C_A}$.
- **Region 2 –Before equivalence point (i.e., a*fter addition of the titrant but before the equivalence point):*** Here, the volume of reagent added to analyte is not sufficient to make the reaction complete (when there is excess of analyte). Thus, in this region T becomes the limiting reagent, and hence there will be very little T in solution (in fact [T] in the flask could be zero if the reaction went totally to completion). Therefore, only A, $\mathbf{P_x}$ and $\mathbf{P_y}$ would be present in measurable quantities.
- **Region 3 –At equivalence point:** In this region, the reagent added is the amount that is chemically equivalent to the amount of substance being determined (analyte). The equivalence point is defined as the point at which there would be neither T nor A present if the reaction went to completion. In reality though, there is often very little of either T or A present and there exists a very simple relationship between [T] and [A]. As is expected, only $\mathbf{P_x}$ and $\mathbf{P_y}$ would be present in measurable amounts.
- **Region 4 –After equivalence point**: Here, the amount of reagent added is higher than the amount of substance being determined. In this region, **A** now becomes the limiting reagent, and therefore there will be very little **A** (if any, depending on whether the reaction went totally to completion, in which case [A] = 0) in solution. Only T, $\mathbf{P_x}$, and $\mathbf{P_y}$ are present in measurable amounts in the titration flask.

In view of the aforementioned, it is clear that the method for determining what is trully present in a titration flask during a titration depends on the region under consideration. To demonstrate what happens and how the concentrations of all substances present varies during a titration process, acid/base titrations will be used as examples of titrations in general. The types of acid/base titrations that will be considered in this unit are:

A) Titration of strong acid with strong base
B) Titration of weak acid with strong base
C) Titration of weak base with strong acid
D) Titration of polyprotic weak acids with strong base

Note that the behaviour in each of the stages mentioned above is a function of the type of acid-base titration process. This behaviour is best depicted or described by making plots of pH as a function of the volume of base added. This plot is known as a ***titration curve***.

Let us now examine each of the types of acid/base titrations mentioned above.

Titration of a Strong acid with a Strong Base

The reaction between HCl (considered here as the unknown) and NaOH (the titrant) will be used as an example. As discussed earlier, strong acids are 100% dissociated in water (i.e., $H^+Cl^- + H_2O \rightarrow H_3O^+ + Cl^-$) and strong bases are 100% hydrolysed (i.e., $Na^+OH^- + H_2O \rightarrow H_2O + OH^- + Na^+$). The reaction therefore between HCl and NaOH can be expressed as:

$$H_3O^+ + OH^- \rightarrow 2H_2O$$

Here, Na^+ and Cl^- are spectator ions and do not enter into the titration reaction. In this reaction, Cl^- is neither added to the flask nor is it consumed in the reaction in the course of the titration process. Thus the number of moles of Cl^- remains constant while its concentration decreases due dilution. (Remember that the volume of solution in the flask is increasing as titration progresses and this dilution process has an effect on the concentrations.)

If $\mathbf{C_t}$ is the concentration of the titrant in the buret and whose value is a fixed; $\mathbf{C_A}$ is the concentration of the unknown analyte, A in the flask before the titration and is also a fixed value; $\mathbf{V_t}$ is the volume of the titrant added to the titration flask; and $\mathbf{V_A}$ is the volume of the unknown analyte placed initially in the titration flask, then the concentration of Cl^-, $[Cl^-]$ which does not depend on the region of the titration is given by

$$[Cl^-] = \frac{mol}{Volume} = \frac{C_A V_A}{(V_A + V_t)} \text{ and } pCl = -\log[Cl^-]$$

Na^+ is continuously being added to the titration flask in the course of the titration process but is not reacting. Hence, the concentration of Na^+, $[Na^+]$ will continuously increase and its concentration will not depend on the region of the titration and is given as

$$[Na^+] = \frac{mol}{Volume} = \frac{C_t V_t}{(V_A + V_t)} \text{ and } pNa = -\log[Na^+]$$

Since the species H_3O^+ and OH^- are involved in the titration reaction, the calculations of $[H_3O^+]$ and $[OH^-]$ in the titration flask will now depend on the titration region. This is now examined below.

Suppose $\mathbf{C_a}$ is the concentration of the strong acid that is present in the flask at any point during the titration process, and $\mathbf{C_b}$ is the concentration of the strong base actually present in the titration flask at any point in the titration. Note that these values will always be different from $\mathbf{C_t}$ and $\mathbf{C_A}$.

Let us now examine what happens to the concentrations of $[H_3O^+]$ and $[OH^-]$ in each of the titration regions discussed above.

Region 1: This is simple a solution of the strong acid present in the titration flask.

$[H_3O^+] = \mathbf{C_a} = \mathbf{C_A}$ and pH = -log$[H_3O^+]$ and pOH = 14.00 – pH

Region 2: As titrant (strong base) is added, some of the strong acid get consumed, but no strong base is yet present. Thus, only the strong acid affects the overall pH of the solution in the titration flask.

Moles of acid remaining = (moles of original acid – moles of base added)

$$\mathbf{C_a} = \frac{(\text{moles of acid remaining})}{(\text{total resultant volume})} = \frac{\left(V_a C_a - V_t C_t\right)}{(V_a + V_t)}$$

$$[H^+] = C_a = \frac{(V_a C_A - V_t C_t)}{(V_a + V_t)} \quad \text{if } \mathbf{C_a} >> 2K_W^{1/2}$$

Region 3: In this region, there is neither strong acid nor strong base present in the titration flask. The solution simply contains the salt, NaCl, the product of the acid-base reaction. Since neither Na^+ nor Cl^- affect pH of the solution mixture, the pH will be that of pure water.

$[H+] = (K_W)^{1/2}$ or pH = 7.00

Region 4: In this region, all the strong acid is now exhausted and there is excess strong base present. Therefore, the pH of the soultion mixture is determined by the excess strong base present.

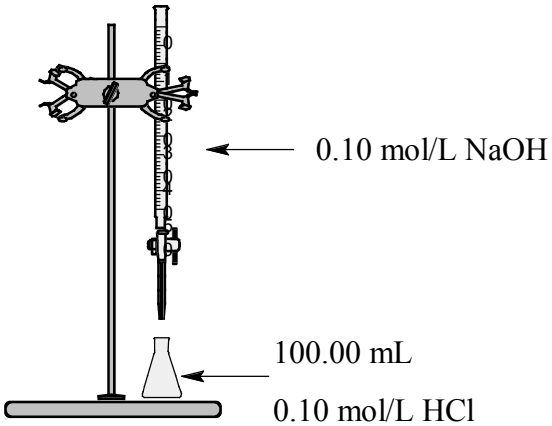
Moles of base present = (total moles of base added so far – moles of original acid present in flask at beginning of titration)

$$\mathbf{C_b} = \frac{(\text{moles of base present})}{(\text{total resultant volume})} = \frac{\left(V_t C_t - V_A C_A\right)}{(V_a + V_t)}$$

$$[OH^-] = C_b = \frac{(V_t C_t - V_a C_A)}{(V_a + V_t)} \quad \text{if } \mathbf{C_b} >> 2K_W^{1/2}$$

$$[H_3O^+] = \frac{K_w}{[OH^-]}$$

Example: Consider titration of 100.0 mL of 0.100 mol/L HCl solution with 0.100 mol/L standard NaOH solution.



Region 1: *Before addition of any titrant.* The 100.0 mL solution contains a strong HCl acid and the total volume is 100 mL (0.100 L).

$[Na^+] = 0.0$ mol/L

$$[Cl^-] = \frac{(0.100\ \text{L})(0.100\ \text{mol/L})}{(0.100\ \text{L})} = 0.100\ \text{mol/L}$$

$$[H^+] = \mathbf{C_a} = \mathbf{C_A} = \frac{(0.100\ \text{L})(0.100\ \text{mol/L})}{(0.100\ \text{L})} = 0.100\ \text{mol/L}$$

$$[OH^-] = \frac{1.00 \times 10^{-14}}{(0.100)} = 1.00 \times 10^{-13}\ \text{mol/L}$$

Region 2: After *addition of, say 50.00 mL of NaOH.* The solution still contains a strong acid and the total volume is 150.0 mL.

$$[Na^+] = \frac{(0.0500\ L)(0.100\ mol/L)}{(0.1500\ L)} = 0.0333\ mol/L$$

$$[Cl^-] = \frac{(0.100\ L)(0.100\ mol/L)}{(0.1500\ L)} = 0.0667\ mol/L$$

$[H^+] = \mathbf{C}_a =$

$$\frac{(0.100\ L)(0.100\ mol/L)-(0.0500\ L)(0.100\ mol/L)}{(0.1500\ L)} = 0.0333\ mol/L$$

$$[OH^-] = \frac{1.00 \times 10^{-14}}{(0.0333)} = 3.00 \times 10^{-13}\ mol/L$$

Region 3: After *addition of, say 99.00 mL of NaOH.* The solution contains very little of the strong acid and the total volume is 199.0 mL.

$$[Na^+] = \frac{(0.0990\ L)(0.100\ mol/L)}{(0.1990\ L)} = 0.0498\ mol/L$$

$$[Cl^-] = \frac{(0.100\ L)(0.100\ mol/L)}{(0.1990\ L)} = 0.0502\ mol/L$$

$[H^+] = \mathbf{C}_a =$

$$\frac{(0.100\ L)(0.100\ mol/L)-(0.0990\ L)(0.100\ mol/L)}{(0.1990\ L)} = 5.03 \times 10^{-4}\ mol/L$$

$$[OH^-] = \frac{1.00 \times 10^{-14}}{(5.03 \times 10^{-4})} = 1.99 \times 10^{-11}\ mol/L$$

Region 3 Continued: After *addition of, say 99.90 mL of NaOH.* The solution contains further reduced strong acid and the total volume is 199.90 mL.

$$[Na^+] = \frac{(0.0999\ L)(0.100\ mol/L)}{(0.1999\ L)} = 0.04998\ mol/L$$

$$[Cl^-] = \frac{(0.100\ L)(0.100\ mol/L)}{(0.1999\ L)} = 0.05003\ mol/L$$

$[H^+] = \mathbf{C_a} =$

$$\frac{(0.100\ L)(0.100\ mol/L)-(0.0999\ L)(0.100\ mol/L)}{(0.1999\ L)} = 5.00 \times 10^{-5}\ mol/L$$

$$[OH^-] = \frac{1.00 \times 10^{-14}}{(5.00 \times 10^{-5})} = 1.999 \times 10^{-10}\ mol/L$$

Region 3 Continued: After *addition of, say 99.99 mL of NaOH.* The solution contains even further reduced strong acid and the total volume is 199.90 mL.

$$[Na^+] = \frac{(0.09999\ L)(0.100\ mol/L)}{(0.19999\ L)} = 0.049998\ mol/L$$

$$[Cl^-] = \frac{(0.100\ L)(0.100\ mol/L)}{(0.19999\ L)} = 0.050003\ mol/L$$

$[H^+] = \mathbf{C_a} =$

$$\frac{(0.100\ L)(0.100\ mol/L)-(0.09999\ L)(0.100\ mol/L)}{(0.19999\ L)} = 5.00 \times 10^{-6}\ mol/L$$

$$[OH^-] = \frac{1.00 \times 10^{-14}}{(5.00 \times 10^{-6})} = 2.00 \times 10^{-9}\ mol/L$$

Region 3 Continued: After *addition of 100.00 mL of NaOH.* The solution contains neither a strong acid nor a strong base and the total volume is 200.00 mL

$$[Na^+] = [Cl^-] = \frac{(0.100\ L)(0.100\ mol/L)}{(0.200\ L)} = 0.0500\ mol/L$$

$$[H^+] = [OH^-] = 1.00 \times 10^{-7}\ mol/L$$

Region 4: After *addition of, say 100.01 mL of NaOH.* The solution contains a little strong base and the total volume is 200.01 mL.

$$[Na^+] = \frac{(0.10001\ L)(0.100\ mol/L)}{(0.20001\ L)} = 0.0500025\ mol/L$$

$$[Cl^-] = \frac{(0.100\ L)(0.100\ mol/L)}{(0.20001\ L)} = 0.0499975\ mol/L$$

$[OH^-] = \mathbf{C_b} =$

$$\frac{(0.10001\ L)(0.100\ mol/L)-(0.100\ L)(0.100\ mol/L)}{(0.20001\ L)} = 4.99975 \times 10^{-6}\ mol/L$$

$$[H^+] = \frac{1.00 \times 10^{-14}}{(4.99975 \times 10^{-6})} = 2.00 \times 10^{-9}\ mol/L$$

Region 4 Continued: After *addition of 100.10 mL of NaOH.* The solution contains a little strong base and the total volume is 200.10 mL.

$$[Na^+] = \frac{(0.1001\ L)(0.100\ mol/L)}{(0.2001\ L)} = 0.050025\ mol/L$$

$$[Cl^-] = \frac{(0.100\ L)(0.100\ mol/L)}{(0.2001\ L)} = 0.049975\ mol/L$$

$[OH^-] = \mathbf{C_b} =$

$$\frac{(0.1001\ L)(0.100\ mol/L)-(0.100\ L)(0.100\ mol/L)}{(0.2001\ L)} = 4.9975 \times 10^{-5}\ mol/L$$

$$[H^+] = \frac{1.00 \times 10^{-14}}{(4.9975 \times 10^{-5})} = 2.001 \times 10^{-10} \text{ mol/L}$$

Region 4 Continued: After *addition of 110.00 mL of NaOH.* The solution contains more strong base and the total volume is 210.00 mL.

$$[Na^+] = \frac{(0.110 \text{ L})(0.100 \text{ mol/L})}{(0.210 \text{ L})} = 0.05238 \text{ mol/L}$$

$$[Cl^-] = \frac{(0.100 \text{ L})(0.100 \text{ mol/L})}{(0.210 \text{ L})} = 0.04762 \text{ mol/L}$$

$[OH^-] = \mathbf{C_b} =$

$$\frac{(0.110 \text{ L})(0.100 \text{ mol/L}) - (0.100 \text{ L})(0.100 \text{ mol/L})}{(0.210 \text{ L})} = 4.762 \times 10^{-3} \text{ mol/L}$$

$$[H^+] = \frac{1.00 \times 10^{-14}}{(4.762 \times 10^{-3})} = 2.1 \times 10^{-12} \text{ mol/L}$$

Region 4 Continued: After *addition of 150.00 mL of NaOH.* The solution contains more strong base and the total volume is 250.00 mL.

$$[Na^+] = \frac{(0.150 \text{ L})(0.100 \text{ mol/L})}{(0.250 \text{ L})} = 0.06 \text{ mol/L}$$

$$[Cl^-] = \frac{(0.100 \text{ L})(0.100 \text{ mol/L})}{(0.250 \text{ L})} = 0.04 \text{ mol/L}$$

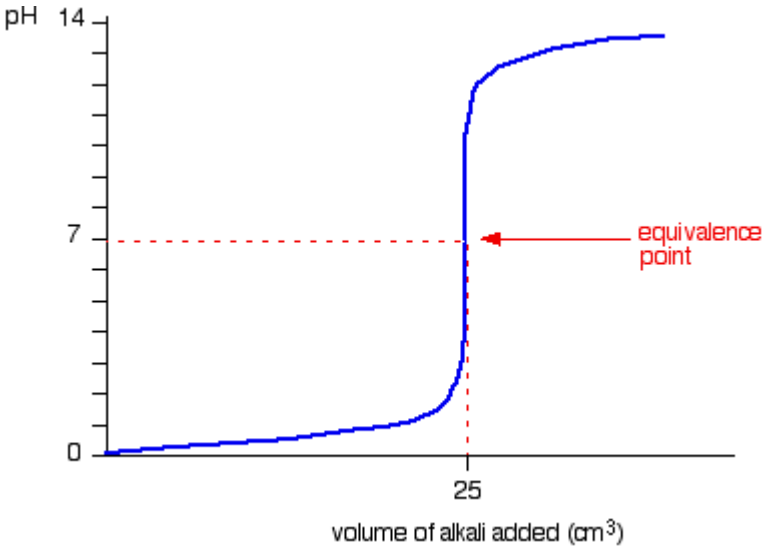
$[OH^-] = \mathbf{C_b} =$

$$\frac{(0.150 \text{ L})(0.100 \text{ mol/L}) - (0.100 \text{ L})(0.100 \text{ mol/L})}{(0.250 \text{ L})} = 0.02 \text{ mol/L}$$

$$[H^+] = \frac{1.00 \times 10^{-14}}{(0.02)} = 5.0 \times 10^{-13} \text{ mol/L}$$

The result of a series of such calculations can now be ploted as a graph of pH versus volume of NaOH to generate what is referred to as a ***titration curve***. In such a plot, it becomes evident that the concentrations of the reactants, but not the products or the spectator ions, go through a large change exactly at the equivalence point. It is this change that allows one to pinpoint the equivalence point. The equivalence point can therefore be determined, say in this case, by monitoring either the concentration of OH^- or H^+ ions.

A typical titration curve for a strong acid versus a strong base is given in the figure below. (We'll take hydrochloric acid and sodium hydroxide as typical of a strong acid and a strong base; i.e., $NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$).



It is clear from this figure that the pH only rises a very small amount until quite near the equivalence point. Then there is a really steep rise.

In order for you to appreciate the generation of a titration curve from such calculations as above, you are encouraged to do the exercise problem below.

Exercise: Using the above calculations, plot the corresponding titration curve for the titration of 100.00 mL of 0.10 mol/L HCL solution with 0.10 mol/L standard NaOH solution.

Let us now consider the case of ***titration of a weak acid with a strong base*** and see how it compares with that of a ***strong acid with a strong base*** dealt with above.

Titration of a Weak acid with a Strong Base

At first glance, it might seem that weak acid/strong base titrations are just like the strong acid/strong base titration encountered in the preceding section. However, there is a significant difference that makes this case more complicated. Whereas the product of the titration reaction and the spectator ions in a strong acid/strong base titration (such as H_2O, Na^+, and Cl^-) do not affect the pH of the solution in the titration flask and can thus be neglected, the same cannot be said of the weak acid/strong base titration. In fact, when a weak acid is titrated with a strong base, one of the products is a weak base which does affect the pH in all the regions discussed above except Region 1, and this must be taken into consideration.

The titration reaction involving a weak acid (HA) with a strong base such as NaOH is often expressed as:

$$HA + NaOH \rightarrow NaA + H_2O$$

which can be more accurately represented as:

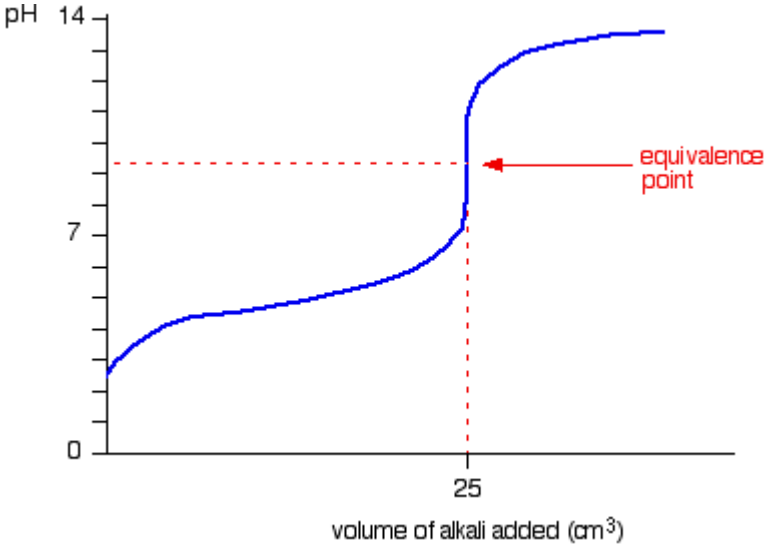
$$HA + OH^- \rightarrow A^- + H_2O$$

with a corresponding equilibrium constant expressed as:

$$K_{eq} = \frac{[A^-]}{[HA][OH^-]} = \frac{1}{K_b} = \frac{K_a}{K_W}$$

Note that $\boldsymbol{K_{eq}}$ for the titration of a weak acid with an $\boldsymbol{K_a}$ of about 1.0×10^{-5} will be only 1.0×10^9 (i.e., $K_{eq} = \frac{1}{K_b} = \frac{K_a}{K_W} = \frac{K_a}{10^{-14}}$), a value that is not as large as that for a strong acid. However, this is still considered large enough for the reaction to proceed to completion. In fact, as the value of $\boldsymbol{K_a}$ of the weak acid decreases, so does the value of K_{eq} for the titration. Therefore, if the acid is too weak, it cannot be easily titrated.

A typical titration curve for a weak acid versus a strong base is given in the figure below. (We'll take ethanoic acid and sodium hydroxide as typical of a waek acid and a strong base; i.e., $CH_3COOH_{(aq)} + NaOH_{(aq)} \rightarrow CH_3COONa_{(aq)} + H_2O_{(l)}$).



The start of the graph shows a relatively rapid rise in pH but this slows down as a buffer solution containing ethanoic acid and sodium ethanoate is produced. Beyond the equivalence point (when the sodium hydroxide is in excess) the curve is just the same as that end of the HCl-NaOH graph shown previously.

Let us now consider the four regions of the titration in the same manner as for the strong acid/strong base titration. Here again, we shall assume that the weak acid of concentration $\mathbf{C_A}$ is the unknown and that the titrant of concentration $\mathbf{C_t}$, is a strong base.

Region 1: Prior to addition of any base, the solution in the titration flask basically contains only the weak acid, HA and that $\mathbf{C_a} = \mathbf{C_A}$. In order to calculate $[H^+]$, a weak acid equation need to be used. Thus

$$[H^+] = (K_a C_A)^{\frac{1}{2}}, \text{ i.e., } pH = -\log\sqrt{K_a C_A}$$

Region 2: Upon addition of some titrant, the solution contains some unreacted acid, HA (since the acid is not 100% dissociated) and some conjugate base, A^-, due to the titration reaction.

Therefore, moles of acid remaining = original moles of acid-moles of strong base added.

$$C_a = \frac{(\text{moles of acid remaining})}{\text{Total volume}} = \frac{(V_A C_A - V_t C_t)}{(V_A + V_t)}$$

Moles of weak base formed = moles of strong base added.

Therefore $C_B = \frac{V_t C_t}{(V_A + V_t)}$, where $\mathbf{C_B}$ is concentration of the weak base formed.

To calculate the $[H^+]$, we need to use the simplified equation for a mixture of a weak acid and its conjugate base, i.e.,

$$[H^+] = \frac{K_a C_a}{C_B}, \text{ i.e., } pH = pK_a + \log\frac{C_B}{C_a}$$

Region 3: At the equivalence point, all the weak acid has been completely neutralized by the strong base and only the weak base remains. There is no excess strong base present. Since the solution contains a weak base, the pH of the solution in the flask cannot be equal to 7.00 and must be greater than 7.00.

Moles of weak base present = moles of strong base added.

$$C_B = \frac{V_t C_t}{(V_A + V_t)}$$

$[OH^-]$ can be calculated using the simplified weak base equation, i.e.,

$$[OH^-] = (K_b C_B)^{\frac{1}{2}}$$

Region 4: After the equivalence point , both the weak base, A-, and excess strong base, OH-, will be present.

moles of weak base = moles of original weak acid

Concentration of weak base, $\mathbf{C_w} = \frac{V_A C_A}{(V_A + V_t)}$

Moles of strong base present = moles of titrant added – moles of original weak acid

Thus, concentration of strong base, $\mathbf{C_S} = \frac{(V_t C_t - V_A C_A)}{(V_A + V_t)}$

The $[OH^-]$ can be calculated by using an equation for a mixture of a weak base and a strong base, i.e.,

$[OH^-] = \mathbf{C_S}$

Example: Consider the titration of a 50.0 mL solution of weak acid of butanoic ($pK_a = 4.98$, i.e., $K_a = 1.05 \times 10^{-5}$) of concentration 0.10 mol/L with a 0.10 mol/L standard NaOH solution. For convenience, we shall calculate only the pH of the solution mixture in the titration flask.

Region 1: Before addition of NaOH, $\mathbf{C_A} = 0.10$ mol/L.

$$[H^+] = (K_a C_A)^{\frac{1}{2}} = \{(1.05 \times 10^{-5})(0.10)\}^{\frac{1}{2}} = 1.02 \times 10^{-3} \text{ mol / L}$$

$$[OH^-] = \frac{1.00 \times 10^{-14}}{1.02 \times 10^{-3}} = 9.77 \times 10^{-12} \text{ mol / L}$$

Region 2: After addition of, say, 20.0 mL of NaOH. Total volume in the titration flask becomes 70.0 mL and the solution is a mixture of a weak acid and its conjugate base.

$$C_a = \frac{(\text{moles of acid remaining})}{\text{Total volume}} = \frac{(0.050\text{L})(0.10\text{mol / L}) - (0.020\text{L})(0.10\text{mol / L})}{(0.050\text{L} + 0.020\text{L})} = 0.0429\text{mol / L}$$

$$C_B = \frac{(0.10\text{mol / L})(0.020\text{L})}{0.070\text{L}} = 0.0286\text{mol / L CB}$$

Using the simplified equation for a mixture of a weak acid and its conjugate base to solve for [H+] and therefore pH,

$$[H^+] = \frac{K_a C_a}{C_B} = \frac{(1.05 \times 10 - 5)(0.0429)}{0.0286} = 1.57 \times 10^{-5} \text{ mol / L and pH} = -\log(1.57 \times 10^{-5}) = 4.80$$

$$[OH^-] = \frac{1.00 \times 10^{-14}}{1.57 \times 10^{-5}} = 6.37 \times 10^{-10} \text{ mol / L}$$

Region 3: After addition of, say, 50.0 mL of NaOH. Total volume in the titration flask becomes 100.0 mL and the solution contains only a weak base.

$$C_B = \frac{V_t C_t}{(V_A + V_t)} = \frac{(0.050\,L)(0.10\,mol/L)}{0.10\,L} = 0.050\,mol/L$$

$$K_b = \frac{1.00 \times 10^{-14}}{K_a} = 9.55 \times 10^{-10}$$

With the simplified equation for a weak base

$$[OH^-] = (K_b C_B)^{\frac{1}{2}} = \{(9.55 \times 10^{-10})(0.050)\}^{\frac{1}{2}} = 6.91 \times 10^{-6}\,mol/L$$

$[H^+] = \frac{1.00 \times 10^{-14}}{6.91 \times 10^{-6}} = 1.45 \times 10^{-9}\,mol/L$, and pH = -log(1.45 x 10^{-9}) = 8.84

Region 4: After addition of, say, 60.0 mL of NaOH. Total volume in the titration flask becomes 110.0 mL and the solution contains both a weak base and a strong base.

Concentration of weak base, $\mathbf{C_w}$ =

$$\frac{V_A C_A}{(V_A + V_t)} = \frac{(0.050\,L)(0.10\,mol/L)}{0.110\,L} = 0.0455\,mol/L$$

Concentration of strong base, $\mathbf{C_S}$ =

$$\frac{(V_t C_t - V_A C_A}{(V_A + V_t)} = \frac{\{(0.060\,L)(0.10\,mol/L) - (0.050\,L)(0.10\,mol/L)\}}{0.110\,L} = 0.00909\,mol/L$$

Using the simplified equation for a mixture of a strong and weak base,

$[OH^-] = C_S = 0.00909$ mol/L

$[H^+] = \frac{1.00 \times 10^{-14}}{0.00909} = 1.10 \times 10^{-12}\,mol/L$, and pH = -log(1.10 x 10^{-12}) = 11.96

Note that the complete titration curve can be plotted when a series of additional calculations similar to those above are carried out.

Exercise: Titration of weak acid with strong base. Using the information provided below, plot the titration curve for the titration of 100.00 mL of 0.10 mol/L CH_3COOH solution with 0.10 mol/L standard NaOH solution. Hint: Consider the four titration stages given above.

Illustration

Calculating pH at Initial Stage:

Let ***n*** moles of **HA** (i.e., a monoprotic weak acid such as the CH_3COOH) be available in a titration flask. The pH is dependent on extent of dissociation of the weak acid. If K_a of the weak acid is very small (i.e., $K_a < 1.0 \times 10^{-4}$), then it is possible to calculate the pH from the dissociation of weak acid using the relation:

$$pH = -\log[\sqrt{K_a[Acid]}$$

Before equivalence point:

Again, let ***n*** moles of **HA** be available in titration flask. To this solution let ***m*** moles of NaOH be added. In this titration, "***Before Equivalence Point***" means ***n > m.***

	HA	$+ NaOH \rightarrow$	NaA	$+ H_2O$
Start	***n***	***m***	***0***	***0***
n > m				
Final	***n-m***	***0***	***m***	***m***

Question: What is left in the solution in the titration flask?

The solution left in the flask contains excess weak acid by an amount of ***(n-m) moles*** and salt of weak acid of an amount of equivalent to ***m moles.*** The solution is a buffer solution. Therefore, the pH of the solution can be calculated using the Henderson-Hasselbalch equation:

$$pH = pKa + \log\frac{[salt]}{[Acid]} =$$

$$pK_a + \log\frac{\frac{m}{(V_{Acid} + V_{base\ added})}}{\frac{(n-m)}{(V_{Acid} + V_{base\ added})}} = pK_a + \log\frac{m}{(n-m)}$$

At equivalence point:

The acid is completely neutralized by the base added. Hence the pH is dependent on the salt solution. The resultant salt obtained is a salt of a weak acid and strong base. Therefore the anion part of the salt will hydrolyze as follows.

$$NaA \rightarrow Na^{+}(aq) + A^{-}(aq)$$

$$A^{-} + H_2O \Leftrightarrow HA + OH^{-}$$

$$pH = \frac{1}{2}\{(pK_w + pK_a - pC_{salt\ produced})\}$$

$$= \frac{1}{2}\{(pK_w + pK_a + \log(\frac{m}{V_{acid} + V_{base}})\}$$

After equivalence point:

The amount of strong base added is more than the amount required to neutralize the acid. Hence an excess amount of strong base will remain in solution. The pH can be calculated from the excess strong base left in the solution using the following equation.

$$pH = pK_w + \log[\frac{(C_{Base}V_{base\ added}) - (C_{Acid}V_{acid})}{(V_{acid} + V_{base\ added})}]$$

Exercise: Titration of weak acid with strong base. Plot a titration curve for titrating 75 mL of 0.12 mol/L CH_3COOH with 0.09 mol/L NH_3. K_a for CH_3COOH = 1.8 x 10^{-5} and K_b for NH_3 = 1.8 x 10^{-5}. Hint: Consider the four titration stages discussed earlier.

Polyprotic Acids:

In our previous discussion of acid-base reactions, we dealt with acids (e.g., HCl, HNO_3, and HCN) that contain only one ionizable hydrogen atom in each molecule. This group of acids that have only one ionizable hydrogen atom per molecule is known as ***monoprotic acid***. The corresponding reactions of the monoprotic acids given above with a base like water are as follows:

$$HCl + H_2O \rightarrow H_3O^{+} + Cl^{-}$$
$$HNO_3 + H_2O \rightarrow H_3O^{+} + NO_3^{-}$$
$$HCN + H_2O \leftrightarrow H_3O^{+} + CN^{-}$$
$$HNO_3 + H_2O \rightarrow H_3O^{+} + NO_3^{-}$$
$$HCN + H_2O \leftrightarrow H_3O^{+} + CN^{-}$$

In general, however, acids can be classified by the number of protons present per molecule that can be given up in a reaction. For acids that can transfer more than one proton to a base, the term ***polyprotic acid*** is used. ***Diprotic acids*** contain two ionizable hydrogen atoms per molecule and their ionization occurs in two stages. Examples of diprotic acids include, H_2SO_4, H_2S, H_2CO_3, etc. An illustration of the two-stage ionization of H_2S is as follows:

$H_2S + H_2O \rightleftharpoons H_3O^+ + HS^-$ (primary ionization)

$HS^- + H_2O \rightleftharpoons H_3O^+ + S^{2-}$ (secondary ionization)

Each of the above steps is characterized by a different acid ionization constant.

The primary ionization step has an acid ionization constant, $K_1 = \frac{[HS^-][H_3O^+]}{[H_2S]}$

whereas the secondary has an acid ionization constant, $K_2 = \frac{[S^{2-}][H_3O^+]}{[HS^-]}$.

If $K_1 \approx K_2$, the two steps occur simultaneously and both must be considered in solving any problems involving the pH of solutions of the acid. If however, $K_1 \gg K_2$ (by atleast a factor of 10^4), then only the one reaction involving the species present need be considered. This then makes one apply the simple monobasic equations that have been dealt with previously in unit 2.

Of the two steps above, the primary ionization always takes place to a greater extent than the secondary ionization.

The most common ***triprotic acid*** is phosphoric acid or sometimes called ortho-phosphoric acid (H_3PO_4), which can ionize in solution in three steps as follows:

$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO^-_4$ (primary ionization)

$H_2PO^-_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO^{2-}_4$ (secondary ionization)

$H_2PO^{2-}_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO3^-_4$ (tertiary ionization)

The corresponding experimentally determined acid ionization constants for phosphoric acid (H_3PO_4) are: $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.6 \times 10^{-8}$, and $K_3 = 1.0 \times 10^{-12}$

Thus, a solution of phosphoric acid will usually comprise a mixture of three different acids; H_3PO_4, $H_2PO_4^-$, and HPO_4^{2-} and their corresponding conjugate bases.

It is important to note that successive ionization constants for a given acid generally have widely different values as can be seen in the case of phosphoric acid (i.e., $K_1 >> K_2 >> K_3$). Thus, as mentioned in the case of the diprotic acid above, no more than two of the successive species associated with the ionization of a particular polyprotic acid are present in significant concentrations at any particular pH. Hence, the equilibria or any calculations can be determined by only one, or at most two,of the acid ionization constants.

Titration of a Polyprotic Weak acid with a Strong base

In accordance with the stepwise dissocitation of di- and polyprotic weak acids, their neutralization reactions are also stepwise. For instance, in the titration of orthophosphoric acid (H_3PO_4) with a strong base such as NaOH, the following stepwise reactions occur:

$$H_3PO_4 + NaOH \leftrightarrow NaH_2PO_4 + H_2O$$

$$NaH_2PO_4 + NaOH \rightarrow Na_2HPO_4 + H_2O$$

$$Na_2HPO_4 + NaOH \leftrightarrow Na_3PO_4 + H_2O$$

Accordingly, the H_3PO_4–NaOH titration curve has not one but three equivalence points. The first equivalence point is reached after one mole of NaOH has been added per mole of H_3PO_4; the second after addition of two moles of NaOH; and the third after addition of three moles of NaOH.

Example: If 10.00 mL of 0.10 mol L^{-1} H_3PO_4 solution is titrated, the first equivalence point is reached after addition of 10.00 mL, the second after addition of 20.00 mL, and the third after addition of 30.00 mL of 0.10 mol L^{-1} NaOH solution.

Titration of a Diprotic weak acid (H_2A) with NaOH

For a diprotic weak acid represented by $\boldsymbol{H_2A}$,

1. ***The pH at the beginning of the titration*** is calculated from the ionization (dissocitation) of the first proton, i.e.,

$$H_2A \rightleftharpoons H^+ + HA^-$$

If $\boldsymbol{K_{a1}}$, *the acid dissociation constatant* $\left(= \dfrac{[H^+][HA^-]}{[H_2A]}\right)$, is not too large and the

amount of dissociated $\boldsymbol{H_2A}$ is ignored compared to the analytical concentration of the acid, then

$$[H^+] = \sqrt{K_{a1}[H_2A]}$$

Otherwise the quadratic formula must be used to solve pH (see section on …. Of unit 2).

2. The pH during titration upto the first equivalence point

An ***HA^-/H_2A*** buffer region (a region where the solution attempts to resist any change in pH upon addition of base during the titration) is established such that

$$pH = pK_{a1} + \log\left(\frac{HA^-}{H_2A}\right)$$

3. At the first equivalence point

$$pH = \frac{pK_{a1} + pK_{a2}}{2}$$

4. Beyond the first equivalence point an A^{2-}/HA^- buffer exists

$$pH = pK_{a2} + \log\left(\frac{[A^{2-}]}{[HA^-]}\right)$$

5. At the second equivalence point the pH is determined from the hydrolysis of A^{2-} salt (i.e., $A^{2-} + H_2O \rightleftharpoons HA^- + OH^-$), such that

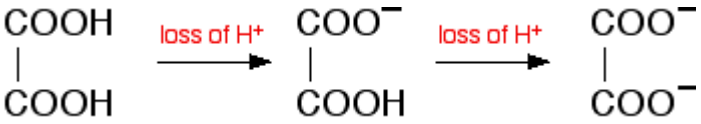
$$[OH^-] = \sqrt{\frac{K_w}{K_{a2}}[A^{2-}]}$$

6. Beyond the second equivalence point

The pH will be dependent on the concentration of excess strong base added (i.e., concentration of the titrant).

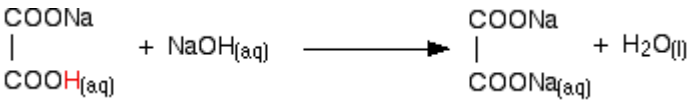
Illustration:

Consider addition of sodium hydroxide solution to dilute ethanedioic acid (oxalic acid). Ethanedioic acid is a diprotic acid which means that it can give away 2 protons (hydrogen ions) to a base. (Note that something which can only give away one (like HCl) is known as a monoprotic acid).

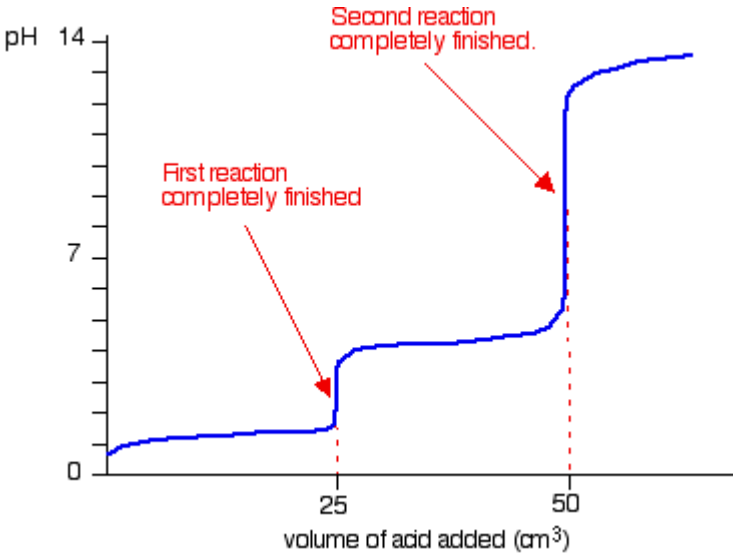


The reaction with NaOH takes place in two stages because one of the hydrogens is easier to remove than the other. The two successive reactions can be represented as:

and



By running NaOH solution into ethanoic acid solution, the pH curve shows the end points for both of these reactions as shown in the figure below.



The curve is the reaction between NaOH and ethanedioic acid solutions of equal concentrations.

Exercise 1. Plot a titration curve for the titration of 75 mL of 0.12 mol L^{-1} H_2CO_3 with 0.09 mol L^{-1} NaOH, given that $K_{a1} = 4.3 \times 10^{-7}$ and $K_{a2} = 5.6 \times 10^{-11}$. Hint: You are expected to consider the six titration stages shown above to collect data in order to plot the titration curve.

Exercise 2. In the titration of a triprotic acid, H_3A with NaOH where $K_{a1}/K_{a2} \geq 10^4$ and $K_{a2}/K_{a3} \geq 10^4$,

(a) Identify the eight titration stages that need to be considered in order to plot the corresponding titration curve.

(b) Derive the expressions for pH in each of the eight stages.

Titration of Anions of a weak acid with strong acid, HA

For the titration of $\mathbf{Na_2A}$ salt:

1. The pH at the beginning of the titration is calculated from the hydrolysis of A^{2-} salt i.e.,

   $$A^{2-} + H_2O \rightleftharpoons HA^- + OH^-$$

2. During the titration up to the first equivalence point

   $$A^{2-} + H^+ \rightleftharpoons HA^-$$

The solution mixture of H^{A-} and A^{2-} is a buffer solution and so,

$$pH = pK_{a2} + \log\frac{[A^{2-}]}{[HA^-]}$$

3. At the first equivalence point

   $$A^{2-} + H^+ \rightleftharpoons HA^-$$

We have HA^- in solution and pH arises from the dissociation of HA^-, i.e.,

$$HA^- + H_2O \rightleftharpoons H_3O^+ + A^{2-} \text{ and}$$

$$pH = \frac{pK_{a1} + pK_{a2}}{2}$$

4. Beyond the first equivalence point:

   $$HA^- + H^+ \rightleftharpoons H_2A$$

The resultant solution is a mixture of H_2A and HA^-, hence a buffer solution and so

$$pH = pK_{a1} + \log\frac{[HA^-]}{[H_2A]}$$

5. At second equivalence point:

   $$HA^- + H^+ \rightleftharpoons H_2A$$

Here, only H_2A is left in solution and hence pH is dependent on the dissociation of H_2A, and so

$$H_2A + H_2O \rightleftharpoons H_3O^+ + HA^-$$

$$[H^+] = \sqrt{K_{a1}[H_2A]}$$

6. Beyond the second equivalence point:

Excess strong acid is added and the pH is determined by the concentration of excess strong acid.

Exercise: Plot the titration curve of 75mL of 0.12 mol L^{-1} CH_3COONa with 0.09 mol L^{-1} HCl. K_a for CH_3COOH = 1.80 x 10^{-5}. Hint: Consider the four possible titration stages.

Exercise: Plot the titration curve of 75mL of 0.12 mol L^{-1} Na_2CO_3 with 0.09 mol L^{-1} HCl. $K_{a1} = 4.3 \times 10^{-7}$ *and* $K_{a2} = 5.6 \times 10^{-11}$. Hint: You are expected to consider six possible titration stages to collect data in order to plot the titration curve.

Table. Summary of relevant equations used to calculate pH for different acid-base titrations.

	pH of solution at various stages calculated by			
Type of Acid-base titration	**Initial stage**	**Before equivalence point**	**At equivalence point**	**After equivalence point**
Strong acid, HCl with strong base, NaOH	pH = -log[HCl]	$pH = -\log\left\{\frac{\left([HCl]V_{HCl}\right)-\left([B]V_B added\right)}{\left(V_{HCl}+V_B added\right)}\right\}$ pH from the concentration of excess HCl	pH=7 Neither of the ions of the salt undergoes hydrolysis	$pH = -\log\left\{\frac{\left([NaOH]V_{NaOH} added\right)-\left([HCl]V_{HCl}\right)}{\left(V_{HCl}+V_{NaOH} added\right)}\right\}$ pH from the concentration of excess strong base
Weak acid, HA with strong base, NaOH	$pH = -\log\left(\sqrt{K_a[HA]}\right)$ pH from dissociation of weak acid	$pH = pK_a + \log\frac{[Salt]}{[HA]}$ The resulting solution is an acid buffer.	$pH = \frac{1}{2}\left(pK_W + pK_a - p[salt_{produced}\right.$ pH from hydrolysis of salt of weak acid and strong base	$pH = pK_W + \log\left\{\frac{\left([NaOH]V_{NaOH}\right)-\left([HA]V_{HA}\right)}{\left(V_{NaOH}+V_{HA}\right)}\right\}$ pH from the excess strong base
Weak base, B with strong acid, HCl	$pH = pK_W + \log\sqrt{K_b[B]}$ pH from dissociation of weak base	$pH = pK_W - pK_b + \log\left\{\frac{[B_{left}]}{[Salt_{produced}]}\right\}$ The resulting solution is a base buffer.	$pH = \frac{1}{2}\left(pK_W - pK_a + p[salt_{produced}\right.$ pH from hydrolysis of salt of weak base and strong acid	$pH = -\log\left\{\frac{\left([HCl]V_{HCl}\right)-\left([B]V_B\right)}{\left(V_{HCl}+V_B\right)}\right\}$ pH from the excess strong acid

Acid-Base Indicators

Indicators	Acid Colour	Range	Base Colour
Methyl Violet	yellow	0.0 – 1.6	blue
Malachite green	yellow	0.2 – 1.8	blue-green
Cresol red	red	1.0 – 2.0	yellow
Thymol blue	red	1.2 – 2.8	yellow
Benzopurpurin 4B	violet	1.2 – 3.8	red
Orange IV	red	1.4 – 2.6	yellow
Phloxine B	colourless	2.1 – 4.1	pink
2,4-Dinitrophenol	colourless	2.8 – 4.0	yellow
Methyl yellow (in ethanol)	red	2.9 – 4.0	yellow
Bromophenol blue	yellow	3.0 – 4.6	blue-violet
Congo red	blue	3.1 – 4.9	red
Methyl orange	red	3.2 – 4.4	yellow
Bromocresol green	yellow	4.0 – 5.6	blue
alpha-Naphthyl red	red	4.0 – 5.7	yellow
Methyl red	red	4.8 - 6.0	yellow
Litmus (azolitmin)	red	5.0 - 7.0	blue
Bromocresol purple	yellow	5.2 - 6.8	violet
4-Nitrophenol	colourless	5.4 - 6.6	yellow
Bromothymol blue	yellow	6.0 - 7.6	blue
Phenol red	yellow	6.4 - 8.0	red

Brilliant yellow	yellow	6.6 - 7.9	orange
Cresol red	yellow	7.0 - 8.0	red
Metacresol purple	yellow	7.4 - 9.0	violet
2,6-Divanillyldenecyclohexanone	yellow	7.8 - 9.4	red
Thymol blue	yellow	8.0 - 9.6	blue
Phenolphthalein	colourless	8.3 - 10.0	dark pink
Thymolphthalein	colourless	9.4 - 10.6	blue
Alizarin yellow R	yellow	10.0 - 12.0	red
Malachite green hydrochloride	green-blue	10.2 - 12.5	colourless
Methyl blue	blue	10.6 - 13.4	pale-violet
Sodium indigosulphonate	blue	11.4 - 13.0	yellow
Orange G	yellow	11.5 - 14.0	pink
2,4,6-Trinitrotoluene	colourless	11.7 - 12.8	orange
1,3,5-Trinitrobenzene	colourless	12.0 - 14.0	Orange

Example: In the titration of 30.0 mL of 0.10 M HF with 0.20 M KOH, the pH of the solution mixtures at 10.0, 15.0, and 20.0 mL additions of the strong alkali are 3.76, 8.14, and 12.30, respectively. If phenol red (whose *pK* value is 7.5 and its acid colour is yellow and its base colour is red) were to be used as an indicator for the titration reaction, what colour would the indicator be at the 10, 15, and 20 mL additions of KOH?

Solution:

At 10 mL, the pH is 3.76. This is very acidic; the colour will be yellow.

At 15 mL, the pH is 8.14. This is just within the of the pK, so it will be orange. Likely a reddish-orange colour.

At 20 mL, the pH is 12.30. This is very basic; and hence the colour will be red.

Since it changes colour at the equivalence point (it doesn't have to hit exactly), this would be a reasonable choice indicator.

Exercise: Refer to the example above. The indicator methyl orange has a pK of about 3.5. It is red in its acidic form and yellow in its basic form. What colour will the indicator be at 10, 15, and 20 mL additions of KOH? Would this be a good indicator for this titration?

Learning activity # 3

Title of Learning Activity : Redox Reactions and Titrations

Specific Learning Objectives

- Define oxidation, reduction, oxidizing agent and reducing agent.
- Define oxidation state and oxidation number.
- Have a knowledge of the oxidation state rules and assign oxidation numbers to atoms in molecules and ions.
- Identify a redox reaction by assigning oxidation numbers to each element.
- Write the oxidation and reduction half reactions for a redox reaction.
- Distinguish between a redox reaction and a non-redox reaction.
- Write balanced Oxidation/Reduction Equations.
- Apply the Nernst equation in all directions to determine missing quantities.
- Describe and discuss Redox titrations.
- Carry out redox-type titrations and associated calculations.

Summary of learning activity # 3

Chemical reactions in which there is a transfer of electrons from one substance to another are known as oxidation-reduction reactions or ***redox reactions***. In this unit, we will consider the class of reactions called ***oxidation-reduction,*** or redox and examine the oxidation-reduction process and use the oxidation state and oxidation number concepts to not only identify redox reactions but also keep track of electrons transferred in a chemical reaction. The introductory sections of the unit explains the fundamental principles of galvanic cells, the thermodynamics of electrochemical reaction. Some applications of the concept of redox equilibria in explaining oxidation-reduction titrations as a technique for volumetric chemical analysis are also discussed.

Key Concepts

Nernst equation: relates the electrochemical potential to the concentration of reactants and products participating in a redox reaction.

Oxidation: the process by which a compound looses or appears to loose electrons. It corresponds to an increase in the *oxidation number*.

Oxidizing agent: species that causes *oxidation*. An ***oxidizing agent*** accepts electrons from the species it oxidizes and therefore, an oxidizing agent is always *reduced*.

Oxidation number: these are used to keep track of electron transfer. *Oxidation numbers* are assigned to ionic as well as molecular compounds. *Oxidation numbers* are assigned per atom.

Oxidation reaction: refers to the half-reaction that involves loss of electrons.

Redox reactions: these are or oxidation-reduction reactions that involve transfer of electrons. As the electron transfer occurs, substances undergo changes in *oxidation number*.

Reduction: the process by which a compound gains or appears to gain electrons. It corresponds to a decrease in *oxidation number*.

Reduction reaction: is a half-reaction that involves gain of electrons.

Reducing agent: species that causes *reduction*. A reducing agent donates electrons to the species it reduces and therefore, a ***reducing agent*** is always *oxidized*.

Introduction to activity # 3

Oxidation-reduction (redox) reactions or processes are very much a part of the world that we live in. These processes or reactions range from the burning of fossil fuels to the action of the oxidizing power of sodium hypochlorite, the active ingredient in household bleach. It is very likely that all of us have at one time or another come across atleast a process or feature that is as a result of a redox process. It is very probable that we have seen many examples of corrosion around us such as rust on iron, tarnish on silverware, and the greening on copper or brass surfaces or material. All these changes that we observe on almost day to day basis without thinking of their chemical origin or nature are examples of processes resulting from redox reactions. Most metallic and nonmetallic elements which find important uses in modern day world, are obtained from their ores by the process of oxidation or reduction reactions.All of these examples are some of the consequences of oxidation-reduction reactions. These are basically reactions that involve electron-transfer. Oxidation-reduction analysis has been used over the years as an alternate method of analyzing for materials that have multiple oxidation states. This unit in part, will help us to link what is happening at the submicroscopic level to macroscopic events in electrochemistry that we see.

List of other compulsory readings

A text that contains vital information on the Nernst Equation, the significance of the equation and analytical applications in quantitative analysis of metal ions in solution (Reading #24)

A text on "Redox Equilibria in Natural Waters" (Reading #25)

A text with sub-sections containing sample problems dealing with chemical equilibrium, oxidation-reduction reactions (Reading #13)

Balancing Redox Equations by Using Half-reactionsBalancing Redox Equations (Reading # 26)

Oxidation NumbersRules for Oxidation Numbers (Reading #27)

Reactions in Aqueous solutions (Reading #28)

Balance redox (Reading #29)

List of relevant resources

List of relevant useful links

http://www.chemguide.co.uk/inorganic/redoxmenu.html#top
http://www.chemguide.co.uk/physical/redoxeqia/combinations.html#top
http://www.voyager.dvc.edu/~lborowski/chem120index/Redox/RedoxIndex.htm

Detailed description of activity #3

Redox (Reduction – Oxidation) Reactions

Introduction*:* Chemical reactions involve the exchange of electrons between two or more atoms or molecules. The species involved, exchange electrons which, leads to a change in the charge of both the atoms of that species. This change in the charges of atoms (change in the atom's oxidation number) by means of electron exchange is defined as a ***Reduction-Oxidation*** (***Redox***) reaction. Chemists usually use the terms oxidizing and reducing agents to describe the reactants in redox reactions. Because oxidation is the process of losing electrons, an ***oxidizing agent*** is defined simply as *any substance that can cause a loss of electrons in another substance in a chemical reaction*. Thus, an ***oxidizing agent*** gains electrons, and its ***oxidation number*** *(a positive or negative number which represents the oxidation state of an atom* as defined below*)* thereby decreases. ***Reduction*** on the other hand, is the process of gaining electrons and therefore a ***reducing agent*** is *a substance that can cause another substance to gain electrons*. The reducing agent therefore loses electrons, and its ***oxidation number*** thereby

increases. Therefore, as a reducing agent reduces the other reagent, it is itself being oxidized. Conversely, as an oxidizing agent oxidizes the other reagent, it is itself being reduced.

To keep track of electrons in redox reactions, it is useful to assign ***oxidation numbers*** to the reactants and products. An atom's ***oxidation number***, also referred to as ***oxidation state***, signifies the *number of charges the atom would have in a molecule (or an ionic compound) if electrons were transferred completely*.

For example, we can write equations for the formation of HCl and SO_2 as follows:

$$\overset{0}{H_2\,(g)} + \overset{0}{Cl_2\,(g)} \rightarrow \overset{+\,-1}{2HCl\,(g)}$$

$$\overset{0}{S\,(s)} + \overset{0}{O_2\,(g)} \rightarrow \overset{+4\,-2}{SO_2\,(g)}$$

The numbers above the elements symbols are the ***oxidation numbers***. In both of the reactions shown, there is no charge on the atoms in the reactant molecules. Thus their oxidation number is zero. For the product molecules, however, it is asumed that complete electron transfer has taken place and that atoms have gained or lost electrons. The oxidation numbers reflect the number of electrons "transferred".

Oxidation numbers enables us to identify elements that are oxidized and reduced at a glance. The elements that show an increase in oxidation number- hydrogen and sulfur in the preceding examples – are oxidized. Chlorine and oxygen are reduced, so their oxidation numbers show a decrease from their initial values. Note that the sum of the oxidation numbers of H and Cl in HCl (+1 and -1) is zero. Likewise, if we add the charges on S (+4) and two atoms of O [2 x (-2)], the total is zero. The reason is that the HCl and SO_2 molecules are neutral, so the charges must cancel.

The following rules are used by chemists to assign oxidation numbers:

1. In free elements (i.e., in the uncombined state), each atom has an oxidation number of zero. Thus each atom in H_2, Br_2, Na, K, O_2 and P_4 has the same oxidation number: zero.
2. For ions composed of only one atom (i.e., monoatomic ions) the oxidation number is equal to the charge on the ion. Thus Li^+ ion has an oxidation number of +1, Ba^{2+} ion, +2; Fe^{3+}, +3; I^- ion, -1; O^{2-} ion, -2; etc. All alkali metals have an oxidation number of +1 and all alkaline earth metals have an oxidation number of +2 in their compounds. Aluminum has an oxidation number of +3 in all its compounds.

3. The oxidation number of oxygen in most compounds (e.g., MgO and H_2O) is -2, but in hydrogen peroxide (H_2O_2) and peroxide ion (O_2^{2-}), it is -1.
4. The oxidation number of of hydrogen is +1, except when it is bonded to metals in binary compounds. In these case (for example, LiH, NaH, CaH_2), its oxidation number is -1.
5. Fluorine has an oxidation number of -1 in all its compounds. Other halogens (Cl, Br, and I) have negative oxidation numbers when they occur as halide ions in their compounds. When combined with oxygen – for example in oxoacids and oxoanions – they have positive oxidation numbers.
6. In a neutral molecule, the sum of the oxidation numbers of all the atoms must be zero. In a polyatomic ion, the sum of oxidation numbers of all the elements in the ion must be equal to the net charge of the ion. For example, in the ammonium ion, NH_4^+, the oxidation number of N is -3 and that of H is +1. the sum of the oxidation numbers is -3 + 4(+1) = +1, which is equal to the net charge of the ion.
7. Oxidation numbers do not have to be integers. For example, the oxidation number of O in the superoxide ion O_2^-, is -1/2.

Example: Using the rules above, assign oxidation numbers to all the elements in the following compounds and ion: (a) Li_2O, (b) HNO_3, (c) $Cr_2O_7^{2-}$

Solution:

(a) By rule 2, we see that lithium has an oxidation number of +1 (Li^+) and oxygen's oxidation number is -2 (O^{2-}).

(b) HNO_3 yields H^+ and NO_3^- ion in solution. From rule 4 we see that H has an oxidation number of +1. Thus the other group (nitrate ion) must have a net oxidation number of -1. Oxygen has an oxidation number of -2, and if we use x to represent the oxidation number of nitrogen, then the nitrate ion can be written as: $[N^{(x)} O_3^{(2-)}]^-$ so that x + 3(-2) = -1 or x = +5

(c) From Rule 6, we see that the sum of the oxidation numbers in the dichromate ion $Cr_2O_7^{2-}$ must be -2. We know that the oxidation number of O is -2, so all that remains is to determine the oxidation number of Cr, which we can call y. the dichromate ion can be written as: $[Cr_2^{(y)} O_7^{(2-)}]^{2-}$ so that 2(y) + 7(-2) = -2 or y = +6.

Exercise 1. Assign oxidation numbers to all the elements in the following anions (a) NO_3^-, (b) MnO_4^- (c) $SbCl_5$

Question : How does one tell a redox reaction from an ion exchange reaction? How does one know that electron transfer has taken place?

Answer: Electron transfer is manifested in change in oxidation number or oxidation state. We know electron transfer has taken place if the oxidation number of an element has changed.

Example: (The numbers written above the symbols are their corresponding oxidation states)

a) $\overset{+1\ +5\ -2}{2\ AgNO_3\ (aq)} + \overset{+2\ -1}{CuCl_2\ (aq)} \rightarrow \overset{+1\ -1}{2\ AgCl\ (s)} + \overset{+2\ +5\ -2}{Cu(NO_3)_2\ (aq)}$

b) $\overset{+1\ +5\ -2}{2\ AgNO_3\ (aq)} + \overset{0}{Cu\ (s)} \rightarrow \overset{0}{2\ Ag\ (s)} + \overset{+2\ +5\ -2}{Cu(NO_3)_2\ (aq)}$

Which of the two reactions is a redox reaction? Explain!

Solution: (b) is a redox reaction since reaction involves electron transfer. Note that the oxidation state of Cu has moved from zero to +2, while that of Ag has changed from +1 to zero. Ag^+ is the oxidizing agent (it gains an electron) while Cu is the reducing agent (it loses two electrons).

Exercise 1: Which is the reducing agent in the following reaction?

$$2\ VO + 3Fe_3O_4 \rightarrow V_2O_5 + 9\ FeO$$

Balancing of a Redox Reaction

The rules for balancing half reactions are the same as those for ordinary reactions; that is, the number of atoms of each element as well as the net charge on both sides of the equation must be equal.

The following are the steps for balancing a Redox reaction:

1. Identify the species being oxidized and the species being reduced.
2. Write the oxidation and reduction half-reactions. For each half-reaction:
   (a) Balance the elements except for O and H.
   (b) Balance the number of electrons gained or lost.
   (c) Balance the net charges by adding H^+ (acidic) or OH^- (basic).
   (d) Balance the O and H by adding H_2O.

Strategy for balancing redox reactions in acidic solutions:

Example 1: Balance the equation for the reaction between dilute nitric acid and copper metal leading to the production of copper ions and the gas nitric oxide, NO given below:

$Cu(s) + H^+(aq) + NO_3^-(aq) \rightarrow Cu^{2+}(aq) + NO(g)$

Solution:

Step 1: Determine the oxidation state for every atom in the skeleton equation above.

0		+1		+5 -2		+2		+2-2
$Cu(s)$	+	$H^+(aq)$	+	$NO_3^-(aq)$	$\rightarrow$	$Cu^{2+}(aq)$	+	$NO(g)$

Changes in Oxidation status:

CU:	0	$\rightarrow$	+2	Oxidation
N:	+5	$\rightarrow$	+2	Reduction

Step 2: Write the skeleton half reactions.

Oxidation:	Cu	$\rightarrow$	Cu^{2+}
Reduction:	NO_3^-	$\rightarrow$	NO

Step 3: Balance each half-reaction "atomically).

- consider all atoms other than H and O (use any of the species that appear in the skeleton equation of step 1 above)
- balance O atoms by adding H_2O
- balance H atoms by adding H^+

Oxidation:	Cu	$\rightarrow$	Cu^{2+}
Reduction:	NO_3^-	$\rightarrow$	$NO + 2H_2O$
Reduction:	$NO_3^- + 4H^+$	$\rightarrow$	$NO + 2H_2O$

Step 4: Balance the electric charges by adding electrons (electrons have to appear on the right hand side of the oxidation half-reaction and on the left hand side of the reduction half-reaction).

Oxidation: $Cu \rightarrow Cu^{2+} + 2e^-$

Reduction: $NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$

Step 5: Make the number of electrons the same in both the half reactions by finding the least common multiple as we prepare to sum the two half equations.

i.e., 3 x Oxidation reaction: $3Cu \rightarrow 3Cu^{2+} + 6e^-$

and 2 x Reduction reaction: $2NO_3^- + 8H^+ + 6e^- \rightarrow 2NO + 4H_2O$

Step 6: Now combine the two half-reactions.

$3Cu + 2NO_3^- + 8H^+ + 6e^- \rightarrow 3Cu^{2+} + 6e^- + 2NO + 4H_2O$

Step 7: Simplify the summation.

$3Cu + 2NO_3^- + 8H^+ \rightarrow 3Cu^{2+} + 2NO + 4H_2O$

Step 8: Indicate the state of each species to obtain the fully balanced net ionic equation..

$3Cu(s) + 2NO_3^-(aq) + 8H^+(aq) \rightarrow 3Cu^{2+}(aq) + 2NO(aq) + 4H_2O(l)$

Strategy for redox reactions in basic solutions: (First balance the reaction as though it was in acid (use H+ to balance hydrogen atoms)

Example 2: Balance the equation $NO_3^- + Al \rightarrow NH_3 + Al(OH)_4^-$ in basic solution.

Solution:

Step 1: Write the skeleton equation and determine the oxidation state per atom.

+5 -2		0		+3 -1		+3 -2 -1
NO_3^-	+	Al	$\rightarrow$	NH_3	+	$Al(OH)_4^-$

Al is being oxidized. Its oxidation number changes from 0 to +3

N in NO_3^- is being reduced. Its oxidation number changes from +5 to +3

Changes in Oxidation status:

Al:	0	$\rightarrow$	+3	Oxidation
N:	+5	$\rightarrow$	+3	Reduction

Step 2: Write the skeleton half reactions.

Oxidation:	Al	$\rightarrow$	$Al(OH)_4^-$
Reduction:	NO_3^-	$\rightarrow$	NH_3

Step 3: Balance each half-reaction "atomically).

NOTE: In basic solutions, no H^+ are available to balance H. Hence, we pretend that the solution is acidic and carry out a neutralization reaction at the end.

As was the case with acidic solution above,

- consider all atoms other than H and O (use any of the species that appear in the skeleton equation of step 1 above)
- balance O atoms by adding H_2O
- balance H atoms by adding H^+

Oxidation: $Al + 4H_2O \rightarrow Al(OH)_4^-$

Oxidation: $Al + 4H_2O \rightarrow Al(OH)_4^- + 4H^+$

Reduction: $NO_3^- \rightarrow NH_3 + 3H_2O$

Reduction: $NO_3^- + 9H^+ \rightarrow NH_3 + 3H_2O$

Step 4: Balance the electric charges by adding electrons (electrons have to appear on the right hand side of the oxidation half-reaction and on the left hand side of the reduction half-reaction).

Oxidation: $Al + 4H_2O \rightarrow Al(OH)_4^- + 4H^+ + 3e^-$

Reduction: $NO_3^- + 9H^+ + 8e^- \rightarrow NH_3 + 3H_2O$

Step 5: Make the number of electrons the same in both the half reactions by finding the least common multiple as we prepare to sum the two half equations.

i.e., 8 x Oxidation reaction: $8Al + 32H_2O \rightarrow 8Al(OH)_4^- + 32H^+ + 24e^-$

and 3 x Reduction reaction: $3NO_3^- + 27H^+ + 24e^- \rightarrow 3NH_3 + 9H_2O$

Step 6: Now combine the two half-reactions.

$8Al + 32H_2O + 3NO_3^- + 27H^+ + 24e^- \rightarrow 8Al(OH)_4^- + 32H^+ + 24e^- + 3NH_3 + 9H_2O$

Step 7: Simplify the summation.

$8Al + 23H_2O + 3NO_3^- \rightarrow 8Al(OH)_4^- + 3NH_3 + 5H^+$

Step 7b: Change to basic solution by adding as many OH^- to both sides as there are H^+.

$8Al + 23H_2O + 3NO_3^- + 5OH^- \rightarrow 8Al(OH)_4^- + 3NH_3 + 5H^+ + 5OH^-$

Neutralization procedure: Combine the H^+ and the OH^- to form H_2O.

$8Al + 3NO_3^- + 23\ H_2O + 5OH^- \rightarrow 8Al(OH)_4^- + 3NH_3 + 5H_2O$

Now simplify: (by cancelling out redundant H_2O molecules from each side)

$8Al + 3NO_3^- + 18H_2O + 5OH^- \rightarrow 8Al(OH)_4^- + 3NH_3$

Step 8: Indicate state of each species

$8Al(s) + 3NO_3^-(aq) + 18H_2O(l) + 5OH^-(aq) \rightarrow 8Al(OH)_4^-(aq) + 3NH_3(g)$

This is the fully balanced net ionic equation.

Example 2: Balance the following reaction that occurs in basic solution. Write complete, balanced equations for the oxidation and reduction half-reactions and the net ionic equation.

$N_2H_4 + BrO_3^- \rightarrow NO + Br^-$

Solution:

Step 1: Check the oxidation numbers to determine what is oxidized and what is reduced.

Bromine goes from +5 in BrO_3^- to -1 in Br^-. Thus BrO_3^- is being reduced.

Nitrogen goes from -2 in N_2H_4 to +2 in NO. Hence N_2H_4 is being oxidized.

The unbalance half-reactions are:

Oxidation: $N_2H_4 \rightarrow NO$

Reduction: $BrO_3^- \rightarrow Br^-$

Step 2: Balance atoms other than H and O:

Oxidation: $N_2H_4 \rightarrow 2NO$

Reduction: $BrO_3^- \rightarrow Br^-$

Step 3: Balance O with H_2O and then H with H^+.

Oxidation: $2H_2O + N_2H_4 \rightarrow 2NO + 8H^+$

Reduction: $6H^+ + BrO_3^- \rightarrow Br^- + 3H_2O$

(Now the atoms are balanced but the charges are not)

Step 4: Balance the charge with electrons.

Oxidation: $2H_2O + N_2H_4 \rightarrow 2NO + 8H^+ + 8e^-$

Reduction: $6H^+ + BrO_3^- + 6e^- \rightarrow Br^- + 3H_2O$

Step 5: Make the number of electrons the same in both the half reactions by finding the least common multiple as we prepare to sum the two half equations.

3 x Oxidation: $6H_2O + 3N_2H_4 \rightarrow 6NO + 24H^+ + 24e^-$

4 x Reduction: $24H^+ + 4BrO_3^- + 24e^- \rightarrow 4Br^- + 12H_2O$

Step 6: Now combine the two half-reactions.

$6H_2O + 3N_2H_4 + 24H^+ + 4BrO_3^- + 24e^- \rightarrow 6NO + 24H^+ + 24e^- + 4Br^- + 12H_2O$

Step 7: Simplify the summation.

$3N_2H_4 + 4BrO_3^- \rightarrow 6NO + 4Br^- + 6H_2O$

Step 8: Indicate state of each species

$3N_2H_4\,(g) + 4BrO_3^-\,(aq) \rightarrow 6NO\,(g) + 4Br^-\,(aq) + 6H_2O\,(l)$

This is the fully balanced net ionic equation.

Exercice 1: Balance the equation: $I^- + Br_2 \rightarrow IO_3^- + Br^-$ in acidic solution.

Oxidation: $3H_2O + I^- \rightarrow IO_3^- + 6e^- + 6H^+$

Reduction: $Br_2 + 2e^- \rightarrow 2Br^-$

Overall: $3Br_2 + I^- + 3H_2O \rightarrow 6Br^- + IO_3^- + 6H^+$

Redox Titrations

Redox titration is a titration in which the reaction between the analyte and titrant is an oxidation/reduction reaction. Like acid-base titrations, redox titrations normally require an indicator that clearly changes colour. In the presence of large amounts of reducing agent, the colour of the indicator is characteristic of its reduced form. The indicator normally assumes the colour of its oxidized form when it is present in an oxidizing medium. At or near the equivalence point, a sharp change in the indicator's colour will occur as it changes from one form to the other, so the ***equivalence point*** can be readily identified.

Since all redox titrations involve the flow of electrons, all redox titrations can be monitored by looking at the electrical potential of the solution. All one needs to monitor the potential of a solution is a reference electrode and an inert electrode. The details of the workings of such a setup is however, outside the scope of this unit and will not be covered. Nevertheless, the relevant expression that utilizes the experimentally measurable elctrochemical potential, E as a function of titrant volume will be discussed later.

Titrimetic methods that are based on the use of the principles of redox reactions have been used widely in the determination of metals which have two well-defined ***oxidation states***. The process of analysis often involves either:

(i) converting all the metal ions to be analysed (analyte) to a higher oxidation state by use of an oxidizing agent such as sodium peroxide and sodium bismuthate, or

(ii) converting all the analyte metal ions to a lower oxidation state by using a reducing agent such as sulphur dioxide or sodium bisulphite.

In both situations, an excess of reagent is needed which is then destroyed or removed before the sample is titrated.

There are other ways of carrying out quantitative reduction experiments but these are outside the scope of this Unit and will not be covered here.

Redox Titration Curves

To evaluate a redox titration we must know the shape of its titration curve. In an acid–base titration (see previous unit) or a complexation titration (see unit 4), a titration curve shows the change in concentration of hydronium ions, H_3O^+ (as pH) or M^{n+} (as pM) as a function of the volume of titrant. For a *redox titration*, it is convenient to monitor electrochemical potential. ***Nernst equation***, which relates the electrochemical potential to the concentration of reactants and products participating in a redox reaction is often used in determining the concentration of an analyte. Consider, for example, a titration in which the analyte in a reduced state, $\boldsymbol{A}_{red}$, is titrated against a titrant in an oxidized state, $\boldsymbol{T}_{ox}$. The titration reaction can therefore be expressed as:

$$\boldsymbol{A}_{red} + \boldsymbol{T}_{ox} \rightleftharpoons \boldsymbol{T}_{red} + \boldsymbol{A}_{ox}$$

The corresponding electrochemical potential for the reaction, $\boldsymbol{E}_{rxn}$, is the difference between the potentials for the reduction and oxidation half-reactions; i.e.,

$$\boldsymbol{E}_{rxn} = \boldsymbol{E}_{Tox/Tred} - \boldsymbol{E}_{Aox/Ared}$$

During the titration process, upon each addition of titrant, the reaction between the analyte and titrant reaches a state of equilibrium. Under these equilibrium conditions, the reaction's electrochemical potential, $\boldsymbol{E}_{rxn}$, becomes zero, and

$$E_{Tox/Tred} = E_{Aox/Ared}$$

This is true since the two redox systems we are titrating together are in equilibrium and hence the potential of the two pairs are equal. Thus, the potential of the reactant mixture can be found by calculating the electrochemical potential, E for either of the redox pairs.

Consequently, the electrochemical potential for either half-reaction may be used to monitor the titration's progress.

It is significant to note that before the equivalence point is reached during the course of the titration process, the resultant mixture consists of appreciable quantities of both the oxidized ($\boldsymbol{A}_{ox}$) and reduced ($\boldsymbol{A}_{red}$) forms of the analyte, but very little unreacted titrant. The potential, therefore, is best calculated using the ***Nernst equation*** for the analyte's half-reaction. Although $E°\boldsymbol{A}_{ox}/\boldsymbol{A}_{red}$ is the standard-state potential for the analyte's half-reaction, a matrix-dependent **formal potential,** *the potential of a redox reaction for a specific set of solution conditions, such as pH and ionic composition*, is used in its place.

After the ***equivalence point***, the electrochemical potential is also calculated using the ***Nernst equation*** for the titrant's half-reaction, since significant quantities of its oxidized and reduced forms are present in solution.

There are only three equations needed when working with Redox titration curves. One equation is applied to get the titration curve up to the equivalence point, a second to get the E at the equivalence point, and the third (that looks very much like the first) is used after the equivalence point.

Illustration of How to Calculate a Redox Titration Curve

Example: Let us calculate the titration curve for the titration of 50.0 mL of 0.100 mol/L Fe^{2+} with 0.100 mol/L Ce^{4+} in a matrix of 1 mol/L $HClO_4$. The reaction in this case is

$$Fe^{2+}(aq) + Ce^{4+}(aq) \square Ce^{3+}(aq) + Fe^{3+}(aq)$$

The equilibrium constant for this reaction is quite large (it is approximately $6x10^{15}$), so we may assume that the analyte and titrant react completely.

The first task in calculating the titration curve is to calculate the volume of Ce^{4+} needed to reach the equivalence point. From the stoichiometry of the reaction we know that

Number of moles of Fe^{2+} = number of moles of Ce^{4+} or

$$M_{Fe}V_{Fe} = M_{Ce}V_{Ce}$$

where M_{Fe} is the concentration of Fe^{2+} and V_{Fe} is the volume of solution of Fe^{2+}; and M_{Ce} is the concentration of Ce^{4+} and V_{Ce} is the volume of solution of Ce^{4+}. Solving for the volume of Ce^{4+} gives the equivalence point volume as 50.0 mL (i.e., $V_{Ce} = M_{Fe}V_{Fe} / M_{Ce}$).

Before the equivalence point the concentration of unreacted Fe^{2+} and the concentration of Fe^{3+} produced by the reaction are easy to calculate. For this reason we find the electrochemical potential, E using the ***Nernst equation*** for the analyte's half-reaction

$$E = E^{0}_{Fe^{3+}/Fe^{2+}} - 0.05916 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

Illustration:

The concentrations of Fe^{2+} and Fe^{3+} in solution after adding 5.0 mL of titrant (i.e., Ce^{4+} solution) are:

$$[Fe^{2+}] = \frac{\text{moles of unreacted } Fe^{2+}}{\text{total volume}} = \frac{M_{Fe}V_{Fe} - M_{Ce}V_{Ce}}{V_{Fe} + V_{Ce}} = \frac{(0.100x50) - (0.100x5)}{(50+5)} = 8.18x10^{-2}\ M$$

$$[Fe^{3+}] = \frac{\text{moles of } Ce^{4+} \text{ added}}{\text{total volume}} = \frac{M_{Ce}V_{Ce}}{V_{Fe} + V_{Ce}} = 9.09x10^{-3}\ mol/L$$

Substituting these concentrations into the **Nernst equation** for Fe along with the formal potential for the Fe^{3+}/Fe^{2+} half-reaction from a table of reduction potentials, we find that the electrochemical potential is:

$$E = +0.767\ V - 0.05916\log\left(\frac{8.18 \times 10^{-2}}{9.09 \times 10^{-3}}\right) = +0.711\ V$$

Similar electrochemical potential calculations can be carried out for various volumes of titrant (Ce^{4+}) added.

At the equivalence point, the moles of Fe^{2+} initially present and the moles of Ce^{4+} added become equal. Now, because the equilibrium constant for the reaction is large, the concentrations of Fe^{2+} and Ce^{4+} become exceedingly small and difficult to calculate without resorting to a complex equilibrium problem. Consequently, we cannot calculate the potential at the equivalence point, $\boldsymbol{E_{eq}}$ using just the Nernst equation for the analyte's half-reaction or the titrant's half-reaction. We can, however, calculate $\boldsymbol{E_{eq}}$ **by combining the two Nernst equations.** To do so we recognize that the potentials for the two half-reactions are the same; thus,

$$E_{eq} = E^0_{Fe^{3+}/Fe^{2+}} - 0.05916\log\frac{[Fe^{2+}]}{[Fe^{3+}]} \text{ and}$$

$$E_{eq} = E^0_{Ce^{4+}/Ce^{3+}} - 0.05916\log\frac{[Ce^{3+}]}{[Ce^{4+}]}$$

Adding the two ***Nernst equations*** yields

$$2E_{eq} = E^0_{Fe^{3+}/Fe^{2+}} + E^0_{Ce^{4+}/Ce^{3+}} - 0.05916\log\frac{[Fe^{2+}][Ce^{3+}]}{[Fe^{3+}][Ce^{4+}]}$$

At the equivalence point, the titration reaction's stoichiometry requires that

$[Fe^{2+}] = [Ce^{4+}]$ and $[Fe^{3+}] = [Ce^{3+}]$

This will make the log term in the above equation equals zero. The equation simplifies to

$$E_{eq} = \frac{E^0_{Fe^{3+}/Fe^{2+}} + E^0_{Ce^{4+}/Ce^{3+}}}{2} = \frac{0.767V + 1.70V}{2} = 1.23$$

After the equivalence point, the concentrations of Ce^{3+} and excess Ce^{4+} are easy to calculate. The potential, therefore, is best calculated using the Nernst equation for the titrant's half-reaction,

$$E = E^0_{Ce^{4+}/Ce^{3+}} - 0.05916\log\frac{[Ce^{3+}]}{[Ce^{4+}]}$$

Illustration:

After adding 60.0 mL of titrant, the concentrations of Ce^{3+} and Ce^{4+} are

$$[Ce^{3+}] = \frac{\text{initial moles } Fe^{2+}}{\text{total volume}} = \frac{M_{Fe}V_{Fe}}{V_{Fe} + V_{Ce}}$$

$$= \frac{(0.100 \text{ mol/L})(50.0 \text{ mL})}{50.0 \text{ mL} + 60.0 \text{ mL}} = 4.55 \times 10^{-2} \text{ mol/L}$$

$$[Ce^{4+}] = \frac{\text{moles of excess } Ce^{4+}}{\text{total volume}} = \frac{M_{Ce}V_{Ce} - M_{Fe}V_{Fe}}{V_{Fe} + V_{Ce}}$$

$$= \frac{(0.100 \text{ mol/L})(60.0 \text{ mL}) - (0.100 \text{ mol/L})(50.0 \text{ mL})}{50.0 \text{ mL} + 60.0 \text{ mL}} = 9.09 \times 10^{-3} \text{ mol/L}$$

Substituting these concentrations into the ***Nernst equation*** for Ce^{4+}/Ce^{3+} half-reaction equation gives the potential as

$$E = +1.70\ V - 0.05916 \log \frac{4.55 \times 10^{-2}}{9.09 \times 10^{-3}} = 1.66\ V$$

Additional data for the plot of the titration curve can be generated following the same procedure above.

How to Sketch a Redox Titration Curve using minimum number of calculations:

Example: Sketch a titration curve for the titration of 50.0 mL of 0.100 mol/L Fe^{2+} with 0.100 mol/L Ce^{4+} in a matrix of 1 M $HClO_4$.

Solution:

This is the same titration that we previously calculated the titration curve for.

We begin as usual, by drawing the axes for the titration curve Potential E versus volume of titrant added in mLs. Having shown that the equivalence point volume is 50.0 mL, we draw a vertical line intersecting the *x*-axis at this volume.

Before the equivalence point, the solution's electrochemical potential is calculated from the concentration of excess Fe^{2+} and the concentration of Fe^{3+} produced by the titration reaction. Using tabulated values of the matrix-dependent **formal potential** values, we can now calculate the corresponding electrochemical potential values **E** and plot **E** for 5.0 mL and 45.0 mL of titrant in the graph.

After the equivalence point, the solution's electrochemical potential is determined by the concentration of excess Ce^{4+} and the concentration of Ce^{3+}. Using tabulated values of the matrix-dependent **formal potential** values, we can now calculate the corresponding electrochemical potential values **E** and again plot points for 60.0 mL and 80.0 mL of titrant.

To complete an approximate sketch of the titration curve, we draw separate straight lines through the two points before and after the equivalence point. Finally, a smooth curve is drawn to connect the three straight-line segments.

Selecting and Evaluating the End Point

The ***equivalence point*** of a redox titration occurs when stoichiometrically equivalent amounts of analyte and titrant react. As with other titrations, any difference between the equivalence point and the end point is a **determinate** (see unit 1) source of error.

The most obvious question to ask is: **Where is the Equivalence Point?**

Previously, in discussing acid–base titrations, we noted that the equivalence point is almost identical with the inflection point located in the sharply rising part of any titration curve. When the stoichiometry of a redox titration is symmetrical (i.e., one mole analyte per mole of titrant), then the equivalence point is equally **symmetrical.** If however, the stoichiometry is not symmetrical, then the equivalence point will lie closer to the top or bottom of the titration curve's sharp rise. In this case the equivalence point is said to be **asymmetrical.** The following example shows how to calculate the equivalence point potential in this situation.

Example: Derive a general equation for the electrochemical potential at the equivalence point for the titration of Fe^{2+} with MnO_4^-. The stoichiometry of the reaction is such that

$$5Fe^{2+}(aq) + MnO_4^-(aq) + 8H_3O^+(aq) \rightarrow 5Fe^{3+}(aq) + Mn^{2+}(aq) + 12H_2O(l)$$

Solution:

The redox half-reactions for the analyte and the titrant are:

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

$$MnO_4^-(aq) + 8H_3O^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 12H_2O(l)$$

for which the corresponding ***Nernst equations*** are:

$$E_{eq} = E^0_{Fe^{3+}/Fe^{2+}} - 0.05916 \log \frac{[Fe^{2+}]}{[Fe^{3+}]}$$

$$E_{eq} = E^0_{MnO_4^-/Mn^{2+}} - \frac{0.05916}{5} \log \frac{[Mn^{2+}]}{[MnO_4^-][H_3O^+]^8}$$

Before adding together these two equations, the second equation must be multiplied by 5 so that the log terms can be combined; thus at the equivalence point, we know that

$$[Fe^{2+}] = 5 \times [MnO_4^-]$$

$$[Fe^{3+}] = 5 \times [Mn^{2+}]$$

Substituting these equalities into the equation for E_{eq} and rearranging gives

$$E_{eq} = \frac{E^0_{Fe^{3+}/Fe^{2+}} + 5E^0_{MnO_4^-/Mn^{2+}}}{6} - \frac{0.05916}{6}\log\frac{5[MnO_4^-][Mn^{2+}]}{5[Mn^{2+}][MnO_4^-][H_3O^+]^8}$$

$$= \frac{E^0_{Fe^{3+}/Fe^{2+}} + 5E^0_{MnO_4^-/Mn^{2+}}}{6} - \frac{0.05916}{6}\log\frac{1}{[H_3O^+]^8}$$

$$= \frac{E^0_{Fe^{3+}/Fe^{2+}} + 5E^0_{MnO_4^-/Mn^{2+}}}{6} + \frac{(0.05916)(8)}{6}\log[H_3O^+]$$

$$= \frac{E^0_{Fe^{3+}/Fe^{2+}} + 5E^0_{MnO_4^-/Mn^{2+}}}{6} - 0.0788pH$$

For this titration, the electrochemical potential at the equivalence point consists of two terms: The first term is **a weighted average of the standard state or formal potentials for the analyte and titrant,** in which the weighting factors are the number of electrons in their respective redox half-reactions. The second term shows that E_{eq} is **pH-dependent.** The Figure below shows a typical titration curve for the analysis of Fe^{2+} by titration with MnO_4^-, showing the asymmetrical equivalence point. Note that the change in potential near the equivalence point is sharp enough that selecting an end point near the middle of the titration curve's sharply rising portion does not introduce a significant titration error.

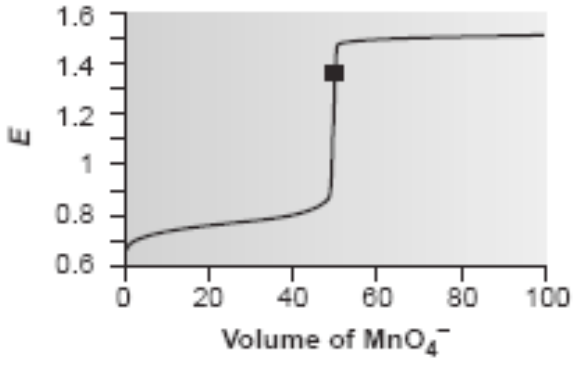


Figure: Titration curve for Fe^{2+} with MnO_4^- in 1 mol/L H_2SO_4. The equivalence point is shown by the symbol •.

Detection of End Point:

The end point of a redox titration can be determined by either an electrode via measuring the electrochemical potential with an indicating electrode relative to a reference electrode and plotting this electrochemical potential against the volume of titrant or by a colour indicator. However, as in other titrations, it is usually more convenient to use visual indicators.

Finding the End Point with a Visual Indicator

There are three methods used for visual indication of the end point in a redox titration. These are:

A. Self-Indication: A few titrants, such as MnO_4^-, have oxidized and reduced forms whose colors in solution are significantly different: Solutions of MnO_4^- are intensely purple. In acidic solutions, however, the reduced form of permanganate, Mn^{2+}, is nearly colourless. When MnO_4^- is used as an oxidizing titrant, the solution remains colourless until the first drop of excess MnO_4^- is added. The first permanent tinge of purple signals the end point.

B. Starch Indicator: A few substances indicate the presence of a specific oxidized or reduced species. Starch, for example, forms a dark blue complex with I_3^- and can be used to signal the presence of excess I_3^- (color change: colourless to blue), or the completion of a reaction in which I_3^- is consumed (color change: blue to colourless). Another example of a specific indicator is thiocyanate, which forms a soluble red-colored complex, $Fe(SCN)^{2+}$, with Fe^{3+}.

C. Redox Indicators: The most important class of visual indicators, however, are substances that do not participate in the redox titration, but whose oxidized and reduced forms differ in color. When added to a solution containing the analyte, the indicator imparts a color that depends on the solution's electrochemical potential. Since the indicator changes color in response to the electrochemical potential, and not to the presence or absence of a specific species, these compounds are called general **redox indicators.**

The relationship between a redox indicator's change in color and the solution's electrochemical potential is easily derived by considering the half-reaction for the indicator

$$In_{ox} + ne- \square In_{red}$$

where In_{ox} and In_{red} are the indicator's oxidized and reduced forms, respectively. The corresponding ***Nernst equation*** for this reaction is

$$E = E^0_{In_{ox}/In_{red}} - \frac{0.05916}{n} \log \frac{[In_{red}]}{[In_{ox}]}$$

If we assume that the indicator's color in solution changes from that of In_{ox} to that of In_{red} when the ratio $[In_{red}]/[In_{ox}]$ changes from 0.1 to 10, then the end point occurs when the solution's electrochemical potential is within the range

$$E = E^{0}_{In_{ox}/In_{red}} \pm \frac{0.05916}{n}$$

Table below shows some examples of general redox indicators

Table showing Redox Indicators

Indicator	Colour		Solution	E^{o}(V)
	Reduced form	Oxidized form		
Nitroferroin	Red	Pale Blue	1 mol/L H_2SO_4	1.25
Ferroin	Red	Pale Blue	1 mol/L H_2SO_4	1.06
Diphenylamine sulfonic acid	Colourless	Purple	Dilute acid	0.84
Diphenylamine	Colourless	Violet	1 mol/L H_2SO_4	0.76
Methylene Blue	Blue	Colourless	1 mol/L acid	0.53
Indigo tetrasulfonate	Colourless	Blue	1 mol/L acid	0.36

Exercise 1: A 25.0 mL solution of sodium ethanedioate (Sodium oxalate) of concentration 0.10 mol/L was placed in a titration flask. A solution of potassium manganate(VII) of concentration 0.038 mol/L was run from a burette into the titration flask. To ensure that the reaction takes place at a suitable rate, the solution was heated to nearly 60°c before potassium manganate (VII) solution was run in from burette.

A. Write the balanced overall redox reaction given the following half-reactions:

Oxidation half-reaction: $C_2O_4^{2-} \rightarrow 2\ CO_2 + 2e^-$

Reduction half-reaction: $MnO_4^-(aq) + 8H_3O^+(aq) + 5e^- \square Mn^{2+}(aq) + 12H_2O(l)$

B. Which indicator is the most suitable to use in this titration?

C. Derive the expression for $\boldsymbol{E_{eq}}$

D. What volume of the manganate(VII) solution would be needed to reach the end point of the titration?

Learning activity # 4

Title of Learning Activity : Complex ion Equilibria and Complexometric Titrations

Specific Learning Objectives

- Define and use the relevant terminologies of complex ion equilibria
- Compare and contrast between complex ion and Lewis acid-base equilibria
- Describe and explain the concept of complex equilibria and stepwise equilibrium reactions.
- Use the concept of chemical equilibria in complexometric titrations and calculations.
- Distinguish among the f the various types of EDTA titrations and their uses.
- Carry out complexometric titrations and related calculations.

Summary of learning activity # 4

In this unit, the concept of complex ion formation and associated stepwise equilibrium reactions will be examined and discussed. Particular emphasis will be given to the application of the complex ion reactions in complexometric titrations, *titrimetric methods based upon complex formation*, as a means to quantitative analysis of metal ions in solution. The emphasis will be on how complex ion formation can be used as a basis of a titrimetric method to quantify metal ions in solution. Here, ethylenediamine tetraacetic acid (EDTA) will be studied as an analytical reagent or titrant that forms very stable complexes with many metal ions in complexometric titration. EDTA (a tertiary amine that also contains carboxylic acid groups) is the most widely used polyaminocarboxylic acid. A discussion on the factors that influence the stability of metal-EDTA complexes and their significance as well as the types of EDTA titrations will also be covered.

Key Concepts

Acid-base indicators: acids or bases which exhibits a visual change on neutralization by the basic or acidic *titrant* at or near the *equivalence point*.

Chelation: the process involved in formation of a chelate.

Chemical stoichiometry: measurement based on exact knowledge of chemical combination

Colorimetric indicator: intensely coloured substances in atleast one form (bound or unbound to a metal) and do change colour when the metal ion analyte binds with it.

Complex: a substance composed of two or more components capable of an independent existence.

Complexation: the *association of two or more chemical species that are capable of independent existence by sharing one or more pairs of electrons*.

Complexometric indicator: water soluble organic molecules that undergoe definite colour change in the presence of specific metal ions and are used in complexometric titrations.

Complexometric titration: A titration based on the formation of coordination complexes between a metal ion and complexing agent (or chelating agent) to form soluble complexes.

Complexing agent or ligand: molecules and/or anions with one or more donor atoms that each donate a lone pair of electrons to the metal ion to form a covalent bond.

Coordination complex: a complex in which a central atom or ion is joined to one or more ligands through what is formally a coordinate covalent bond in which both of the bonding electrons are supplied by a ligand.

***Metal chelate*:** a species that is simultaneously bound to two or more sites on a ligand.

Monodentate (or Unidentate) ligand: A ligand that shares a single pair of electrons with a central metal ion in a complex.

Multidentate ligand: A ligand which shares more than one pair of electrons with a central metal ion in a complex. Those ligands which share 2, 3, 4, 5, or 6 are referred to as bidentate, tridentate, tetradentate (or quadridentate), pentadentate (or quinqui dentate), and hexadentate, respectively.

Stability constant of a complex: a *measure of the extent of formation of the complex at equilibrium*.

Introduction to activity #4

Complex-forming reactions involving many metal ions can serve as a basis for accurate and convenient titrations for such metal ions. These kinds of complex ion titration procedures referred to as complexometric titrations, have high accuracies and offer the possibility of determinations of metal ions at the millimole levels. They have their applications in many chemical and biological processes. The processes involved in the formation of complex ions are basically acid-base type reactions in which the metal ion acts as an acid and the anions or molecules as the base (see unit 2 that deals with acids and bases). In this activity, the theory and applications of complex ion formation, and specifically complexometric titrations in quantifying metal ions in solution will be examined. In addition, the significance of using a reagent that forms a chelate over one that merely forms a complex with a metal ion in volumetric analysis will be explained. Since much attention has recently been focused on the use of ethylenediamine tetraacetic acid (EDTA) in titrimetry, its various applications will be highlighted in this unit.

List of other compulsory readings

Complex Formation (Reading #30)

Ethlyne diamine tetraacetic acid (Reading #31, Reading #32)

List of relevant resources :

List of relevant useful links

http://www.chem.vt.edu/chem-edu/index.html

http://www.chem.vt.edu/chem-edu/a.html

http://www.chem.vt.edu/chem-edu/titration/titratn.html

http://www.chem.vt.edu/chem-edu/general/complexes.html

Detailed description of the activity

Introduction to Complexation Equilibria and Processes:

In this introduction, important terminologies that will be encountered when dealing with the topic of complexation titration are provided. Also included is a brief description of what a complex is and how their very nature contrast Lewis acid-base systems.

In the broadest sense, ***complexation*** is the *association of two or more chemical species that are capable of independent existence by sharing one or more pairs of electrons*. Although this type of a chemical reaction can be classified as a *Lewis acid-base reaction*, it is more commonly known as a **complexation reaction**. As

applied to chemical analysis, this definition is generally taken to mean *the bonding of a central metal ion, capable of accepting an unshared pair of electrons with a ligand that can donate a pair of unshared electrons*.

Consider the addition of anhydrous copper (II) perchlorate to water. The salt dissolves readily according to the reaction,

$$Cu(ClO_4)_2(s) + 4H:O:H \xrightarrow{water} Cu(H_2O)_4^{2+}(aq) + 2ClO_4^-$$

in which a pair of electrons on the oxygen atom of each H_2O molecule forms a *coordinate covalent bond*, *a bond in which both electrons originate from one atom* (in this case one oxygen atom of H_2O), to Cu^{2+} ion. In this reaction, Cu^{2+} acts as a ***Lewis acid*** and H_2O as a ***Lewis base***. Such binding of solvent molecules to a metal ion is called *solvation* or, in the special case of solvent water, *hydration*. The $Cu(H_2O)_4^{2-}$ ion is called an *aquo complex*.

In a complexation reaction, the product of the reaction is termed a **complex**. The species which donates the electron pairs by acting as a *Lewis base* is known as a **complexing agent or ligand**, and the ion which accepts the donated electrons, the *Lewis acid*, is called the **central ion or central atom**. Central ions are generally metallic cations. The ligand can be either a neutral molecule such as water or ammonia; or an ion such as chloride, cyanide, or hydroxide. The complex can have either a positive or a negative charge, or it can be neutral.

For most analytical applications, complexation occurs between a dissolved metal ion and a dissolved ligand capable of displacing water from the metal ion. This is illustrated for the reaction between a hydrated copper (II) ion and dissolved NH_3 ligand below.

$$[Cu(H_2O)_4]^{2+} + NH_3 \xrightarrow{water} [CuNH_3(H_2O)_3]^{2+} + H_2O$$

Normally for reactions that occur in water, H_2O is omitted and the ***complexation reaction*** is written simply a

$$Cu^{2+} + NH_3 \rightleftharpoons [CuNH_3]^{2+}$$

Classification of Ligands

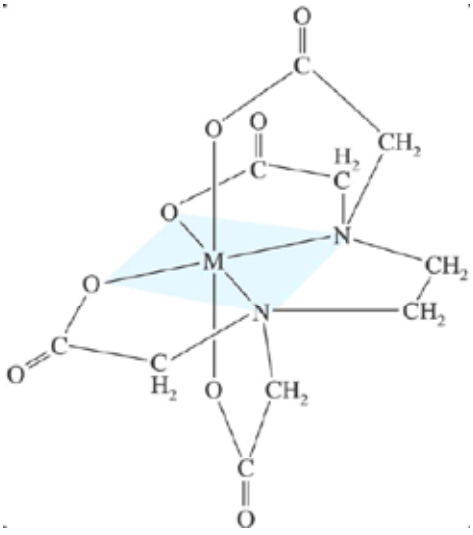
Ligands are classified according to the number of pairs of electrons which they can share with the central metal or metal ion. A ligand that shares a single pair of electrons (such as ammonia, water, cyanide, F^-, Cl^-, Br^-, I^-, CN^-, SCN^-, NO_2^-, NH_3, H_2O, $N(CH_2CH_3)_3$, CH_3COCH_3, etc.) is a ***monodentate*** or ***unidentate ligand***; a ligand, which shares more than one pair of electrons, is a ***multidentate ligand***. A multidentate ligand, which shares two (such as $NH_2CH_2CH_2NH_2$, $C_2O_4^{2-}$, etc,), three, four, five, or six pairs of electrons is a bidentate, tridentate (or terdentate), tetradentate (or quadridentate), pentadentate (or quinqui dentate), or hexadentate (or sexadentate) ligand, respectively. The maximum number of electron pair donor groups that a metal ion can accommodate in complexation reaction is known as its *coordination number*. Typical values are 2 for Ag^+, as in $Ag(CN)_2^-$, 4 for Zn^{2+}, as in $Zn(NH_3)_4^{2+}$; and 6 for Cr^{3+}, as in $Cr(NH_3)_6^{3+}$.

Nature of Linkage in complex ions

A central metal ion can form a single bond with a ligand which is able to donate a pair of electrons from one of its atoms only, as in the examples given above for the formation of $Zn(NH_3)_4^{2+}$, $Cr(NH_3)_6^{3+}$ etc. However, with multidentate (or sometimes known as polydentate) ligands, it can form a bond in more than one location to form a ring structure. Generally, ring formation results in increased stability of the complex. A species that is simultaneously bonded to two or more sites on a ligand is called a **metal chelate**, or simply a ***chelate*** and the process of its formation is called ***chelation***.

A ***chelate*** is formed if two or more donor atoms is coordinated by the simultaneous use of two or more electron pairs to the same metal atom. An example of a metal-EDTA complex is provided in the figure below.

Note that, all types of bidentate, tridentate, tetradentate, pentadentate and hexadentate ligands can act as chelating ligands and their complexes with metals are therefore known as chelates.



Here, EDTA behaves as a hexadentate ligand since six donor groups are involved in bonding the divalent metal cation.

Importance of Chelates

Chelates find application both in industry and in the laboratory where fixing of metal ions is required. In analytical chemistry, chelates are used in both qualitative and quantitative analysis. For example, Ni^{2+}, Mg^{2+}, and Cu^{2+} are quantitatively ***precipitated*** by chelating agents. In volumetric analysis, chelating agents (such as ethylenediamine tetraacetic acid, EDTA) are often used as a reagents or as indicators for the titration of some metal ions. Because of the stability of chelates, polydentate ligands (also called chelating agents) are often used to sequester or remove metal ions from a chemical system. Ethylenediamine tetraacetic acid (EDTA), for example, is added to certain canned foods to remove transition-metal ions that can catalyze the deterioration of the food. The same chelating agent has been used to treat lead poisoning because it binds Pb^{2+} ions as the chelate, which can then be excreted by the kidneys.

In the subsequent sections that follow, the application of the fundamentals of complex ion formation is demonstrated in complexometric titration. This is achieved after briefly considering the subtopic of complex equilibria.

Complex ion Equilibria

Stability constant of a complex is defined as a *measure of the extent of formation of the complex at equilibrium*. Stability of a complex depends on the strength of the linkage between the central metal ion and the ligands (ie., the bond) and therefore, the stronger the metal ligand bond, the more stable the complex.

Metal complexes are formed by replacement of molecules in the solvated shell of a metal ion in aqueous solution with the ligands by ***stepwise reaction*** as shown below:

$$[M(H_2O)_n] + L \rightleftharpoons [M(H_2O)_{n-1}L] + H_2O$$

$$[M(H_2O)_{n-1}L] + L \rightleftharpoons [M(H_2O)_{n-2}L_2] + H_2O$$

$$[M(H_2O)_{n-2}L_2] + L \rightleftharpoons [M(H_2O)_{n-3}L_3] + H_2O$$

Overall reaction is:

$$[M(H_2O)_n] + nL \rightleftharpoons [ML_n] + nH_2O$$

where ***L*** stands for the ligand and ***n*** refers to the number of molecules of a particular species. If we ignore the water molecules in the above equations, one can then write the above equations and their corresponding equilibrium constants as follows:

$$M + L \rightleftharpoons ML \qquad K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \rightleftharpoons ML_2 \qquad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$ML_2 + L \rightleftharpoons ML_3 \qquad K_3 = \frac{[ML_3]}{[ML_2][L]}$$

$$ML_{n-1} + L \rightleftharpoons ML_n \qquad K_n = \frac{[ML_n]}{[ML_{n-1}][L]}$$

The equilibrium constants, K_1, K_2, K_3, …., and K_n are known as the ***stepwise formation constants*** or ***stepwise stability constants*** or ***consecutive stability constants***.

Note that the values of the stepwise stability constants decrease in the order:

$$K_1 > K_2 > K_3 > \ldots > K_n$$

because a previously metal ion-coordinated ligand tends to repel any incoming ligand of a similar kind.

The products of the ***stepwise stability constants*** is known as ***overall stability*** or ***cumulative stability constant*** and is designated as β , i.e.,

$$\beta = K_1 \times K_2 \times K_3 \times \ldots\ldots\ldots \times K_n$$

$$\beta = \frac{[ML]}{[M][L]} \bullet \frac{[ML_2]}{[ML][L]} \bullet \frac{[ML_3]}{[ML_2][L]} \bullet \bullet \bullet \bullet \frac{[ML_n]}{[ML_{n-1}][L]}$$

As previously mentioned, multidentate ligands which form five- or six-membered rings with central metal ions, generally have unusually high stability. To be useful in a titration, the complexation reaction must occur rapidly as compared with the rate of addition of the titrant. Complexes which are formed rapidly are called **labile complexes** and those which are formed slowly are called **nonlabile or inert complexes**. Generally, only titration reactions which form labile complexes are useful.

Consider the simple complexation of copper (II) ion by the unidentate ligand NH_3 in water. The reaction between these two species is

$$Cu^{2+} + NH_3 \rightleftharpoons [CuNH_3]^{2+}$$

(the H_2O is omitted for simplicity). In aqueous solution the copper (II) ion is actually hydrated and NH_3 replaces H_2O. The equilibrium constant for this reaction is the stepwise formation constant, K_1, is expressed as:

$$K_1 = \frac{[[CuNH_3]^{2+}]}{[Cu^{2+}][NH_3]} = 2.0 \times 10^4$$

The equilibrium of the addition of a second ammonia molecule,

$$CuNH_3^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2]^{2+}$$

is described by a second stepwise formation constant, K_2,

$$K_2 = \frac{[[Cu(NH_3)_2]^{2+}]}{[CuNH_3]^{2+}][NH_3]} = 5.0 \times 10^3$$

The overall process for the addition of the two NH_3 molecules to a Cu^{2+} ion and the equilibrium constant for that reaction are given by the following:

$$Cu^{2+} + NH_3 \rightleftharpoons [CuNH_3]^{2+}$$

$$K_1 = \frac{[[CuNH_3]^{2+}]}{[Cu^{2+}][NH_3]} = 2.0 \times 10^4$$

$$CuNH_3^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_2]^{2+}$$

$$K_2 = \frac{[[Cu(NH_3)_2]^{2+}]}{[CuNH_3]^{2+}][NH_3]} = 5.0 \times 10^3$$

$$Cu^{2+} + 2NH_3 \rightleftharpoons [Cu(NH_3)_2]^{2+}$$

$$\beta_2 = \frac{[[Cu(NH_3)_2]^{2+}]}{[Cu^{2+}]][NH_3]^2} = K_1 \times K_2 = 1.0 \times 10^8$$

The formation constant β_2 (= K_1K_2) is called an **overall formation constant**. Recall that the equilibrium constant of a reaction obtained by adding two other reactions is the product of the equilibrium constants of these two reactions, β_2.

Similarly, the stepwise and overall formation constant expressions for the complexation of a third and fourth molecule of NH_3 to copper (II) are given by the following:

$$[Cu(NH_3)_2]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_3]^{2+} \qquad K_3 = \frac{[[Cu(NH_3)_3]^{2+}]}{[[Cu(NH_3)_2]^{2+}][NH_3]}$$

$$[Cu(NH_3)_3]^{2+} + NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} \qquad K_4 = \frac{[[Cu(NH_3)_4]^{2+}]}{[[Cu(NH_3)_3]^{2+}][NH_3]}$$

$$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

$$\beta_4 = \frac{[[Cu(NH_3)_4]^{2+}]}{[Cu^{2+}]][NH_3]^4} = K_1 \times K_2 \times K_3 \times K_4$$

The values of K_3 and K_4 are 1.0 x 10^3 and 2.0 x 10^2, respectively. Therefore, the values of β_3 and β_4 are 1.0 x 10^{11} and 2.0 x 10^{13}, respectively.

The stepwise formation constants of the amine complexes of copper (II) are relatively close together. This means that over a wide range of NH_3 concentrations, there will exist at the same time, at least two (normally more), copper (II) amine complexes in solution at significant concentrations relative to each other. This is generally true of *unidentate ligands* and hence limits their use as titrants for the determination of metal ions (save for a few specialized cases, which is beyond the scope of this module).

A major requirement for titration is a single reaction that goes essentially to completion at the equivalence point. This requirement is generally not met by unidentate ligands because of the fact that their formation constants are not very high.

Dissociation of Complexes

A given complex behaves as a weak electrolyte and dissociates to a small degree. The equilibrium constant for the dissociation of a complex is simply the inverse of its ***formation constant***, K_{form}, and is known as the **instability constant,** K_{ins}. For example, the complex ion $Ag(NH_3)_2^+$ dissociates according to the equilibrium reaction:

$$[Ag(NH_3)_2]^+ \rightleftharpoons Ag^+ + 2NH_3$$

and its ***instability constant*** is given by,

$$K_{ins} = \frac{1}{K_{form}} = \frac{[Ag^+][NH_3]^2}{[Ag(NH_3)_2^+]}$$

In actual practice, the dissociation of a complex ion, just like the ionization of a polyprotic acid, occurs in steps as shown below:

$$Ag(NH_3)_2^+ \rightleftharpoons Ag(NH_3)^+ + NH_3 \qquad K_1 = \frac{[Ag(NH_3)^+][NH_3]}{[Ag(NH_3)_2^+]}$$

$$Ag(NH_3)^+ \rightleftharpoons Ag^+ + NH_3 \qquad K_2 = \frac{[Ag^+][NH_3]}{[Ag(NH_3)^+]}$$

The ***overall instability constant,*** $K_{ins} = K_1 \times K_2$

Exercise. Calculate the percent dissociation of a 0.10 M $Ag(NH_3)_2^+$ solution if its instability constant, $K_{ins} = 6.3 \times 10^{-8}$.

Application of Complex Equilibria in Complexation Titration:

The concept behind formation of complexes can be used as stated earlier (see section on importance of chelates), in quantitative analysis of either metal ions or other anions of interest.

An example to illustrate the use of complex titration exercise is in the determination of cyanide present in a solution via the ***titration of cyanide with silver nitrate solution*** given below**.**

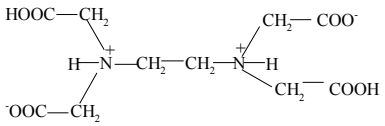
When a solution of silver nitrate is added to a solution containing cyanide ion (alkali cyanide), a white precipitate is formed when the two ligands first come into contact with each another. On stirring, the precipitate re-dissolves due to the formation of an alkali stable salt of silver-cyanide complex, i.e.,

$$Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$$

When the above reaction is complete (following attainement of an ***equivalence point***), further addition of the silver nitrate solution now yields an insoluble *silver cyanoargentate* (some times termed insoluble silver cyanide). The ***end point*** of the reaction is indicated by the formation of a permanent precipitate or turbidity. Such a titration experiment can be used to quantify the amount of cyanide present in a solution. Here cyanide is an example of a ***complexone***; another term for *a complexing agent*.

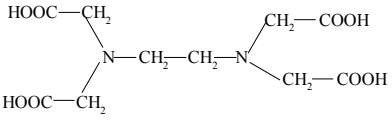
Note that the formation of a single complex species in contrast to a stepwise production of complex species simplifies ***complexation titration*** (i.e., complexometric titrations) and facilitates the detection of ***end points***.

The chelate most commonly used for complexometric titrations is ***ethylenediamine tetraacetic acid*** (EDTA); an aminopolycarboxylic acid which is an excellent complexing agent. It is normally represented by either of the following two structures:



(I)

OR



(II)

Its greatest advantage is that it is inexpensive, chemically inert, and it reacts with many metals with a simple stoichiometry

$$EDTA^{4-} + M^{n+} \rightarrow [M - EDTA]^{n-4}$$

where *n* is the charge on the metal ion, M.

This complexing agent has four (4) ionizable acid groups with the following pK_a (= -logK_a, where K_a is the acid dissociation constant) values: $pK_{a1} = 2$, $pK_{a2} = 2.7$, $pK_{a3} = 6.6$ and $pK_{a4} = 10.3$ at 20°C. These values suggest that the complexing agent behaves as a dicarboxylic acid with two strongly acidic groups and that there are two ammonium protons of which the first ionizes in the pH region of about 6.3 and the second at pH of about 11.5.

If M^{n+} is the metal ion and Y^{4-} stands for the completely ionized form of EDTA, then the metal-EDTA complex can be represented as $MY^{(n-4)+}$. The stability of such a complex is often dependent on a number of factors, that need due consideration as one investigates the application of EDTA titration experiments in quantification of metal ions in solution. These factors affect the various ***multiple equilibria*** shown above, which in turn influences how complexometric titration is carried out. The next section looks at the two important factors that are true for all complexometric titrations.

Factors affecting Stability of Metal-EDTA complexes

- ***Effect of pH on stability of metal-EDTA complexes***

The concentration of each of the complexes shown, say in examples above, will depend on the pH of the solution. So to have any properly defined equilibria, the pH of the solution mixture will have to be buffered. Equally important, the concentration of protons, H^+, which would otherwise compete with the M^{n+} ions, must be held rigorously constant. For instance, at low pH values ***protonation*** (*the act of transferring or donating a proton, a hydrogen ion, H^+, to a species*) of Y^{4-} species occurs and the species HY^{3-}, H_2Y^{2-}, H_3Y^- and even undissociated H_4Y may well be present. (The abbreviations H_4Y, H_3Y^-, H_2Y^{2-}, HY^{3-}, and Y^{4-} are often used to refer to EDTA and its ions.) Thus, the act of lowering the pH of the solution will decrease the concentration of Y^{4-}. On the other hand, Increasing the pH of the solution will cause tendency to form slightly soluble metallic hydroxides owing to the reaction below:

$$(MY)^{(n-4)+} + nOH^- \rightleftharpoons M(OH)_n + Y^{4-}$$

The extent of hydrolysis (*meaning the splitting of water in a reaction such as*)

$$^-OAc + H_2O \rightleftharpoons HOAc + OH^-$$

of $(MY)^{(n-4)}$ depends upon the characteristic of the metal ion and is largely controlled by the *solubility product* of the metallic hydroxide and the *stabiltity constant* of the complex. The larger the stability constant of the complex, the lesser the tendency of the metal hydroxide to form.

- ***The effect of other complexing agents***

If another complexing agent (other than Y^{4-}) is also present in the solution, then the concentration of M^{n+} in solution will be reduced owing to its ability to further complex with the interfering complexing agent. The relative proportions of the complexes will be dependent on the stability constants of the two types of metal-complexing agent complexes.

EDTA titration has been traditionally used in quantitating calcium ions in water, in a process referred to as determining water hardness. Water hardness is customarily referred to as concentration of calcium in the form of calcium carbonate.

In the following section, we shall use the Ca^{2+}-EDTA titration to illustrate the method of complexometric titration. In this method, a ***colorimetric indicator***, [*these are intensely coloured substances in at least one form (bound or unbound to the metal) and do change colour when the metal-ion analyte binds with it*], is used.

The reaction between Ca^{2+} and EDTA proceeds according to the stoichiometry shown below:

$$Ca^{2+} + EDTA^{4-} \rightleftharpoons Ca - EDTA^{2-}$$

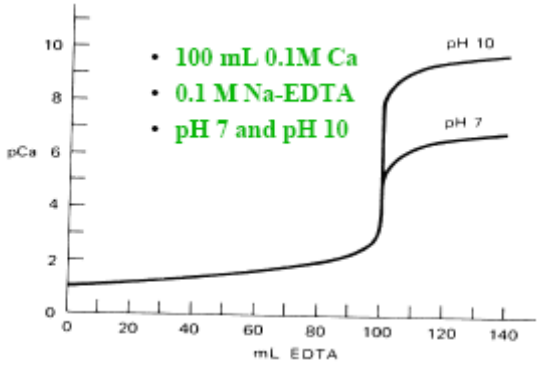
with a corresponding equilibrium constant for ***formation*** expressed as

$$K_f(Ca - EDTA^{2-}) = \frac{[Ca - EDTA^{2-}]}{[Ca^{+}][EDTA^{4-}]}$$

Note that, whereas the equilibrium constants for acids and bases are often tabulated as dissociation constants, equilibrium constants for complex formation are tabulated as *formation constants*.

Titration Curves

In the former unit, we learnt that in the titration of a strong acid versus a strong base, a plot of pH against the volume of the solution of the strong base added yields a point of inflexation at the equivalence point. Similarly, in an EDTA versus metal ion titration, if pM (= -log[M^{n+}], where M^{n+} signifies the metal ion whose concentration is required) is plotted against the volume of EDTA solution added, a point of inflexation occurs at the equivalence point. The general shape of a titration curve obtained following the titration of 100 mL of a 0.1 mol/L solution of Ca^{2+} ion with a 0. 1 mol/L Na-EDTA solution at two separate pH conditions is shown below.



Chemistry of EDTA Titrations

EDTA is used to titrate many ions. For instance, EDTA has been used succesfully over the years for the determination of water hardness (a meassure of the total Ca^{2+} and Mg^{2+} ions in water). Water hardness is often conveniently determined by titration of total Ca^{2+} and Mg^{2+} ions with EDTA. In this subsection, we shall look at the chemistry of EDTA titrations in general.

In the presence of Eriochrome Black T (EBT) as an indicator, a minor difficulty is usually encountered. Note that metal complexes of EBT are generally red in colour. Therefore, if a colour change is to be observed with EBT indicator, the pH of the solution must be between 7 and 11 so that the blue form of the indicator dominates when the titrant breaks up the red metal-EBT complex at the end point. At a pH of 10, the endpoint reaction is:

$$\underset{\text{(Red)}}{MIn^-} + Y^{4-} + H^+ \rightarrow MY^{2-} + \underset{\text{(Blue)}}{HIn^{2-}}$$

EDTA is normally standardized against a solution of Ca^{2+} ions. In the early stages of the EDTA titration with EBT as indicator, the Ca^{2+}-EBT complex does not dissociate appreciably due to a large excess of the untitrated Ca^{2+} ions in solution (i.e., Ca^{2+} ions is plenty in solution). As the titration progresses further and more Ca^{2+} ions is complexed with the titrant, the equilibrium position shifts to the left (i.e., previously complexed Ca-EBT complex, which is red in colour, begins to dissociate to give back more Ca^{2+} ions for complexation with the titrant EDTA), causing a gradual change in colour from the red Ca-EBT complex.

To avoid this problem of gradual change in colour, a small amount of 1:1 EDTA:Mg is often added to the titration flask (this does not affect the stoichiometry of the titration reaction because the quantities of EDTA and Mg are equimolar) because MgIn complex is sufficiently stable that it will not dissociate appreciably prior to attainement of the equivalence point. (Note that at pH 10, Ca-EDTA complex is more stable than Mg-EDTA complex and also, MgIn-complex is more stable than CaIn-complex.)

Note that when 1:1 EDTA:Mg is added to the Ca^{2+} analyte-containing indicator solution, the following reactions take place:

$$MgY^{2-} + Ca^{2+} \rightarrow Mg^{2+} + CaY^{2-} \text{ (more stable)}$$

$$Mg^{2+} + CaIn^- \rightarrow Ca^{2+} + MgIn^- \text{ (more stable)}$$

Explanation:

When EDTA titrant is added, it first binds all the Ca^{2+} as per the reaction shown below (Note that at pH 10, the predominant species of EDTA is HY^{3-}):

$$Ca^{2+} + HY^{3-} \rightarrow CaY^{2-} + H^{+}$$

Upto and including the end point, EDTA replaces the less strongly bound Eriochrome Black T from the Mg^{2+}-EBT complex (represented as $MgIn^{-}$) as shown below:

$$MgIn^{-} + HY^{3-} \rightarrow HIn^{2-} + MgY^{2-}$$

Types of EDTA Titrations

Important metal ions-EDTA titration experiments fall into the following categories:

A. Direct Titration

In ***direct titration***, the solution containing the metal ion to be determined is buffered to the desired pH and titrated directly with a standard EDTA solution. It may be necessary to prevent precipitation of the hydroxide of the metal ion (or a basic salt) by the addition of an ***auxillary complexing agent*** (or sometimes called ***masking agent***, since they form stable complexes with potential interference), such as *tartarate* or *citrate*.

At start (i.e., before addition of titrant):

$M^{n+} + \boldsymbol{Ind} \rightleftharpoons [M\boldsymbol{ind}]^{n+}$

where ***Ind*** is representing the indicator.

During titration:

$M^{n+} + [H_2Y]^{2-} \rightleftharpoons [M\boldsymbol{Y}]^{n-4} + 2H^{+}$

where $[H_2Y]^{2-}$ is representing EDTA titrant

At Endpoint:

$[M\boldsymbol{Ind}]^{n+} + [H_2Y]^{2-} \rightleftharpoons [M\boldsymbol{Y}]^{n-4} + \boldsymbol{Ind} + 2H^{+}$

Note that the ***complexed*** ($[M\boldsymbol{ind}]^{n+}$)and ***free indicator*** (***ind***) have different colours.

At the ***equivalence point*** the magnitude of the concentration of the metal ion being determined decreases abruptly. This ***equivalence point*** is generally determined by the change in color of a ***metal indicator*** that responds to changes in pM.

Example 1. Titration of 100 mL of a water sample at pH 13 in the presence of a calcium specific indicator such as Eriochrome Black T required 14.0 mL of 0.02 M EDTA solution. Calculate the hardness of the water sample as $CaCO_3$ in mg L^{-1}.

Solution

Important infromation to note:

- Molecular weight for $CaCO_3$ is 100g
- The stoichiometry for the reaction between Ca^{2+} and EDTA at pH 13 is given by: $Ca^{2+} + EDTA^{4-} \rightleftharpoons Ca - EDTA^{2-}$
- Both Mg^{2+} and Ca^{2+} contribute to water hardness. Both metal ions have the same stoichiometry with EDTA, hence the titration includes the sum of Mg and Ca ions in the water sample.
- The 14.0 mL of 0.02 M EDTA contains $(\frac{14.0 mL}{1000 ml / L}) \times 0.02 moles / L)$ = 2.80 x 10^{-4} moles of EDTA.
- From the above 1:1 stoichiometry, the number of Ca^{2+} ions present in the 100 mL water sample (equivalent to the combined Ca^{2+} and Mg^{2+} ions responsible for water hardness) should be equal to the number of moles of the titrant, EDTA.
- Hence, number of moles of Ca^{2+} ions present in the 100 mL water sample = 2.80 x 10^{-4} moles.
- 2.80 x 10^{-4} moles of Ca^{2+} is equivalent to (2.80 x 10^{-4} moles) x 100 g $mole^{-1}$ $CaCO_3$ = 2.80 x 10^{-2}g = 2.80 x 10^{-2}g x 1000 mg g^{-1} = 28.0 mg of Ca (as $CaCO_3$).
- Therefore, the hardness of the water is 28.0 mg present in the 100 mL of water = $\frac{28.0 mg}{100 ml / 1000 ml L^{-1}}$ = 280 mg L^{-1} hardness.

Exercise 1. A 50.00 mL water sample required 21.76 mL of 0.0200 mol/L EDTA to titrate water hardness at pH 13.0. What was the hardness in mg L^{-1} of $CaCO_3$?

B. Back titration

This is for the determination of metal ions that cannot be titrated directly with EDTA, say in alkaline solution (e.g., Mn^{2+} and Al^{3+}) due to precipitation of their hydroxides).

In ***back titration***, an excess known amount of a standard EDTA solution is added to the solution of the analyte. The resulting solution mixture is then buffered to the desired pH, and the excess EDTA titrated with a standard solution of a second metal ion. Examples of metal ions often used as the second metal include solutions of; $ZnCl_2$, $ZnSO_4$, $MgCl_2$ or $MgSO_4$. The end point is then detected with the aid of an appropriate metal indicator that responds to the second metal ion introduced in the back titration.

The following steps apply:

$M^{n+} + [H_2Y]^{2-} \rightleftharpoons [M\boldsymbol{Y}]^{n-4} + 2H^+$

where $[H_2Y]^{2-}$ is representing EDTA titrant

$Zn^{2+} + [H_2Y]^{2-} \rightleftharpoons [Zn\boldsymbol{Y}]^{-2} + 2H^+$

At Endpoint:

$Zn^{2+} + \boldsymbol{ind} + \rightleftharpoons [Zn\boldsymbol{ind}]^{2+}$

Back titration becomes necessary if analyte:

- precipitates in the absence of EDTA,
- reacts too slowly with EDTA, or
- blocks the indicator.

Example 1. A 3208 g sample of nickel ore was processed to remove interferences and 50.00 ml of 0.1200 mol L^{-1} EDTA was added in excess to react with Ni^{2+} ions in solution. The excess EDTA was titrated with 24.17 mL of 0.0755 mol L^{-1} standard Mg^{2+}. Calculate the %Ni in the ore.

Solution

- The stoichiometry for the reaction between Ni^{2+} (or Mg^{2+}) and EDTA can be represented as: $Ni^{2+} + EDTA^{4-} \rightleftharpoons Ni - EDTA^{2-}$
- The stoichiometry represents a 1:1, i.e., for every mole of EDTA present, an equivalent number of moles of Ni^{2+} is used up.
- Total number of moles of EDTA initially available in the 50.00 mL (= 0.050 L) solution of 0.1200 mol L^{-1} EDTA = (0.1200 moles L^{-1} x 0.050 L) = 6.0 x 10^{-3} moles.
- Number of moles of the titrant Mg^{2+} ions present in the 24.17 mL (= 0.02417 L) of 0.0755 mol L^{-1} = (0.02417 L x 0.0755 moles L^{-1}) = 1.82 x 10^{-3} moles

- Therefore, the moles of EDTA that must have reacted with the available Ni^{2+} ions originally present = ($6.0 \times 10^{-3} - 1.82 \times 10^{-3}$) moles = 4.18×10^{-3} moles.
- Hence, number of moles of Ni^{2+} ions originally present in the 50.00 mL (= 0.050 L) solution = 4.18×10^{-3} moles.
- This is = 4.18×10^{-3} moles x 58.7g/mol (Atomic weight for Ni = 58.7g) = 0.245366 g

- Therefore, %Ni in the ore = $\frac{0.245366\text{g}}{3208\text{g}} \times 100\% = 0.00765\%$

C. Replacement or substitution titration

Substitution titration may be used for the metal ions that do not react (or react unsatisfactorily) with a metal indicator (e.g., Ca^{2+}, Pb^{2+}, Hg^{2+}, Fe^{3+}), or for metal ions that form EDTA complexes that are more stable than those of other metals such as magnesium and calcium.

In this, there is quantitative displacement of the second metal (Mg^{2+} or Zn^{2+}) from a complex by the analyte metal. Usually, the determination of the metal ions that form weak complexes with the indicator and the colour change is unclear and vague.

The metal cation M^{n+} to be determined may be treated with the magnesium complex of EDTA leading to the following reaction:

$$M^{n+} + MgY^{2-} \rightleftharpoons (MY)^{(n-4)+} + Mg^{2+}$$

The amount of magnesium ion set free is equivalent to the cation present and can be titrated with a standard solution of EDTA.

The following steps apply:

1. Replacement step:

$Ca^{2+} + [MgY]^{2-} \rightleftharpoons [CaY]^{2-} + Mg^{2+}$

2. $Mg^{2+} + \textbf{\textit{Ind}} \rightleftharpoons [Mg\ \textbf{\textit{Ind}}]^{2+}$

$Mg^{2+} + [H_2Y]^{2-} \rightleftharpoons [MgY]^{2-} + 2H^+$

$[Mg\ \textbf{\textit{Ind}}]^{2+} + [H_2Y]^{2-} \rightleftharpoons [MgY]^{2-} + \textbf{\textit{Ind}} + 2H^+$

D. Alkalimetric Titration

When a solution of Na_2H_2Y is added to a solution containing metallic ions, complexes are formed with the liberation of two equivalents of hydrogen ion, i.e.,

$$M^{n+} + H_2Y^{2-} \rightleftharpoons (MY)^{(n-4)} + 2H^+$$

The hydrogen ions thus set free can be titrated with a standard solution of sodium hydroxide using an acid-base indicator or potentiometric end point. Alternatively, an iodate-iodide mixture is added as well as the EDTA solution and the librated iodine is titrated with a standard thiosulphate solution.

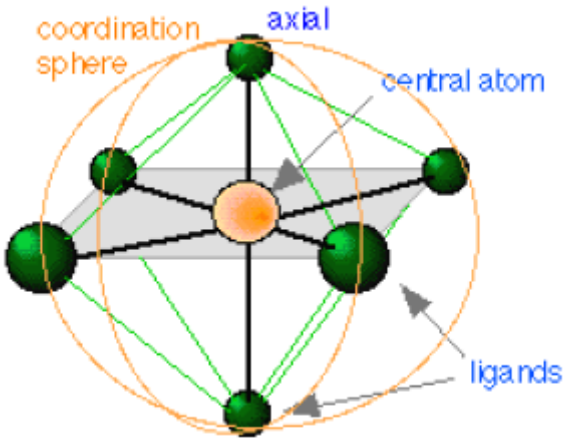
Note that the solution of the metal to be determined must be accurately neutralized before titration; this is often a difficult matter on account of the hydrolysis of many salts, and constitutes a weak feature of alkalimetric titration.

Example 1. A 10.00 mL solution of $FeSO_4$ was added to 50.00 mL of 0.05 mol L^{-1} Na_2H_2Y. The H^+ released required 18.03 mL of 0.080 mol L^{-1} NaOH for titration. What was the molar concentration of the $FeSO_4$ solution?

Solution

- The stoichiometry for the reaction between Fe^{2+} and Na_2H_2Y can be represented as: $Fe^{2+} + Na_2H_2Y \rightleftharpoons Na_2FeY + 2H^+$. Here, 1 mole of Fe^{2+} ions yields 2 moles of H^+ ions.
- The stoichiometry for the acid-base neutralization reaction between the released H^+ ions and NaOH in the titration process can be represented as: $H^+ + OH^- \rightleftharpoons H_2O$. This is 1:1 reaction (i.e., for every 1 mole of H^+ ions released, an equivalent moles of hydroxide is needed for neutralization.
- Therefore, number of moles of H^+ released = number of moles of OH^- ions present in the 18.03 mL (= 0.01803 L) of the 0.080 mol L^{-1} NaOH solution = 0.01803 L x 0.080 mol L^{-1} = 1.4424 x 10^{-3} moles.
- Since for every mole of Fe^{2+} ions consumed, twice as many moles of H^+ ions are released, then the number of moles of Fe^{2+} ions consumed = $\frac{1}{2} \times 1.4424 \text{ x } 10^{-3} \text{moles} = 7.212 \times 10^{-4} \text{ moles}$
- Therefore, 7.212 x 10^{-4} moles of Fe^{2+} ions were present in the original 10.00 mL (= 0.010 L) solution of $FeSO_4$. Thus, Molar concentration of

$$\text{the } FeSO_4 \text{ solution} = \frac{7.212 \times 10^{-4} \text{ moles}}{0.0100\text{L}} = 0.07212\,\text{M}$$



XV. Synthesis of the Module

Analytical chemistry is the branch of chemistry that deals, in part, with the analysis or determination of the composition of chemical substances. This determination or analysis of the composition of substances may be of a quantitative or qualitative nature. In this module, the emphasis has been on the tools for carrying out quantitative chemical analysis. Since the final result of a quantitative analysis is usually a number(s) or a measured quantity there is always some uncertainity associated with measurement. Thus, the first unit of this module covered important statistical methods for describing and reducing, if necessary, such uncertainties in measurements. The second unit dealt with volumetric analysis, as a tool for quantitative methods of analysis based on measurement of volume. Within this unit, the theory of chemical equilibria was discussed with specific emphasis on solubility and acid-base equilibria, two of the four main types of chemical equilibria. Also, the fundamentals of acid-base titrations and their applications in quantitative analysis were highlighted and discussed. The last two units covered separately, oxidation-reduction and complex ion equilibria aspects of volumetric analysis of metal ions in solution. The last unit dealt with complexometric titration with emphasis on the application of complex ion reactions in complexometric titrations as a means to quantitative analysis of metal ions in solution.

XVI. Summative Evaluation

1. Explain or define each of the following terms: (a) Precision (b) Accuracy (c) Determinate error (d) Indeterminate error
2. Normally, we perform only a small number of replicate analyses. Explain!
3. A soil sample was analysed for its magnesium content and the results of the analysis are as tabulated below:

Experiment Number	Mg content (mg/g)
1	19.6
2	20.1
3	20.4
4	19.8

Calculate: (a) the mean concentration of magnesium in the soil sample (b) the median of the data set (c) the absolute deviation from the mean of the second data point (d) the standard deviation of the data set (e) the confidence interval for the data set at the 90% confidence interval.

4. If the true value for magnesium content in the soil of question 3 above, is 20.0 mg/g, calculate the relative error of the mean.
5. In an experiment that involved measurement of temperature, mass, volume and pressure of a gas, values were reported with their corresponding absolute errors as follows: mass = 0.3124g $\pm$ 0.1mg, temperature = 283 K $\pm$ 1K; volume = 150.3 mL $\pm$ 0.2 mL; and pressure = 1257.4 Pa $\pm$ 0.1 Pa. (a) Which of the above measurements will dominate in determining the error in the gas constant, R? (b) Explain your choice.
6. To how many significant figures ought the result of the operation $\frac{(24 \times 6.32)}{100.0}$ be reported and what is the calculated uncertainty?
7. If an analysis is conducted in triplicate and the average obtained in the measurements is 14.35 with a corresponding standard deviation of 0.37, express the uncertainty at the 95% confidence level. The ***t value*** at 95% level from a table is 4.303.
8. Label each of the components in the following equations as acids, bases, conjugate acids or conjugate bases: (a) $HCl + H_2O \rightarrow H_3O^+ + Cl^-$ (b) $NH3 + H_2O \rightarrow NH_4^+ + OH^-$
9. Write equations to show the dissociation of H_2SO_4, HNO_3 and HCl.

10. Determine the base dissociation constant, K_b of a base whose solution of concentration 0.01 mole/L has a pH of 8.63.
11. Calculate the pH of a solution in which the hydronium (H_3O^+) ion concentration is: (a) 1.0 M, (b) 0.01 M, (c) 1.0×10^{-7} M (d) 3.5×10^{-9}
12. Determine the pOH and the hydronium (H_3O^+) ion concentration of a 0.01 M NaOH solution.
13. What is the hydroxide (OH^-) ion concentration of a solution if the pH is: (a) 8.00 (b) 5.30, and (c) 4.68
14. Calculate the hydronium ion concentration if the pH is (a) 2.78 (b) 6.95 (c) 8.30
15. Write the equation for the K_a of the monoprotic benzoic acid, C_6H_5COOH whose sodium salt is C_6H_5COONa.
16. Periodic acid, HIO_4, is a moderately strong acid. In a 0.10 M solution, the $[H_3O^+] = 3.8 \times 10^{-2}$ M. Calculate the K_a and pK_a for periodic acid.
17. Is a solution whose $[H_3O^+] = 4.6 \times 10^{-8}$ M, acidic, neutral or basic? Explain your answer!
18. Define each of the following terminologies: (a) Standard solution, (b) Primary standard (c) Standardized solution (d) Standardization (e) End point of a titration (f) Equivalence point of titration (g) Titration error (h) Titration curve
19. Calculate the pH of a 0.10 M solution of $Ca(OH)_2$. Hint: Ca(OH)2 is a strong base and dissociates to yield 2 moles of OH^- ions ($Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$).
20. Characterize each of the following acids as monoprotic, diprotic, or triprotic and give the corresponding ionization reactions for each hydrogen ion for each acid: (a) CH_3COOH (b) H_2SO_4 (c) H_3PO_4 (d) $C_6H_4(COOH)_2$.
21. A 25.0 mL solution of KIO_3 was placed in a titration flask. 20.0 mL solution of KI and 10.0 mL of dilute sulfuric acid were added to the flask. The liberated iodine was titrated using a solution of $Na_2S_2O_3$ of concentration 0.2mol/L while using starch as the indicator. The end point was reached when 24.0 mL of $S_2O_3^{2-}$ solution was run in.

(a) This is an example of a substitution titration (an indirect titration). First the analyte IO_3^- is reacted with excess I^- to produce stoichiometrically equivalent amount of I_2.

$IO_3^- + I^- \rightarrow I_2$ Not balanced

The librated I_2 is titrated with standard $S_2O_3^{2-}$

$S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I$ Not balanced

Write the two balanced redox reactions responsible for the determination of IO_3^-

(b) What was the concentration of the original IO_3^- solution?

(c) Which indicator is the most suitable to use in this titration?

22. Assign oxidation numbers to each atom in the following species: (a) NO_3^- (b) $CaHAsO_4$
23. Determine whether the following changes are oxidation, reduction, or neither and show the oxidation number change that proves your point. (a) SO_3^{2-} to SO_4^{2-} (b) Cl_2 to ClO_3^- (c) N_2O_4 to NH_3 (d) NO to NO_3^- (e) PbO to $PbCl_4^{2-}$
24. Consider the following unbalanced oxidation/reduction reaction for the next two questions: $Hg^{2+}(aq) + N_2O_4(aq) \rightarrow 6\ NO_3^-(aq) + Hg_2^{2+}(aq)$

(a) What is being oxidized in the reaction?

(b) What is being reduced in the reaction?

25. Find the oxidation number of N in NO_3^- and Hg in Hg^{2+}.
26. Give the complete balanced equation in acidic media for the reaction in question 24 above.
27. Identify the reducing reagent in the following redox reaction,

$$Hg^{2+}(aq) + Cu(s) \rightarrow Cu^{2+}(aq) + Hg(l)$$

28. Select the spectator ions in the following reaction:

$$Pb(NO_3)_2(aq) + 2NaCl(aq) \rightarrow PbCl_2(s) + 2NaNO_3(aq)$$ (a) $Na^+(aq)$, $NO_3^-(aq)$ (b) $Pb^{2+}(aq)$, $NO_3^-(aq)$ (c) $Na^+(aq)$, $Cl^-(aq)$ (d) $Pb^{2+}(aq)$, $Cl^-(aq)$, $Na^+(aq)$, $NO_3^-(aq)$ (e) $Pb^{2+}(aq)$, $Cl^-(aq)$.
29. Permanganate ion is converted to manganese (II) ion by oxalic acid. What is the oxidizing agent? What is the reducing agent? Balance the reaction:

$$MnO_4^-(aq) + H_2C_2O_4(aq) \rightarrow Mn^{2+}(aq) + CO_2(g)$$ (in acidic, aqueous solution).
30. Balance the following reaction that occurs in acidic medium using the ion-electron method: $Fe^{2+} + MnO_4^- \rightarrow Fe^{3+} + Mn^{2+}$

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XVIII. Main Author of the Module

Prof. Paul M. Shiundu is an Associate Professor of Analytical Chemistry, at the Department of Chemistry of the University of Nairobi, Kenya. Prof. Shiundu obtained his early childhood education in Kenya. He graduated from the Department of Chemistry, University of Nairobi in 1986 with a First Class B.Sc. Honours degree in Chemistry. He then proceeded to the University of Cambridge, UK for a Certificate of Postgraduate Studies (CPGS) in Natural Science through a Cambridge Commonwealth Scholarship, before joining the Department of Chemistry of the University of British Columbia (UBC), Canada in 1987 for his postgraduate studies on a University of British Columbia Graduate Fellowship (UGF). At the University of Cambridge, Prof. Shiundu's research topic was "Time Resolved Molecular Attachment to Excited Atoms". Prof. Shiundu obtained his PhD in Analytical Chemistry from the University of British Columbia in 1991 and the title of his thesis was "Automated Methods Development in Flow Injection Analysis". Immediately upon graduating with a PhD. from UBC in 1991, Prof. Shiundu proceeded for a 3 year Postdoctoral Research Fellowship at the Field-Flow Fractionation Research Centre (FFFRC), Department of Chemistry of the University of Utah, USA, where he carried out research in the field of separation science methodology, and specifically Field-Flow Fractionation techniques for the separation and characterization of particulate and macromolecular materials of importance to industry. In 2002, Prof. Shiundu won a Fulbright Senior Research Scientist Award that enabled him undertake a 9-month sabbatical leave at the Department of Chemistry and Geochemistry of the Colorado School of Mines, USA and is a Fellow of the Cambridge Commonwealth Trust. Prof. Shiundu is an author of several scientific publications in internationally reputable journals and is also an author of two Distance Learning Modules for Bachelor of Education Science Courses for the University of Nairobi's Bed. Science by Distance Learning Programme.