Ministry of Education and Science of Ukraine
Kyiv National University of Technologies and Design

T. M. Derkach

ANALYTICAL CHEMISTRY

FOR TECHNOLOGISTS

Part 1

KNUTD Textbook Series
for International Training Programmes

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Dedicated to the 90th anniversary
of Kyiv National University of Technologies and Design

T. M. Derkach

Analytical Chemistry for Technologists

Part 1: Sections 1-9

It is recommended by the Academic Council of
the Kyiv National University of Technology and Design
as lecture notes for students of higher education
in the fields of chemical technology & engineering,
biotechnology & bioengineering, and pharmacy & industrial pharmacy

UDC 543(075.8)=111
D45

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Derkach T. M.
D45 Analytical Chemistry for Technologists: lecture notes for students of technological specialities. Part 1: Sections 1-9. Kyiv : KNUTD, 2020. 198 p.
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The book presents the basic concepts of analytical chemistry, such as qualitative and quantitative chemical analysis, sampling and sample preparation, statistical data processing, separation methods. Modern physicochemical methods of analysis are considered. The theoretical bases of methods are stated, conditions and their branches are specified practical application. The control questions and tasks presented at the end of each section will help to consolidate the studied material.

The book is intended for undergraduate students majoring in chemical technologies & engineering, biotechnology & bioengineering, and pharmacy & industrial pharmacy. The lecture notes consist of two parts. The first part includes Sections 1-9 and covers introductory topics, equations and equilibrium, classic methods of chemical analysis. The second part includes Sections 10-18 and covers instrumental methods.

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Content

Introduction

Analytical chemistry is a branch of chemistry that deals with the study of theory and practice of methods used to determine the composition of matter. Analytical chemistry is often described as a field of chemistry that is responsible for characterizing the composition of a substance, both qualitatively and quantitatively. However, analytical chemistry and chemical analysis are not the same.

The difference between analytical chemistry and chemical analysis is that analyst chemists work to improve and expand established analytical methods. The characteristic detail of analytical chemistry is not to perform routine analysis on a routine sample, which is more appropriately called chemical analysis. The meaning of the analytical chemistry is to improve established methods, to expand them to new types of samples and to develop new analytical methods for measuring chemical phenomena.

Forty to fifty years ago, the chemical analysis focused on three main areas: qualitative determination; quantitative determination using "classical" methods of titrimetry and gravimetry; structural analysis, which required time-consuming procedures and calculations.

Today, chemists have instrumental methods, automated systems, and computers that make analytical measurements easier, faster, and more accurate. However, the chemist has to have profound understanding principles, areas of practical application and limitations of each method to work without mistakes.

Reviews of daily operations of many industrial and other analytical laboratories in the UK, Europe, Japan and the US have identified the most methods widely used. The textbook describes the techniques and methods commonly used by most analytical laboratories today.

The textbook is written as lectures-presentations, which gradually reveal the analytical process. Regardless of the area where the need for analysis arises, the chemist needs to answer the following questions:

- How should a representative sample be obtained?
- How much material is available for analysis and how many samples should be taken?
- What should be determined? With what accuracy?
- What components are in the sample? Will they have interferences?
- What tools should be used?
- How reliable will the data be?

The answers to these questions and related topics are discussed in Sections 1-3.

Statistical methods of processing the results are given somewhat simplified, but enough to obtain reliable results and use them to assess the correctness of the proposed analysis methods.

The following lectures-presentations contain a description of the principles, tools and application of analytical methods. The lecture notes consist of two parts. The first part includes Sections 1-9 and covers introductory topics, equations and equilibrium, classic methods of chemical analysis. The second part includes Sections 10-18 and covers instrumental methods of chemical analysis.

The material of this textbook may be useful to future professionals as an overview of topics to continue learning at a deeper level.

This knowledge is enough for a specialist to be able to work in analytical laboratories and control the quality of various products.

Nobody can do your learning for you. The most important way to master this course is to work tasks and gain experience in the laboratory. Problem-solving may illustrate how to apply what you have just read. Exercises are the minimum set of problems that apply the most significant concepts of each chapter.

Tables of dissociation constants and pK values for acids and bases, solubility-product constants for compounds, standard reduction potentials, formation constants (or stability constants) for complex ions in aqueous solutions, and densities of acids, alkalis and some other substances are shown in the last chapter of the textbook.

Section 1: Common Analytical Problems

Contents:

Introduction

Analytical chemistry is connected with many other chemical and related disciplines. Typical problems that chemists-analysts work on include i) **qualitative analysis** (what does it consist of?), ii) **quantitative analysis** (how much of this component is in the sample?), iii) **analysis of characteristics** (what are the chemical and physical properties of the sample?) and iv) **fundamental analysis** (how does this method work and how can it be improved?).

Many problems of analytical chemistry begin with the need to identify the constituent samples. It is the field of qualitative analysis. Much of the early work on analytical chemistry involved the development of simple chemical tests to detect inorganic ions and organic functional groups. Classical laboratory courses of inorganic and organic qualitative analysis are based on such work.

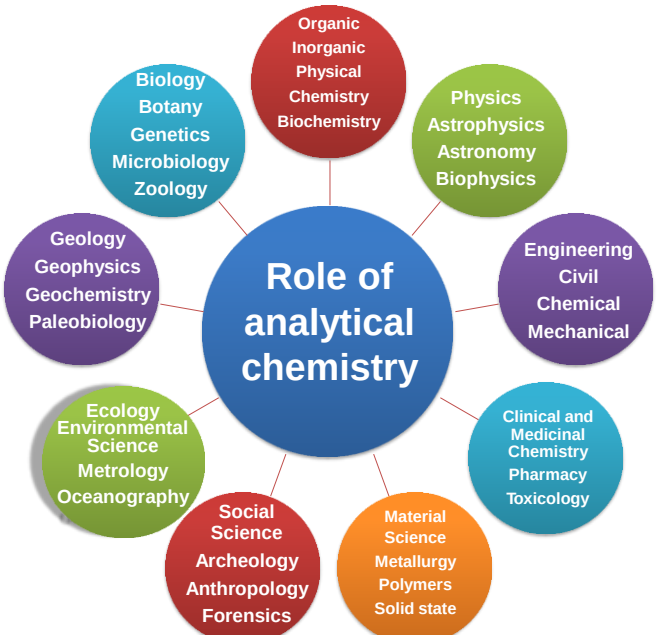
The purpose of the qualitative, quantitative, or characteristic analysis is to solve a problem related to a specific sample. The purpose of fundamental analysis is to improve the understanding of the theory behind the analytical method.

Examples of basic research in analytical chemistry are as follows: expansion and improvement of the theory on which the analytical method is based; study the limitations of the analytical method; development and modification of the existing analytical method.

In this section, we will consider important questions such as "How do we ensure the accuracy of our results?", "How to obtain a representative sample?" and "How to choose the appropriate analytical method?"

Also, in this section, we briefly review the use of units and significant indicators in analytical chemistry.

The set of equipment for analytical measurements is impressive, ranging from simple and inexpensive to complicated and expensive. In section 1, we will discuss the simplest equipment for mass measurement, volume measurement and drying of materials. We postpone the discussion of more complex equipment to later sections, where its application to specific analytical methods is relevant.



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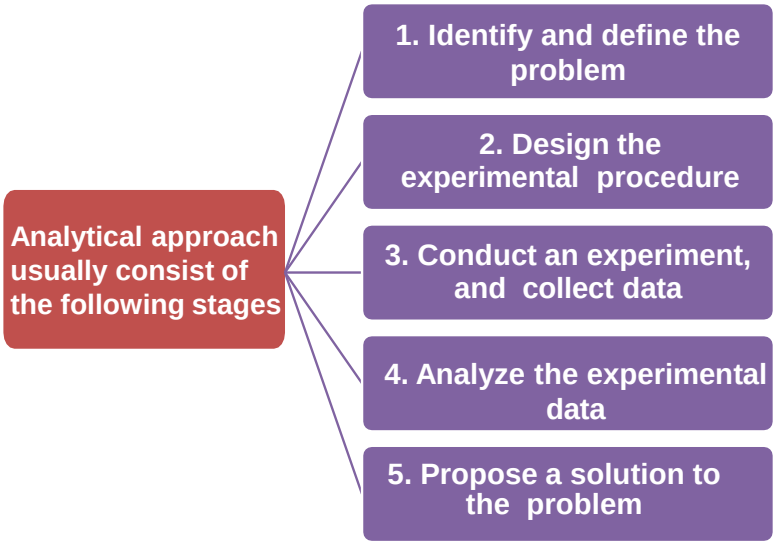


Notes:

The stages are based on the following activities

1. Determine the type of information needed
   Qualitative, Quantitative, characterization or fundamental
2. Identify problem
   Select method
   Establish validation data
   Establish sampling strategy
3. Calibrate Instruments and equipments
   Standardise reagent
   Gather data
4. Reduce or transform data
   Analyze statistics
   Verify results
   Interpretation results
5. Conduct external evaluation

Notes:

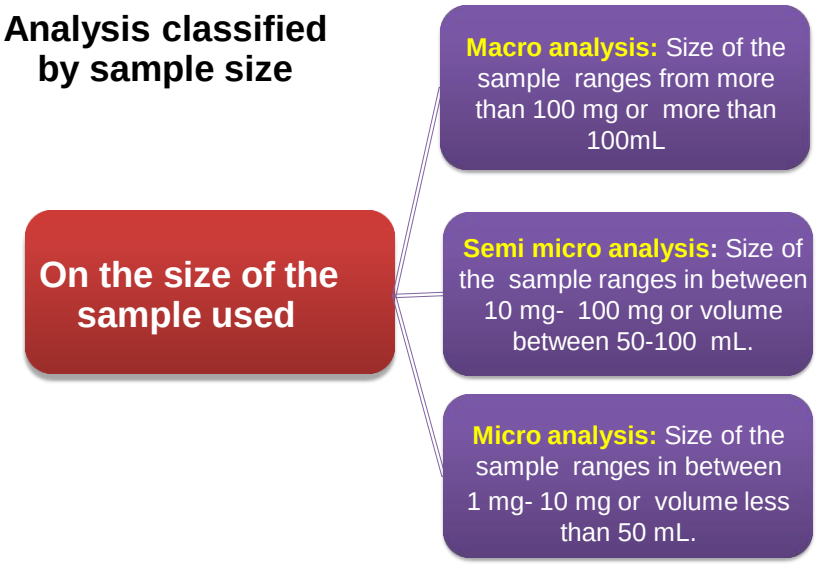
The language of analytical chemistry (continued)

Notes:

6. **Technique:** A chemical or physical principle that can be used to analyze a sample.
7. **Method:** A method is the application of a technique for the determination of a specific analyte in a specific matrix within specific and appropriate measurement parameters.
8. **Procedure:** Written directions outlining how to analyze a sample.
9. **Protocol:** a **protocol is a set of stringent written guidelines detailing the procedure** that must be followed if the agency specifying the protocol is to accept the results of the analysis. Protocols are commonly encountered when analytical chemistry is used to support or define public policy.

Analysis classified by sample size

Notes:



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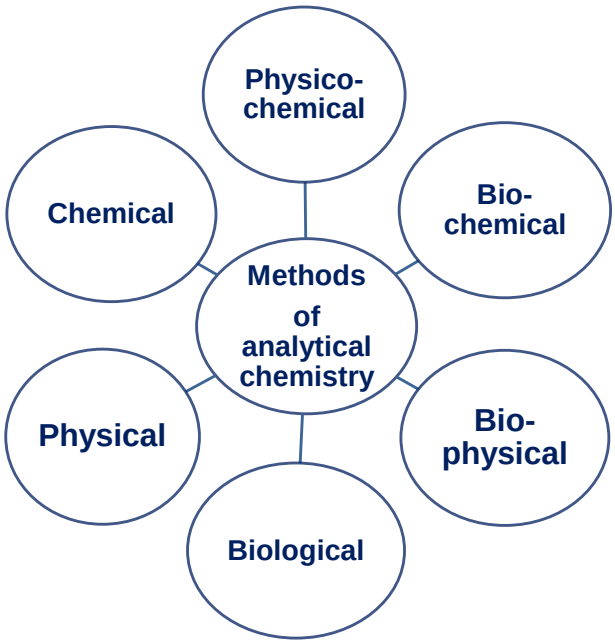

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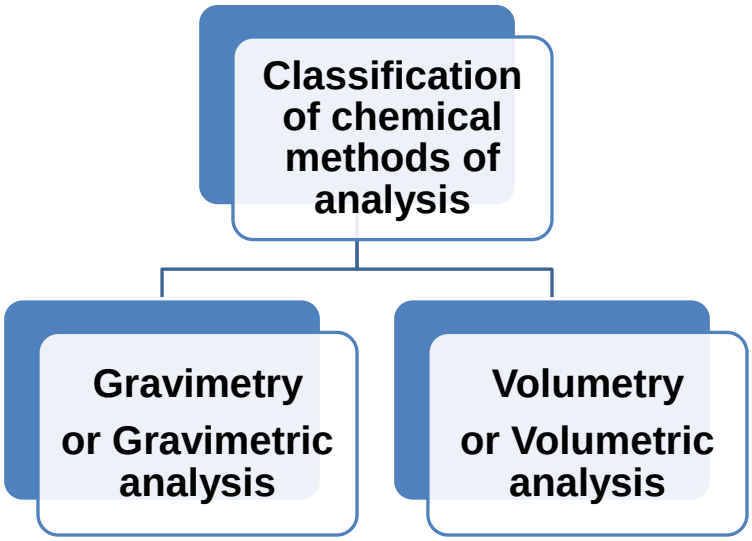


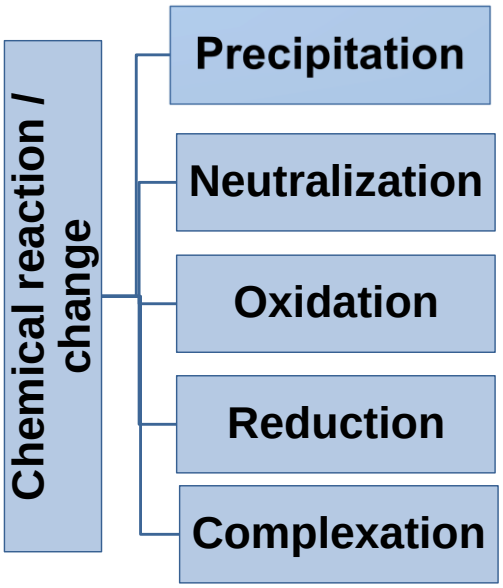
Notes:

Advantages of classical methods

- Simple procedure
- Cheaper equipment
- No specialised training required

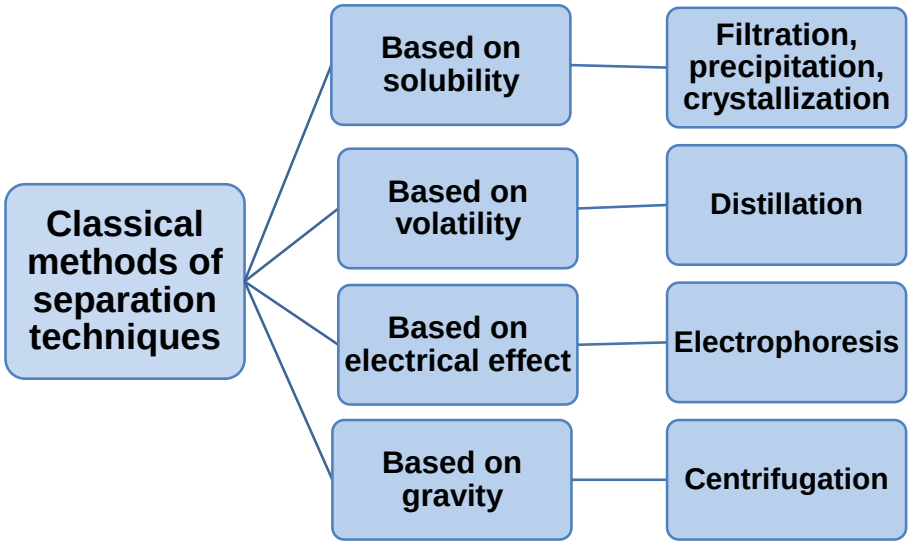
Notes:

Chemical reactions involved in classical analytical methods



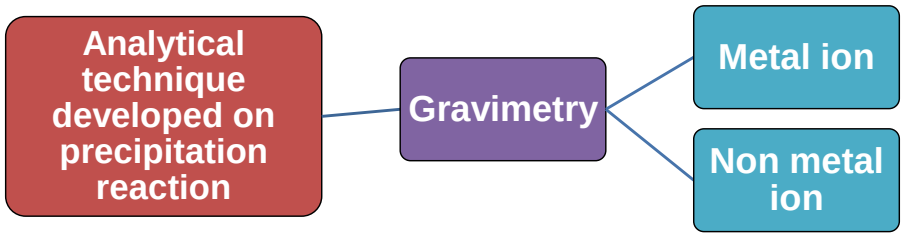
Separation techniques. Why separation is essential?

Notes:



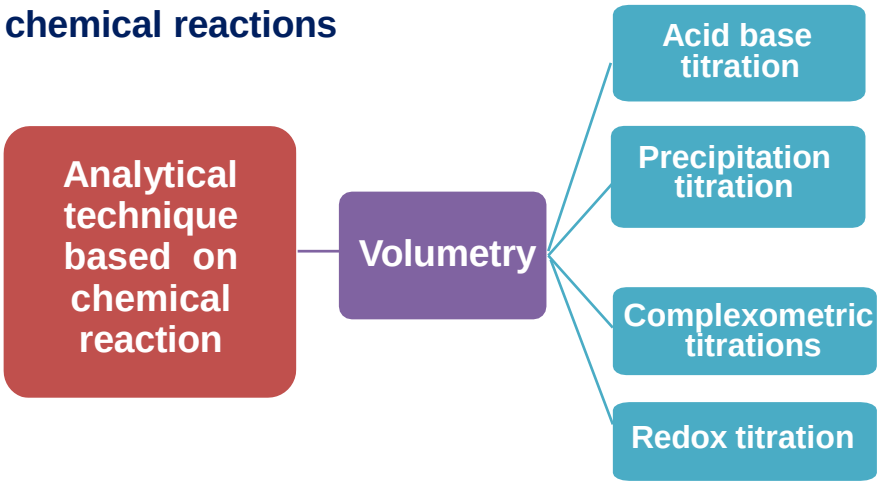
Notes:

Analytical Technique developed on Precipitation Reaction



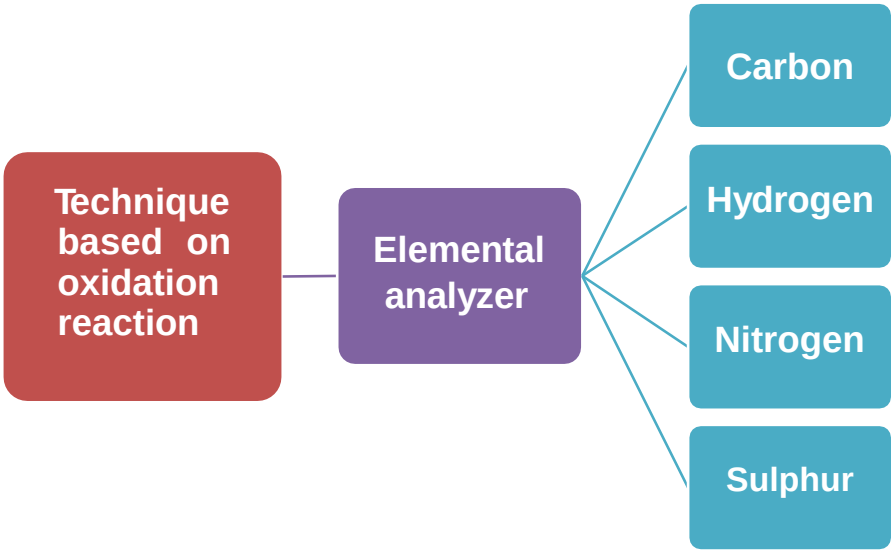
Notes:

Methods based on various chemical reactions



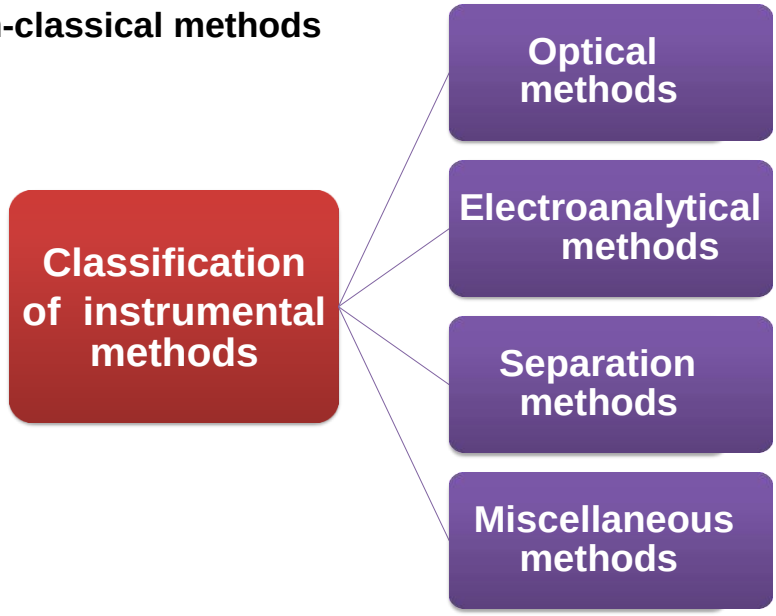
Methods based on oxidation reactions

Notes:



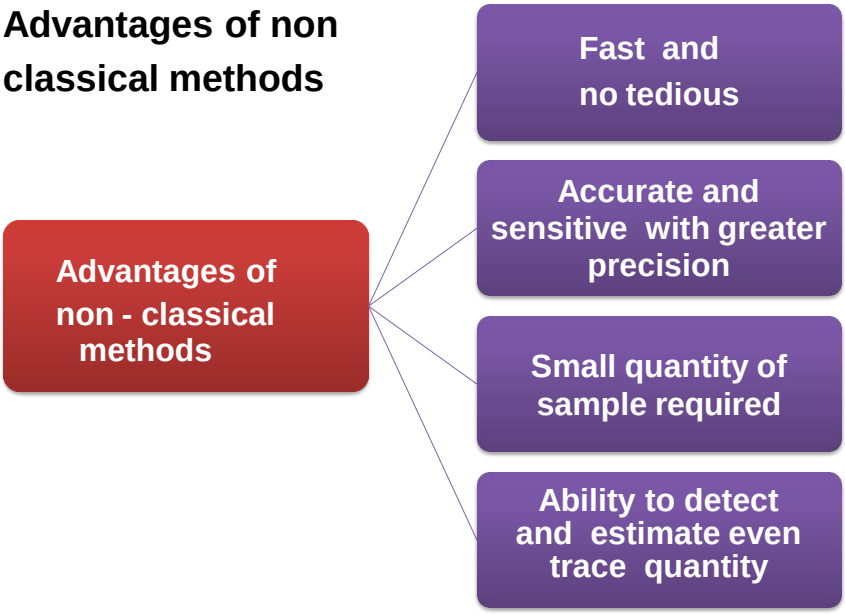
Non-classical methods

Notes:



Advantages of non classical methods

Notes:



Performance characteristics for analytical method

Notes:

1. ***Accuracy:*** The agreement between measured value and true value. Defined as closeness of the observed value with the true value.
2. ***Precision:*** The agreement between individual observation within the same set of observations
3. ***Selectivity:*** It is defined as degree to which the method is free from interferences from other components present in the matrix.
4. ***Sensitivity:*** Ability of a method to discriminate between two small concentration differences in the analyte.
   It is measured in terms of slope of the calibration curve. If the slope is greater, sensitivity of the method is higher and vice-versa.

Performance characteristics for analytical method (cont.)

Notes:

5. ***Dynamic range:*** It is the concentration range from limit of quantification (LOQ) to limit of linearity (LOL).
7. **Limit of Linearity (LOL) :** It is defined as maximum concentration range up to which instrument is produces linear response.
8. ***Limit of detection (LOD):*** Minimum amount of concentration of a component that can be detected with a given degree of confidence.
9. ***Limit of Quantification (LOQ):*** Minimum amount of concentration of a component that can be estimated with a given degree of confidence is termed as LOQ.

Accuracy

Notes:

The **Accuracy** of an analytical procedure expresses the closeness of agreement between the value, which is accepted either as a conventional true value or an accepted reference value, and the value found.

In other words, it is the degree to which an experimental result approaches the true or accepted answer.

For example: The dissociation constant for acetic acid is 1.75×10^{-5} at 25 °C. In an experiment, if a student arrives at exactly this value, his value is said to be accurate.

Ways to Describe Accuracy:

Error is an experimental measure of accuracy.
The difference between the result obtained by a method (X) and the true or accepted value (m) is absolute error.

***Absolute Error* = (X – m)**

***Relative Error* (%) = 100(X – m)/m**

All Methods, except counting, contain errors – *don't know "true" value*

There are two types of error: random or systematic (explain it later)

Precision

Notes:

The precision of an analytical procedure expresses the closeness of agreement (degree of scatter) between a series of measurements obtained from multiple sampling of the same homogeneous sample under the prescribed conditions.

Precision may be considered at three levels: **repeatability, intermediate precision and reproducibility.**

Repeatability

Repeatability expresses the precision under the same operating conditions over a short interval of time. Repeatability is also termed intra-assay precision .

Intermediate precision

Intermediate precision expresses within-laboratories variations: different days, different analysts, different equipment, etc.

Reproducibility

Reproducibility expresses the precision between laboratories (collaborative studies, usually applied to standardization of methodology)

Ways to describe precision

Notes:

Range: the high to low values measured in a repeat series of experiments.

Standard Deviation: describes the distribution of the measured results about the mean or average value.

Absolute Standard Deviation (SD): $SD = \sqrt{\sum_{i=1}^{n} (X_i - \overline{X})^2 / (n-1)}$

Relative Standard Deviation (RSD) or Coefficient of Variation (CV):

$$RSD(\%) = (SD / \overline{X})100$$

where: n = total number of measurements;

X_i = measurement made for the i^{th} trial;

$\overline{X}$ = mean result for the data sample.

Random and systematic errors

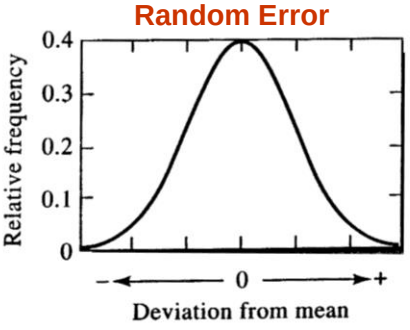
Notes:

Let us plot of the number of occurrences or population of each measurement (Gaussian curve)

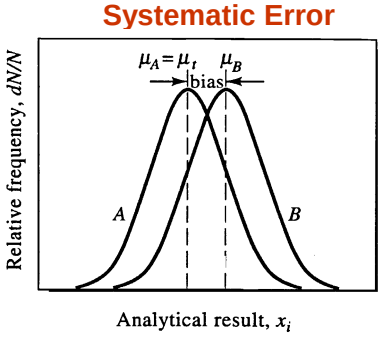
Random Error: results in a scatter of results centered on the true value for repeated measurements on a single sample.

***Systematic Error*:** results in all measurements exhibiting a definite difference from the true value

Random Error



Systematic Error



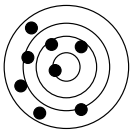
Difference between accuracy and precision

Notes:

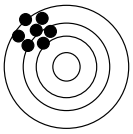
Precision illustrates the reproducibility of results. The degree to which an experimental result varies from one determination to the next.

Precision is related to *random error* and
Accuracy is related to *systematic error.*

Shooting marks illustrate the difference between them

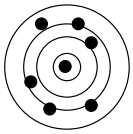


Low accuracy, low precision

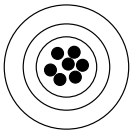


Close shots but past the target

Low accuracy, high precision



High accuracy, low precision



all shots at the target

High accuracy, high precision

Can you define accuracy and precision?

Notes:

Three shooters with three arrows each to shoot.

Both accurate and precise

Precise but not accurate

There is systematic (determinate) error

Neither accurate nor precise

There is random (indeterminate) error

Can you define accuracy and precision?

Response

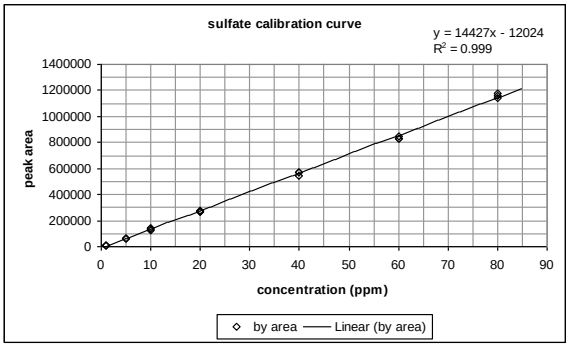
Notes:

This is the way in which the result or signal of a method varies with the amount of compound or property being measured.

Ways to Describe Response:

To plot Calibration Curve:

In calibration curves, the measured concentrations are plotted as a function of known amounts of substance in standard samples.



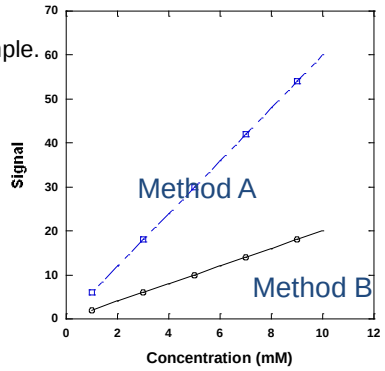
Sensitivity

Notes:

Parameters used to describe a calibration curve: $S = mc + S_{bl}$

S – measured signal;
c – analyte concentration;
S_{bl} – instrument signal for blank (bl) sample.

Sensitivity: is ability to discriminate between small differences in analyte concentration.



calibration sensitivity is:
slope (m) of calibration curve.

analytical sensitivity (γ) is:
slope (m) / standard deviation (S_s)

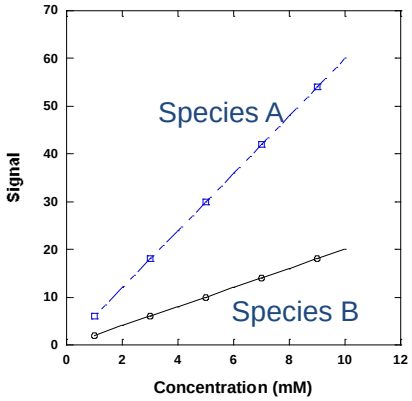
Slope and reproducibility of the calibration curve determine sensitivity.

Best method is more *sensitive* to analyte than interfering species (interferent). The sensitivity of method indicates how responsive it is to a small change in the concentration of an analyte.

Selectivity

Notes:

Selectivity is the degree to which the method is free from interference by other species in the sample. Typically interferences might include impurities and matrix



No method is totally free from interference from other species.
Best method is more ***sensitive*** to analyte than interferent.

Selectivity coefficient (k):

$$k_{B,A} = m_B / m_A$$

Relative slopes of calibration curves indicate selectivity:

$$S = m_A(c_A + k_{B,A}c_b) + S_{bl}$$

Interested in detecting species A, but signal will be a combination of signal from the presence of species A and species B.

Limit of detection

Notes:

Limits of Detection (c_m): is min concentration or mass of analyte that can be detected at a known confidence level.

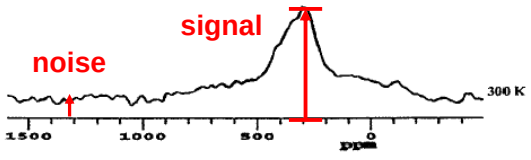
It is calculated as a difference of analyte and blank signals divided by a calibration curve slope:

[minimum analyte signal (S_m) - mean blank signal ($\overline{S}_{bl}$)] / slope(m)

Signal-to-noise Ratio (S/N):

Noise: random variation in signal or background
Signal: net response recorded by a method for a sample

(Note: a value of S/N = 2 or better is considered to be the minimum ratio needed for the reliable detection of a true signal from a sample.)



Estimate S/N:

1) Multiple determination of blank samples.
2) Estimation of best-fit to calibration curves

Detection and quantitation limits

Notes:

DETECTION LIMIT

The detection limit of an individual analytical procedure is the lowest amount of analyte in a sample which can be detected but not necessarily quantitated as an exact value.

QUANTITATION LIMIT

The quantitation limit of an individual analytical procedure is the lowest amount of analyte in a sample which can be quantitatively determined with suitable precision and accuracy. The quantitation limit is a parameter of quantitative assays for low levels of compounds in sample matrices, and is used particularly for the determination of impurities and/or degradation products.

Linearity

The linearity of an analytical procedure is its ability (within a given range) to obtain test results which are directly proportional to the concentration (amount) of analyte in the sample.

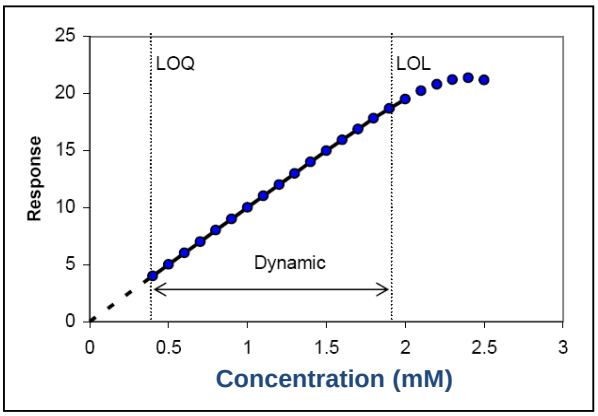
Dynamic range

Notes:

Dynamic Range: linear region of calibration curve where the lower limit is the range between the limits of linearity and quantitation

LOQ - limit of quantitation

LOL - limit of linearity



Robustness

Notes:

The robustness of an analytical procedure is a measure of its capacity to remain unaffected by small, but well-considered variations in method parameters and provides an indication of its reliability during normal usage.

The types of parameters which are assessed in order to determine the robustness of a method include:

the stability of analytical solutions;

the length of the extraction time;

the effect of variations in the pH;

the effect of small variations in mobile phase composition;

the effect of changing chromatographic columns;

the effect of temperature and flow rate during chromatography.

Notes:

Example 1: The data in the table below were obtained during a colorimetric determination of glucose. A sample gave an absorbance of 0.350.

Glucose Concentration, mM	Absorbance, A
0.0	0.002
2.0	0.150
4.0	0.294
6.0	0.434
8.0	0.570
10.0	0.704

Find **the glucose concentration** and its:

- standard deviation,
- calibration sensitivity,
- detection limit and
- dynamic range.

Notes:

Stages of analysis
Development of model and plan for analysis

- The model is an idealized representation of all steps of the analytical method.
- It includes a specific statement of the problem, information about the sample and analyte (concentration levels of concern, potential interferences, location of the analyte in the sample, phase relationships, particle size distribution,….).
- Selection of optimal analytical methods
- The development of a model may require experiments to obtain more information about the sample or to validate assumptions.
- It necessary to perform measurements on the sample to determine its homogeneity.
- Development of a sampling plan to accurately address the goals of the method.
- The results of these preliminary experiments are used to help refine the original model.

Notes:

Qualitative and quantitative methods

The method chosen may provide either qualitative or quantitative information.

❑ Qualitative method: data may include the composition, oxidation states, structural information, or the isotopic distributions of elements contained in a sample.

✓ An understanding of the instrumentation used to make the qualitative measurement also leads one to a rough approximation of the concentration of the species being measured.

✓ Whether the substance is a major (>1%), minor (0.01-1%), trace (10-2 – 10^{-6}%), or ultra-trace (10^{-6}- 10^{-9}%) component.

❑ Quantitative methods: the analyst needs to plan tasks associated with sampling, sample preparation, and calibration more carefully than a qualitative analysis.

✓ Often, preliminary measurements will be required to develop a quantitative method.

Factor to consider selecting analytical method

Notes:

Sample consideration

1. Concentration of the component.
2. The complexity of the materials/presence of interfering material
3. The probable concentration of the species of interest

Method consideration

1. What type of information does the method provide?
2. What are the advantages or disadvantages over other methods?
3. Degree of accuracy
4. Sensitivity and detection limit
5. How much or how little sample is required?
6. What types of samples can the method be used with?

Additional factors

1. Speed, time and cost of analysis
2. Availability of equipment
3. Skill person for handling the instrument

➢ ***All the above factors should be taken into account combinedly, to select the proper method***

Notes:

Sampling

Obtaining a representative sample is the first step of an analysis.

Proper consideration of the sampling and sample handling are equally important

The gross sample is several small portions of the sample.

This is reduced to provide a laboratory sample.

An aliquot of this sample is taken for the analysis sample.

Notes:

Sample preparation

- ✓ The samples must also be treated to make them compatible with the instrumental technique.
- ✓ Transformation of the sample into a form that can be measured using the selected technique is termed sample preparation.
- ✓ Sample selection and preparation usually represent the largest investment of time in the implementation of an analytical method.
- ✓ It is important to realize that the majority of instrumental techniques require the sample to be in a liquid phase.
- ✓ For solid samples, several techniques are taken to transfer the analyte into the liquid phase.
- ✓ Care must be taken in these steps to preserve the integrity of the analyte by considering the possibility of contamination, loss, or chemical and physical changes to the analyte.

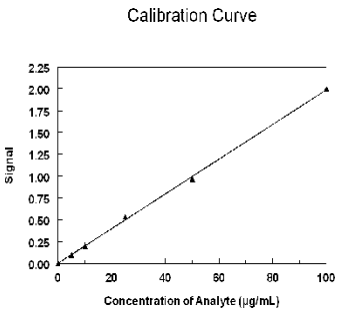
Perform measurements

Notes:

- ✓ Once the sample has been prepared, it is necessary to measure replicate samples to establish the precision of the method.
- ✓ The measurement depends upon the interaction of the technique with a unique chemical or physical property of the analyte.

Compare results with standards

- ✓ Reliable and convincing analytical results must involve a proper, careful comparison of the analyte's signal to that of appropriate standards of known analyte concentration as well as a calibration blank solution.
- ✓ This is known as calibration or standardization.
- ✓ Calibration establishes the mathematical relationship between the analytical signal and the concentration of analyte in the calibration standards.
- ✓ The most common approach is to develop a "working" curve.



Some items of labware

Notes:

Electronic analytical balance

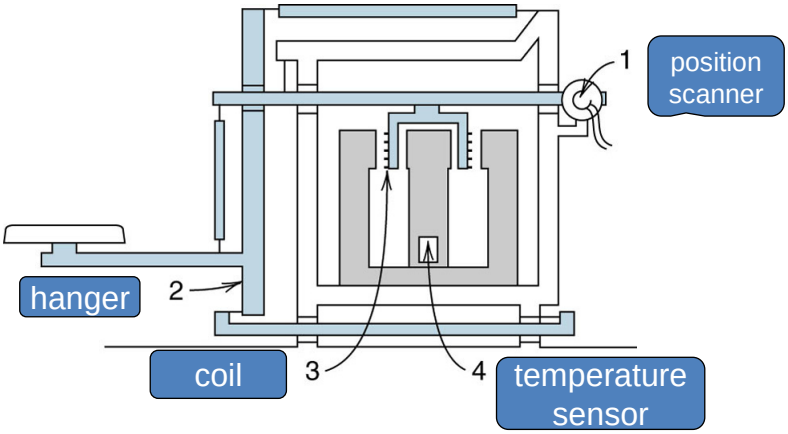
Modern balances are electronic.

They still compare one mass against another since they are calibrated with a known mass.

Common balances are sensitive to 0.1 mg.

Operating principle of electronic balance

Notes:

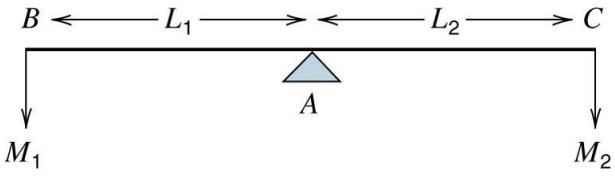


Electronic balances operate on the principle of electromagnetic force compensation .

The compensation current, which brings the pan back to its original position, is proportional to the sample weight.

Notes:

Principle of analytical balance

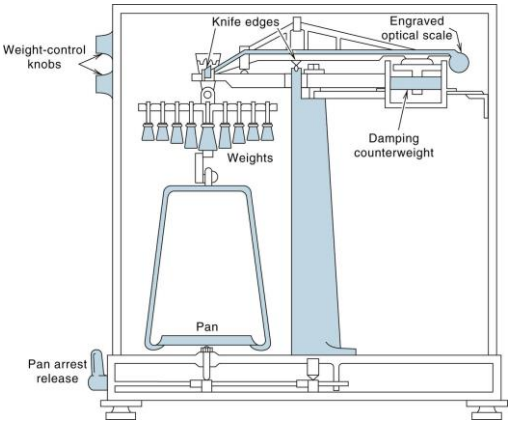


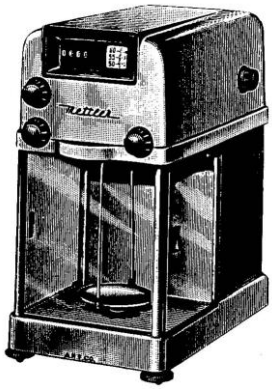
Mechanical balances operate as first class levers.

The unknown mass is calculated as $M_1L_1 = M_2L_2$

Scheme of a typical single-pan balance

Notes:





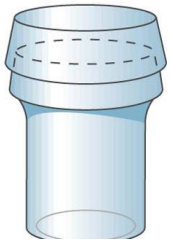
The single pan balance operates by removing weights equal to the mass of the sample. Small residual imbalances are read optically from the deflection of the beam. The balance is as accurate as electronic balances.

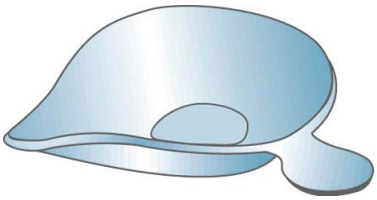
But it can't be interfaced to a computer to collect and process data.

You have to read a scale instead of a digital number.

Weighing bottles and dish

Notes:





Weighing bottles are used for drying samples.

Hygroscopic samples are weighed by difference, keeping the bottle capped except when removing the sample.

A weighing dish or boat is used for direct weighing of samples

Weight in a Vacuum

Notes:

Weights of objects in air can be corrected to the weight in vacuum by using the following calculations:

$$W_{vac} = W_{air} + W_{air}[(0.0012/D_o) - (0.0012/D_w)]$$

Where

W_{vac} is a weight in vacuum, g

W_{air} is a weight in air, g

D_o is a density of an object

D_w is a density of standard weights

0.0012 is the density of air

Muffle furnace and drying oven

Notes:

The furnace is used to ignite (or anneal) samples at high temperatures, e.g., to dry ash organic matter.

Drying oven is used to dry samples before weighing (usually at 110° C).

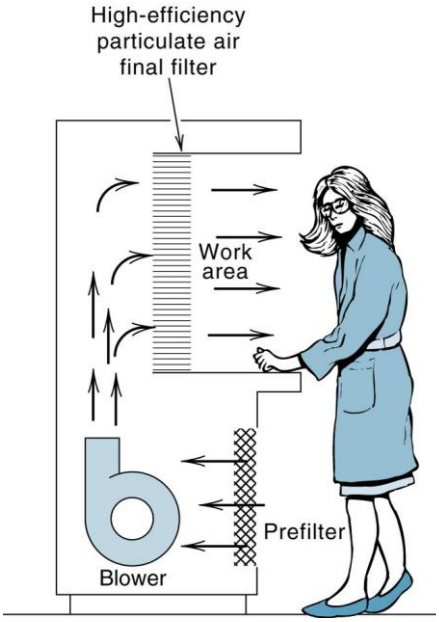
Laminar-flow workstation

Notes:

A fume hood is “dirty” since it draws in laboratory air.

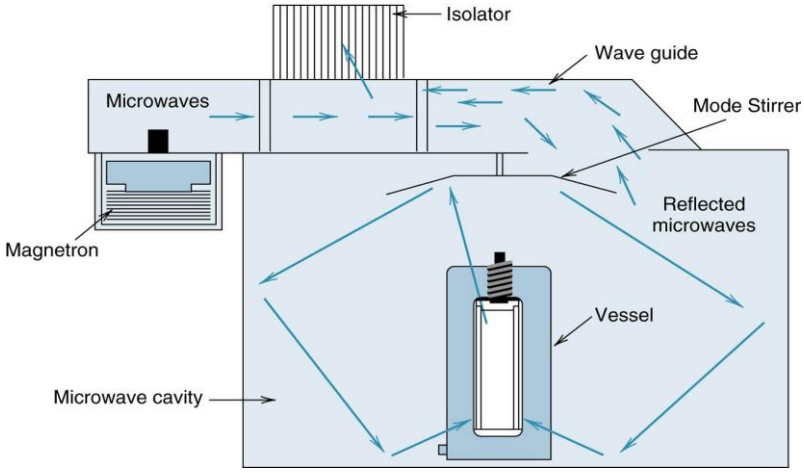
A laminar-flow hood filters air (0.3 mm filter is necessary) and flows it out into the room.

Use it as a workstation for trace analysis.



Schematic of a microwave system

Notes:



Microwave ovens provide rapid drying.

Acid decomposition times are reduced from hours to minutes.

Lower blank levels are achieved with reduced amounts of reagents.

6. Glassware. Materials used in laboratory

Notes:

Material	Recommended Use	Properties
Borosilicate Glass	General applications	Transparent; good thermal properties; fragile; attacked by HF, H_3PO_4, and alkaline solutions.
Fused Quartz	High temperature applications	Transparent; excellent thermal properties (up to 1,100 EC); fragile; more expensive than glass; attacked by HF, H_3PO_4, and alkaline solutions.
Porcelain	High temperature applications and pyrosulfate fusion	Used at temperatures up to 1,100 EC; less expensive than quartz; attacked by HF, H_3PO_4, and alkaline solutions.
Nickel	Molten alkali metal hydroxide and Na_2O_2 fusions	Suitable for use with strongly alkaline solutions. Do not use with HCl.
Platinum	High temperature or corrosive applications	Virtually unaffected by acids, including HF; dissolves readily in mixtures of HNO_3 and HCl, Cl_2 water or Br_2 water; adequate resistance to H_3PO_4; very expensive; forms alloys with Hg, Pb, Sn, Au, Cu, Si, Zn, Cd, As, Al, Bi, and Fe, which may be formed under reducing conditions; permeable to H_2 at red heat, which serves as a reducing agent; may react with S, Se, Te, P, As, Sb, B, and C to damage container; soft and easily deformed, often alloyed with Ir, Au, or Rh for strength. Do not use with Na_2CO_3 for fusion.

Materials used in laboratory (continued)

Notes:

Material	Recommended Use	Properties
Zirconium	Peroxide fusions	Less expensive alternative to platinum; extremely resistant to HCl; resistant to HNO_3; resistant to 50% H_2SO_4 and 60% H_3PO_4 up to 100 EC; resistant to molten NaOH; attacked by molten nitrate and bisulfate; usually available as Zircaloy—98% Zr, 1.5% Sn, trace Fe, Cr, and Ni. Do not use with KF or HF.
Alumina (Al_2O_3)	Acids and alkali melts at low temperatures	Resistant to acids and alkali melts; rapidly attacked by bisulphate melts; brittle, requires thick walled containers.
Polyethylene	Sample and reagent storage	Resistant to many acids; attacked by 16M HNO_3 and glacial acetic acid; begins to soften and lose shape at 60°C; appreciably porous to Br_2, NH_3, H_2S, H_2O, and HNO_3 (aqueous solutions can lose ~1% volume per year when stored for extended periods of time).
Teflon™	Corrosive applications	Inert to almost all inorganic and organic compounds except F_2; porosity to gases is significantly less than that of polyethylene; safe to use below 250°C but decomposes at 300°C; difficulty in shaping containers results in high cost; low thermal conductivity (requires long periods of heating time).
Polystyrene	Sample and reagent storage	Only useful for acid solutions < 0.1 M; brittle

Glasses

Notes:

Laboratory glassware and plastic wares are widely used in medical laboratories.
Glassware are usually manufactured from borosilicate glass.
Borosilicate glass is a material with the following defined characteristics:

- Resistant to the action of chemical with the exception of hydrofluoric and phosphoric acid,
- Made to withstand mechanical breakage,
- Made to withstand sudden change of temperature.

Glassware produced from the soda lime type of glass does not fit the above requirements and is easily broken by mechanical stress produced by a sudden change of temperature.

Hardened glasses, such as Pyrex, monax, and firmasil have low soda-line content and are manufactured especially to resist thermal shock (high temperature).

Glasses (continued)

Notes:

The walls of these vessels are generally thicker than those made from soda lime. The high proportion of borosilicate increases the chemical durability of the glassware.

Precautions:

- All glassware must be handled carefully.
- Breakage can sometimes be dangerous and may result in the loss of valuable and irreplaceable materials.
- Flasks and beakers should be placed on a gauze mat when they are heated over a Bunsen flame. Gauze mat is made from asbestos and its function is to distribute the heat evenly.
- Test tubes exposed to a naked flame should be made of heat resistant glasses.
- If liquids are to be heated in a bath or boiling water, the glass contents should be heat resistant.

Glasses (continued)

Notes:

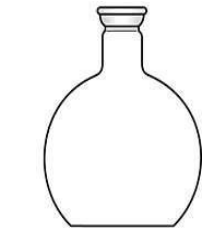
- Sudden cooling of hot glass should be avoided.
- When diluting concentrated acids, thin walled glassware should be used since the heat evolved by the procedure often cracks thick glassware.
  Examples: hydrochloric and sulfuric acid.
- Heat expansion is liable to crack bottles if their caps are screwed on tightly so if heat is to be applied, flasks should not be tightly clamped.
- Containers and their corresponding ground glass stoppers should be numbered in order to ensure direct matching when stoppers are replaced.
- Because of the danger of chemical and bacteriological contamination, pipettes should never be left lying on the bench.

Flasks

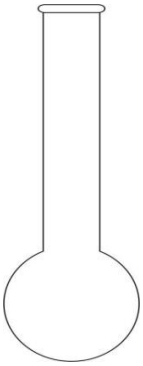
Notes:

There are four types of flasks having 25 to 6,000 millilitre (ml) capacities.

- Flat bottomed round flasks;
- Round bottomed flasks;
- Conical (Erlenmeyer) flasks;
- Volumetric flasks;

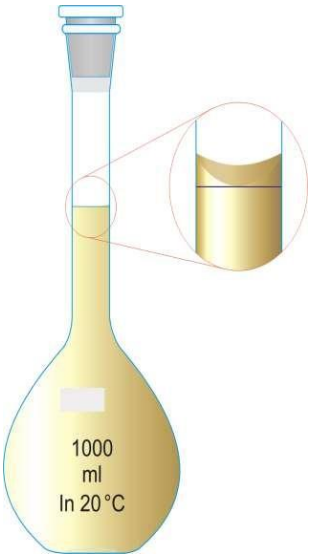


Flat Bottomed Round Flask



Round Bottomed Flask

Conical (Erlenmeyer) flask



Volumetric Flask

Notes:

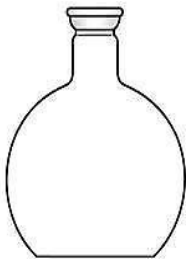
Flasks (continued)

Flat bottomed round flasks:

Flat-bottomed round flasks are convenient containers to heat liquids.

A gauze mat should be interposed between the flask and flame.

These flasks are widely used in the preparation of bacteriological culture media.



Notes:

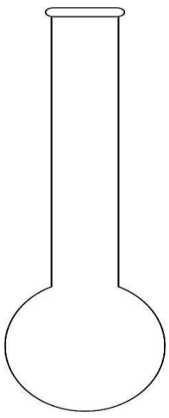
Flasks (continued)

Round bottomed flasks:

Round bottomed flasks can with stand higher temperatures than the flat-bottomed type

They may be heated in a necked flame, or in an electro-thermal mantle.

They can be used for boiling of different kinds of solutions and to make titration.



Flasks (continued)

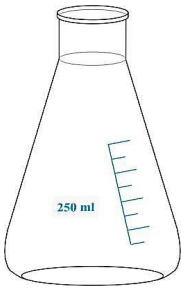
Notes:

Conical (Erlenmeyer) flasks:

Conical (Erlenmeyer) flasks are useful for titrations.

For boiling solutions when it is necessary to keep evaporation to a minimum.

Some have a side arm suitable for attachment to a vacuum pump.



Notes:

Volumetric flasks:

Volumetric flasks are flat - bottomed, pear-shaped vessels with long narrow necks, and are fitted with ground stoppers.

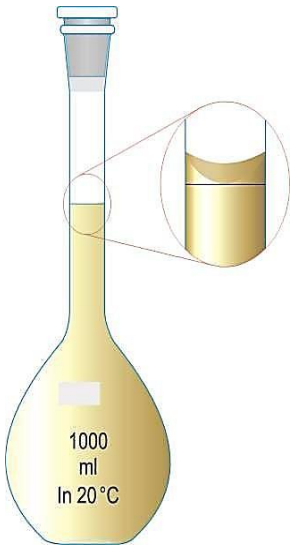
Most flasks are graduated to contain a certain volume, and these are marked with the letter “C”.

Those designed to deliver a given volume are marked with the letter “D”.

A horizontal line etched round the neck denotes the stated volume of water at given temperature, for example at 20^{o}C.

They are used to prepare various kinds of solutions.

The neck is narrow so that slight errors in reading the meniscus results in relatively small volumetric differences (minimizes volumetric differences or errors)

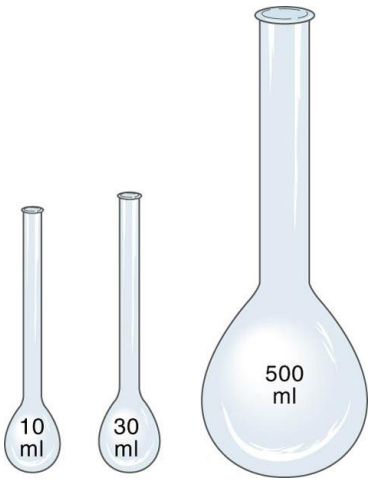


Notes:

Kjeldahl flasks

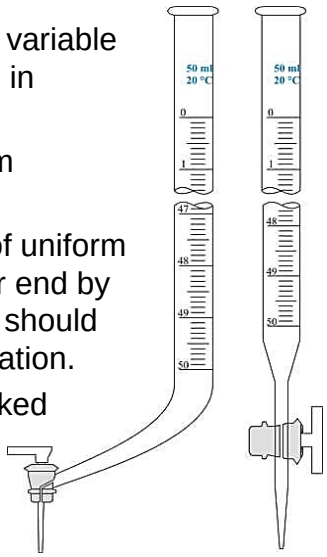
Use these for acid digestions.

They are tilted while heating to avoid losses from “bumping”.



Burettes

- Burettes are used for measuring variable quantities of liquid that are used in volumetric titrations.
- They are made in capacities from 1-100 millilitres.
- They are long graduated tubes of uniform bore and are closed at the lower end by means of a glass stopper, which should be lightly greased for smooth rotation.
- A 50-mL burette (see left) is marked in 0.1 mL increments.
- You interpolate to 0.01 mL, good to about ±0.02 mL.
- Two readings are taken for every volume measurement.



Notes:

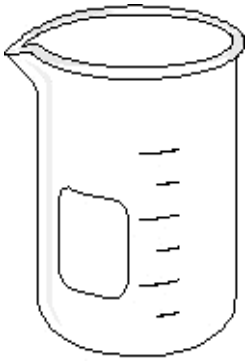
Beakers

Beakers have capacities from 5 to 5,000 ml.

•They are usually made up of heat resistant glass and are available in different shapes.

•The type most commonly used is the squat form, which is cylindrical and has a spout. There is also a tall form, usually without a spout.

•Beakers are often supplied for heating or boiling of solutions.



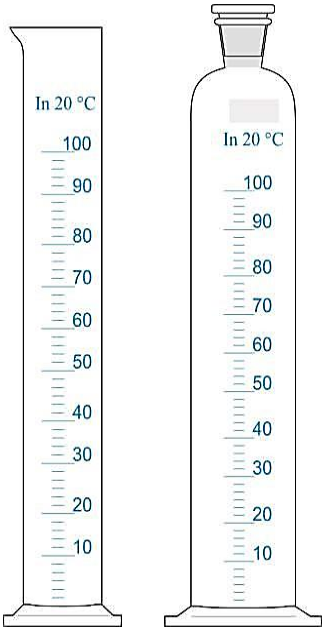
Notes:

Cylinders

Cylinders are supplied in 10 to 2,000 ml capacities.

•Some are made of heat resistant glass or plastic and some are fitted with ground- glass stoppers.

•Measurement of liquids can be made quickly with these vessels, but a high degree of accuracy is impossible because of the wide bore of the cylinders.



Notes:

Types of pipets

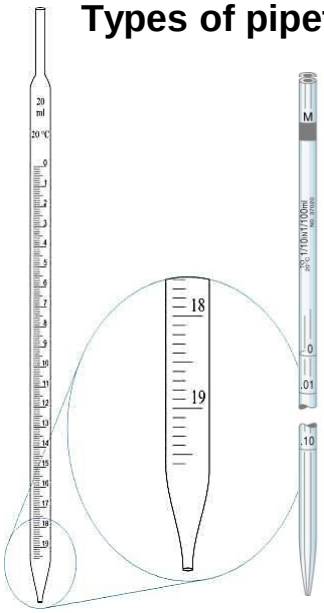
Notes:

- There are several types each having its own advantages and limitations. Pipettes are designated as class “A” or “B” according to their accuracy.
- Class “A” pipettes are the most accurate and the tolerance limits are well defined that is, +0.01, +0.02 and +0.04 ml for 2, 25, and 50 ml pipettes respectively.
- Class “B” pipettes are less accurate but quite satisfactory for most general laboratory purposes.
- Significant errors will result if the temperature of the liquid pipetted is widely different from the temperature of calibration.
- The usual temperature of calibration is 20^{o}C and this is marked on the pipette.

Types of pipets

Notes:

Mohr’s Pipette



Graduated or Measuring Pipette

Volumetric pipette

Graduated pipette (blow-out) (Serological pipette)

Typical accuracies and precisions for single channel pipets

Notes:

Range (m L)	Increment (m L)	Volume (m L)	Accuracy (m L)	Accuracy (%)	Precision[a] s.d. (m L)	Precision[a] CV (%)
0.2–2	0.01	2	±0.050	±2.5	0.040	2.0
		0.2	±0.024	±12.0	0.020	10.0
0.5–10	0.1	10	±0.100	±1.0	0.050	0.5
		1	±0.025	±2.5	0.020	2.0
0.5–10	0.1	10	±0.100	±1.0	0.080	0.8
		1	±0.035	±3.5	0.030	3.0
2–20	0.1	20	±0.200	±1.0	0.080	0.4
		2	±0.060	±3.0	0.030	1.5
5–40	0.5	40	±0.240	±0.6	0.120	0.3
		5	±0.100	±2.0	0.100	2.0
10–100	1.0	100	±0.80	±0.8	0.20	0.2
		10	±0.30	±3.0	0.10	1.0
20–200	1.0	200	±1.20	±0.6	0.40	0.2
		20	±0.36	±1.8	0.14	0.7
200–1000	5.0	1000	±6.00	±0.6	2.00	0.2
		200	±1.80	±0.9	0.60	0.3
100–1000	5.0	1000	±6.00	±0.6	2.00	0.2
		100	±1.00	±1.0	0.60	0.6

Volumetric pipets

Notes:

- Volumetric pipettes are calibrated to deliver a constant volume of liquid.
- The most commonly used sizes are 1, 5, and 10ml capacities. Less frequently used sizes are those which deliver 6, 8, 12, and so on ml.
- They have a bulb mid-way between the mouthpiece and the tip. The main purpose of the bulb is to decrease the surface area per unit volume and diminish the possible error resulting from water film.
- The Volume (capacity) and calibration temperature of the pipettes are clearly written on the bulb. They should be used when a high degree of accuracy is desired.
- The pipette is first rinsed several times with a little of the solution to be used, then filled to just above the mark.
- Then the liquid is allowed to fall to the mark and the tip is carefully wiped with filter paper. The contents are allowed to drain in to the appropriate vessel.
- A certain amount of liquid remains at the tip and this must not be blown out.

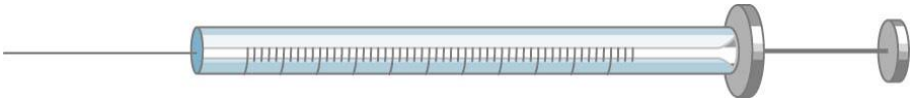
Graduated or Measuring pipettes:

Notes:

- Graduated pipettes consist of a glass tube of uniform bore with marks evenly spaced along the length.
- The interval between the calibration marks depends up on the size of the pipette.
- Two types calibration for delivery are available. These are:
  - One is calibrated between two marks on the stem.
  - The other has graduation marks down to the tip (serological pipette)
- These pipettes are intended for the delivery of predetermined volumes.
- The serological pipette must be blown out to deliver the entire Volume of the liquid and it has an etched ring (pair of rings) near the mouth end of the pipette signifying that it is a blow-out pipette.
- Measuring pipettes are common only in 0.1, 0.2, 0.5, 1.0 5.0, and 10.0 ml sizes. The liquid is delivered by allowing it to fall from one calibration mark to another.

Notes:

Hamilton microliter syringe



Syringe pipets precisely deliver microliter volumes.

They are commonly used to introduce samples into a gas chromatograph.

Single-channel and multichannel digital displacement pipets and microwell plates.

Notes:

These syringe pipets can reproducibly deliver a selected volume.

They come in fixed and variable volumes.

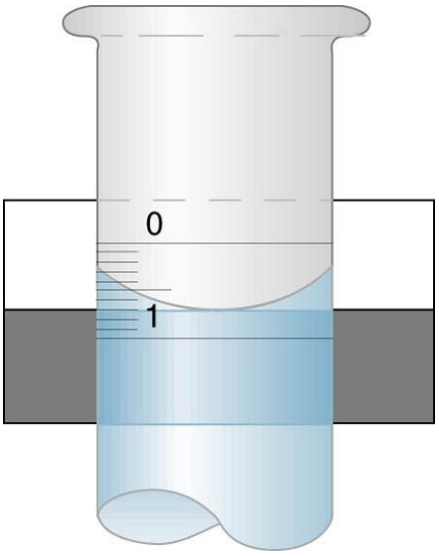
The plastic tips are disposable.

Meniscus illuminator

Notes:

Position the black field just below the meniscus.

Avoid parallax error by reading at eye level.



Cleaning of Glassware

Notes:

- It is clear that volumetric glassware and glass apparatus must be absolutely clean, otherwise volumes measured will be inaccurate and chemical reactions are affected adversely.
- One method generally used to test for cleanness is to fill the vessel with distilled water and then empty it and examine the walls to see whether they are covered by a continuous thin film of water.
- Imperfect wetting or the presence of discrete droplets of water indicates that vessel is not sufficiently clean.
- A wide variety of methods have been suggested for the cleaning of most glassware.
- Chromic-sulfuric acid mixture is the cleaning agent in common usage.
- It is imperative that glassware cleaning should be as mild as possible and should be appropriate to the type of contamination present.

Cleaning of Glassware (continued)

Notes:

- Fats and grease are the most frequent causes of severe contamination present and,
- It is advisable to dissolve these contaminants by a liquid solvent (water-immiscible organic solvent) followed by water washing.
- The most widely used oxidant is a solution of sodium dichromate in concentrated sulfuric acid.
- Because of its oxidizing power, the solution, particularly when hot, removes grease and fats quickly and completely.
- Cleaning solution, as a mixture, is not a general solvent for cleaning all apparatus but only for cleaning borosilicate glassware, including volumetric wares.
- Glassware is generally in contact with the mixture for 1 to 24 hours, depending up on the amount of grease or liquid present.

Cleaning of Glassware (continued)

Notes:

- After removal of the acid and draining, the glass ware should be washed out at least four times with tap water and then rinsed three times with distilled water
- New glass wares should also be washed and socked in 1% HCL since they are slightly alkaline while they are manufactured.

CLEANING OF PIPETTES:

- Pipettes should be placed in a vertical position with the tips up in a jar of cleaning solution in order to avoid the breakage of their tips.
- A pad of glass wool is placed at the bottom of the jar to prevent breakage.
- After soaking for several hours, the tips are drained and rinsed with tap water until all traces of cleaning solution are removed.
- The pipettes are soaked in distilled water for at least an hour.

Cleaning of Glassware (continued)

Notes:

- Filing with water, allowing the pipette to empty, and observing whether drops formed on the side within the graduated portion make a gross test for cleanness.
- Formation of drops indicates greasy surfaces, after the final distilled water rinse the pipettes are dried in an oven at not more than 110^{o}C.
- Most laboratories that use large numbers of pipettes daily use a convenient automatic pipette washer.
- These devices are made of metal or polyethylene and can be connected directly to hot and cold water supplies.
- Polyethylene baskets and jars may be used for soaking and rinsing pipettes in chromic acid cleaning solution.

Cleaning of flasks, beakers, cylinders and other glassware

Notes:

- Pour warm cleaning solution into each vessel and stopper or cover carefully.
- Each vessel should be manipulated so that all portions of the wall are repeatedly brought into contact with the solution.
- This procedure should be followed for at least five minutes.
- The cleaning solution can be poured from one vessel to another and then returned to its original container.
- The vessels should then be rinsed repeatedly with tap water four times and finally rinsed three times with distilled water.
- It is important that the necks of volumetric flasks above the graduation mark be clean because, when solutions are diluted in the flask, drops of water may adhere to an unclean wall and may invalidate the measurement of volume.

Plastic Wares

Notes:

- Plastic wares are usually manufactured from polymers of polyethylene, polypropylene and TEFLON.
- These plastics **are chemically inert and un**affected by acid /alkali.
- Plastic wares are durable and suitable to store alkaline solutions. However, surface bound may be leached to the solution, absorb dyes and proteins.

CLEANING OF PLASTIC WARES:

- After each use Laboratory plastic wares should be immediately soaked in water or if contaminated, soaked overnight in a suitable disinfectant such as 0.5% w/v sodium hypochlorite or bleach.
- Most plastic ware is best clean in a warm detergent solution, followed by at least two rinses in clean water, and ideally a final rinse in distilled water.
- The articles should then be left to drain and dry naturally or dried in a hot air oven, set at a temperature the plastic can withstand. A brush or harsh abrasive cleaner should not be used on plastic ware. Stains or precipitates best removed using dilute nitric acid or 3% v/v acid alcohol

Notes:

Techniques for Calibrating Glassware: Volumetric Flask Calibration

1. Make all operations at constant room temperature.
2. Weigh the clean, dry flask and stopper.
3. Fill to mark with distilled water.
   No droplets on the neck, blot dry
4. Weigh the filled flask.
5. The increase in weight represents the weight in air of the water contained by the flask.
6. Taking the density of water as 1 gram per cubic centimeter, compare the real and nominal volumes of the flask.

Techniques for Calibrating Glassware: Pipet Calibration

Notes:

1. Make all operations at constant room temperature.
2. Weigh a clean, dry conical flask with a rubber stopper or a weighing bottle with a glass stopper or cap.
3. Fill pipet with distilled water and deliver the water into the flask or bottle, stopper container to avoid evaporation loss.
4. Reweigh the container to obtain the weight in air of the water delivered by the pipet.
5. Taking the density of water as 1 gram per cubic centimeter, compare the real and nominal volumes of the pipet

Techniques for Calibration of Glassware: Burette Calibration

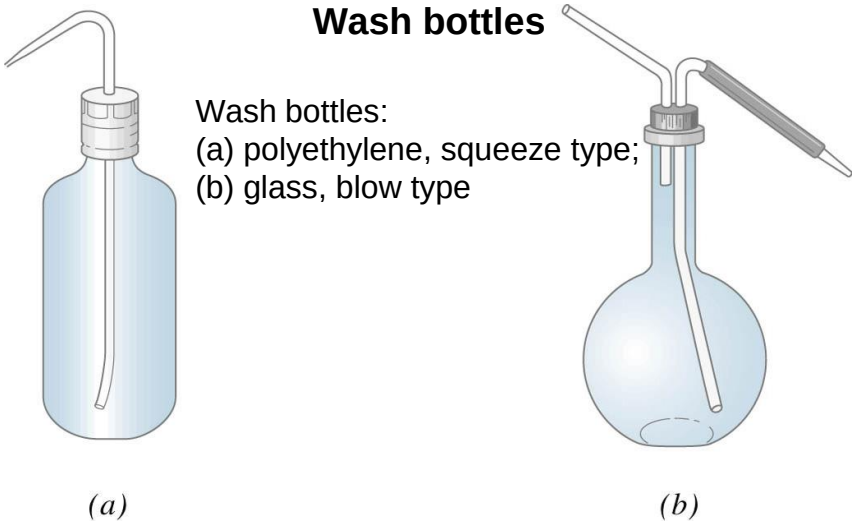
Notes:

1. Weigh a clean, dry conical flask.
2. Take the volume at 20% full-volume increments by filling the burette each time and then delivering the nominal volume into a dry flask.
3. Alternative: make successive deliveries into same flask, filling the burette only once.
4. The delivered volume does not have to be exact, but close to the nominal volume, you can make fairly fast deliveries, but wait 10 to 20s for film drainage.
5. Prepare a plot of volume correction versus nominal volume and draw straight lines between each point.
6. Interpolation is made at intermediate volumes from the lines.

Other chemical vessels, accessories and techniques

Notes:

Wash bottles



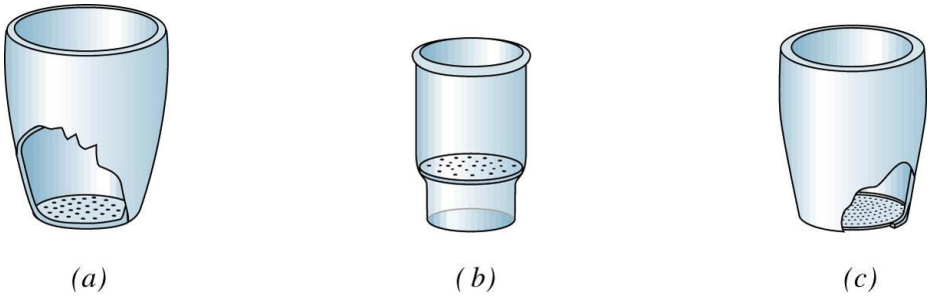
Wash bottles:
(a) polyethylene, squeeze type;
(b) glass, blow type

(a) *(b)*

Use these for quantitative transfer of precipitates and solutions, and for washing precipitates.

Filtering crucibles

Notes:



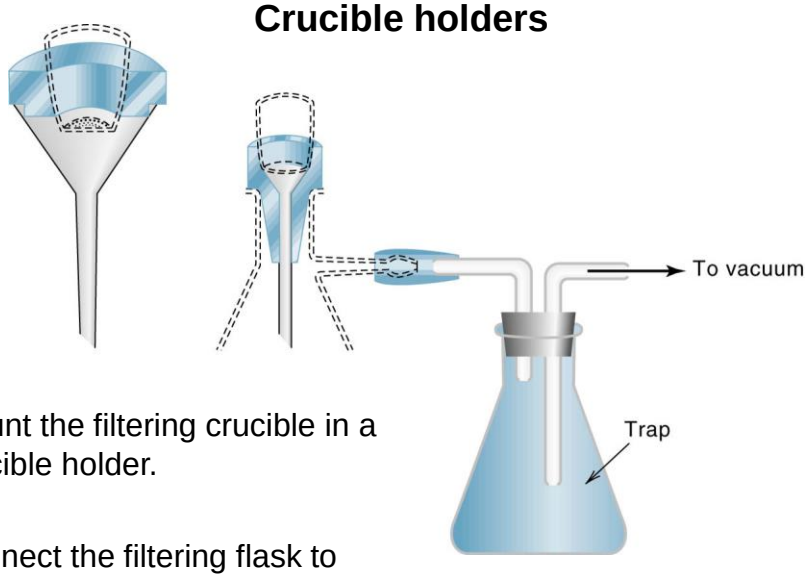
(a) (b) (c)

Filtering crucibles:
(a) Gooch crucible;
(b) sintered-glass crucible;
(c) porcelain filter crucible.

Use for filtering non-gelatinous precipitates

Crucible holders

Notes:



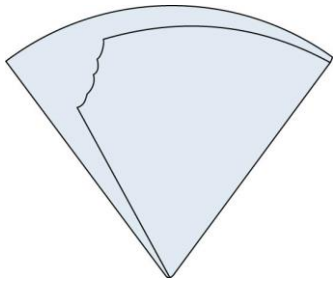
Mount the filtering crucible in a crucible holder.

Connect the filtering flask to a water aspirator.

Types of filter paper

Notes:

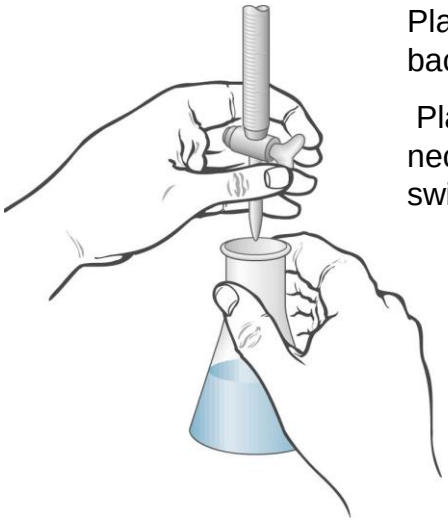
Precipitate	Whatman
Very fine (e.g., $BaSO_4$)	No. 42 (2.5 μm)
Small or medium (e.g., AgCl)	No. 40 (8 μm)
Gelatinous or large crystals (e.g., $Fe_2O_3 \cdot xH_2O$)	No. 41 (20–25 μm)



- Properly folded filter paper.
- This provides a good seal and prevents air bubbles from being drawn in.
- Suction from the weight of the water in the stem increases the filtration rate.
- Let the precipitate settle in the beaker before beginning filtration.

Proper technique for titration

Notes:



Place the flask on a white background.

Place the buret tip in the neck of the flask while your swirl**.**

Notes:

Temperature Dependence of Molarity

The Molarity of a solution is temperature dependent.

Therefore when preparing or standardizing solutions you have to record the temperature of solutions.

Conversion Formula:

$$M_{new\ temp} = M_{old\ temp} \times (D_{new\ temp} / D_{old\ temp})$$

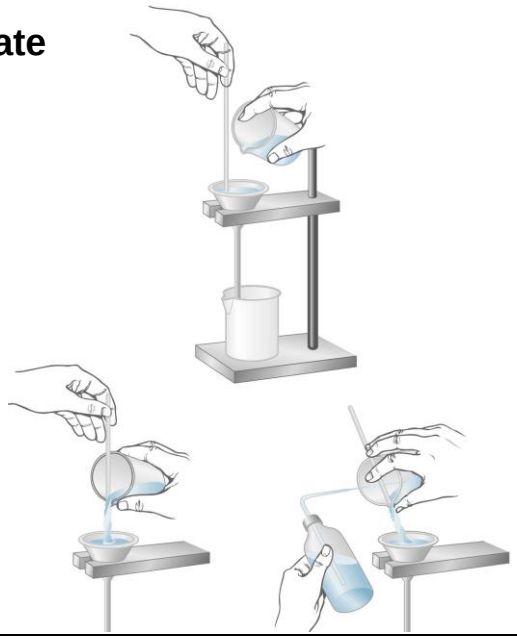
Proper technique for transfer of a precipitate

Notes:

Decant the solution by pouring down the stirring rod.

After decanting the mother liquor, add wash water to the precipitate and decant again, repeating 2-3 times.

Then wash the precipitate into the filter.



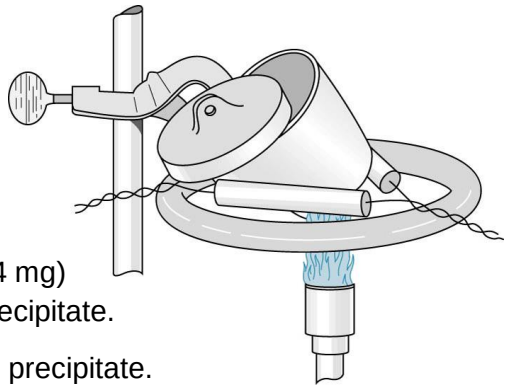
Notes:

Rubber policeman

Use this to scrub the walls of the beaker and collect all the precipitate (by washing).

Crucible and cover supported on a wire triangle for charring off paper

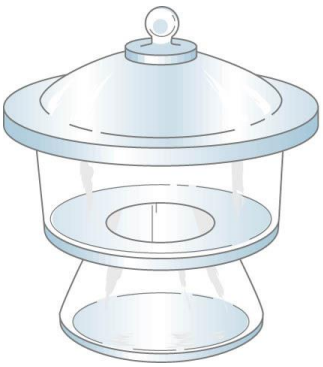
Notes:

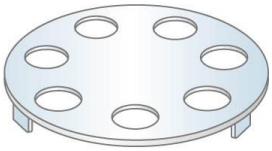


- Heat or ignite the crucible to a constant weight (to 0.3-0.4 mg) before adding the filtered precipitate.
- Fold the filter paper over the precipitate.
- Drive off moisture at low heat.
- Then gradually increase heat till the paper begins to char.
- After the paper is gone, ignite the precipitate.

Desiccator and desiccator plate

Notes:





Use a desiccator to cool a dried or ignited sample.

Cool a red hot vessel before placing in the desiccator.

Do not stopper a hot weighing bottlle (creates a partial vacuum on cooling).

Some commonly used drying agents

Notes:

Agent	Capacity	Deliquescent[a]
$CaCl_2$ (anhydrous)	High	Yes
$CaSO_4$	Moderate	No
CaO	Moderate	No
$MgClO_4$ (anhydrous)	High	Yes
Silica gel	Low	No
Al_2O_3	Low	No
P_2O_5	Low	Yes

[a] Becomes liquid by absorbing moisture.

$CaCl_2$ is most popular; It needs periodic replacement when wet or caked

Tasks to Section 1

1. Give definitions of these terms: analytical chemistry, analytical methods, technique, procedure, performance characteristics, stages of analysis, kinds of labware, sample, sampling, sample preparation.

2. What kind of classification of samples do you know?

3. What differences between methods of analytical chemistry?

4. Why is separation essential?

5. Name the analytical techniques based on various chemical reactions.

6. Describe the performance characteristics for analytical methods.

7. What is robustness?

8. What differences do you know between qualitative and quantitative methods?

9. Imagine you are the head of a new analytical lab at a small pharmaceutical company. List the equipment you would like to purchase.

10. Take into account that:

- determinations of chemical structure, equilibrium constant, particle size, and surface structure are examples of a method of characterisation analyses;

- the purpose of fundamental analyses is to improve our understanding of the theory behind an analytical method;

For each of the problems indicate whether its solution requires a qualitative analysis, a quantitative analysis, a characterisation analysis, or a fundamental analysis? More than one type of analysis may be appropriate for some problems.

(a) A hazardous-waste disposal site is believed to be leaking contaminants into the local groundwater.

(b) An art museum is concerned that a recent acquisition is a forgery.

(c) Airport security needs a more reliable method for detecting the presence of explosive materials in luggage.

(d) The structure of a newly discovered virus needs to be determined.

(e) A new visual indicator is necessary for an acid-base titration.

(f) A new law requires a method for evaluating whether automobiles are emitting too much carbon monoxide.

11. What das mean the term "procedures calibration of glassware"? Describe such procedure for volumetric flask calibration.

Section 2: Treatment of Analytical Data

Contents:

Introduction

The causes of measurement errors are numerous, and their values are variable.

They lead to uncertainty in the results obtained. However, measurement errors can be minimized, and some of their types can be eliminated by careful experimental control.

The effects of errors can be assessed using statistical methods of data analysis and chemometric methods. Gross errors can occur due to faulty equipment or incorrect performance of the technique by personnel. Proper maintenance of equipment, proper staff training and supervision should eliminate them.

Errors need to be monitored and evaluated so that reliable analytical measurements can be made and reported. The reliability of the data must be demonstrated because the end-user need to have an acceptable degree of confidence in the analysis results.

If the readings are repeated several times under the same conditions, the measured parameter will always be characterized by changes.

Several experimental error estimates need to be made. Potential sources of error should be evaluated to ensure that they do not adversely affect our results. It is necessary to make sure that measurement errors remain acceptable during the analysis. The quality of measurements and results should be assessed.

All measurements contain experimental errors, so we can never be entirely sure of the result. Errors may not be detected if the actual value is not known for comparison purposes. If the experiment is repeated many times, and if the errors are random, the results are usually symmetrical about the mean. The more times the experiment is repeated, the closer the results come to an ideal dome-shaped curve, the so-called Gaussian distribution.

Of course, we cannot do too many measurements in the lab. Most often, the experiment is repeated 3 - 5 times. However, even from a small sample of results, we can evaluate the parameters that describe a large sample, evaluate the so-called statistical characteristics.

This chapter provides an overview of possible sources of error, describes the estimation of errors in analytical measurements and statistical analysis of data.

Quality of analytical procedures

Notes:

The International Conference on Harmonisation (ICH) has adopted the following terms for defining how the quality of an assay is controlled.

The analytical procedure provides an exact description of how the analysis is carried out. It should describe in detail the steps necessary to perform each analytical test.

The full method should describe:

(i) the quality and source of the reference standard for the compound being analysed

(ii) the procedures used for preparing solutions of the reference standard

(iii) the quality of any reagents or solvents used in the assay and their method of preparation

(iv) the procedures and settings used for the operation of any equipment required in the assay

(v)the methodology used for calibration of the assay and methodology used for the processing of the sample prior to analysis.

Notes:

Selecting an analytical method

- How reproducible? - **Precision**
- How close to true value? - **Accuracy**
- How small a difference can be measured? - **Sensitivity**
- What range of amounts? - **Dynamic Range**
- How much interference? - **Selectivity**
- How many samples? – **Efficience** (time, money cost)

Notes:

1. Characterisation of the results obtained
Mean value

A mean value is obtained by dividing the sum of a set of replicate measurements by the number of individual results in the set.

For example, if a titration is repeated four times and the titre values are 10.1, 9.9, 10.0 and 10.2 ml, then

$$Mean = \frac{(10.1+9.9+10+10.2}{4} = \frac{40.2}{4} = 10.05$$

This mean value is also called arithmetic mean or average

Notes:

The median

This is a value about which all other values in a set are equally distributed. Half of the values are greater and the other half smaller numerically, compared to the median.

For example: If we have a set of values like

1.1, 1.2, 1.3, 1.4 and 1.5, the median value is 1.3.

When a set of data has an even number of values,

then the median is the average of the middle pair.

Notes:

Absolute error

- The term accuracy is denoted in terms of absolute error E.

  E is the difference between the observed value (X_i) and the expected value (X_t) : $E = | X_i - X_t |$
- If a student obtains a value of 1.69×10^{-5} for the dissociation constant of acetic acid at 25°C, the absolute error in this determination is $E = | 1.69 \times 10^{-5} - 1.75 \times 10^{-5} | = | 0.06 \times 10^{-5} |$

Relative error

- Sometimes the term relative error is used to express the uncertainty in data.
- The relative error denotes the percentage of error compared to the expected value. For the dissociation constant value reported, relative error is

$$r = [0.06 \times 10^{-5} \times 100] / 1.75 \times 10^{-5} = 3.4\%$$

Notes:

Problem:

The actual length of a field is 500 meters.
A measuring instrument shows the length to be 508 meters.

Find:

a.) the absolute error in the measured length of the field.

b.) the relative error in the measured length of the field.

Solution:

- (a)The absolute error in the length of the field is 8 feet.

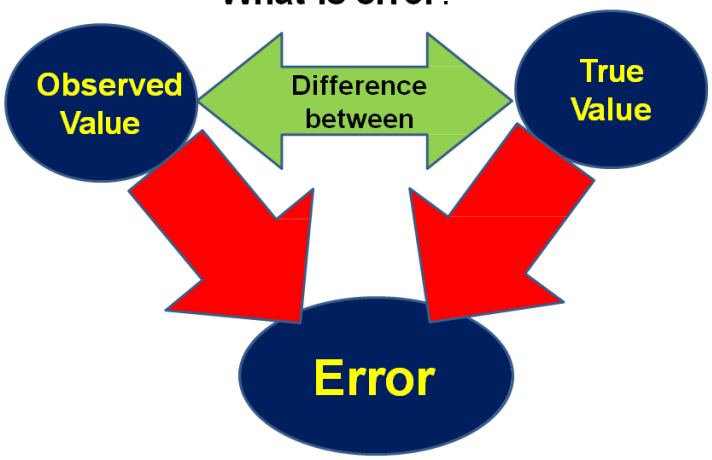
  $E = | X_i - X_t | = 508\text{-}500 = 8$ m.
- b.) The relative error in the length of the field is

  Relative error $= (8 \times 100) / 500 = 1.6\%$

2. Types and reasons for errors

Notes:

What is error?

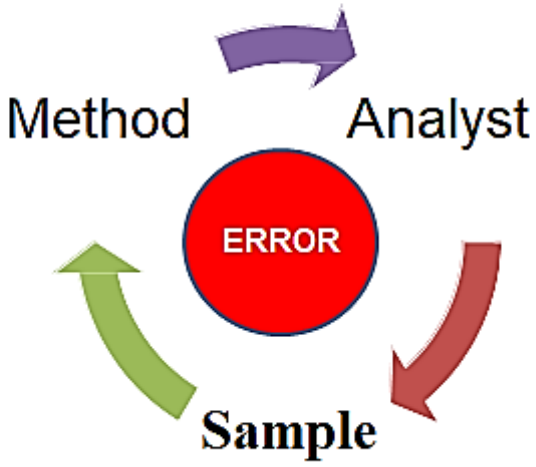


Measurement Error (also called Observational Error) is the difference between a measured quantity and its true value

Who and what may produce errors?

Notes:

Any measurement involves the interaction of the following three components



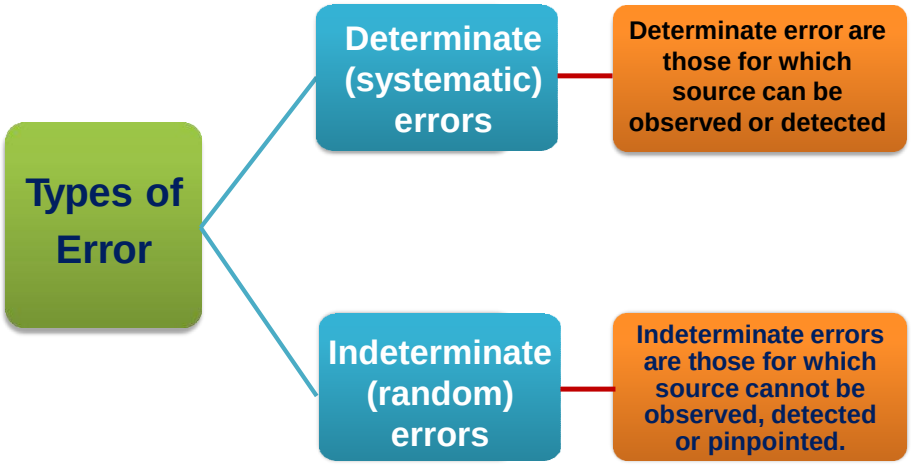
Sources of errors

Notes:

- Incorrect weighing and transfer of analytes and standards
- Inefficient extraction of the analyte from a matrix
- Incorrect use of pipettes, burettes or volumetric flask for volume measurement
- Measurement carried out using improperly calibrated instrumentation
- Failure to use an analytical blank
- Selection of assay conditions that cause degradation of the analyte
- Failure to allow for or to remove interference by excipients in the measurement of an analyte

Types of errors

Notes:



Comparison

Notes:

Sr. No.	Characteristics	Determinate error	Indeterminate Error
1	Origin	Source can be observed	No Source can be observed
2	Magnitude	Large	Small
3	Direction	Unidirectional	No direction
4	Reproducibility	Reproducible	Not Reproducible
5	Effect	Affect the measurement	No Effect on measurement
6	Remedy	Minimization possible, elimination in some cases possible	No elimination

Absolute and relative errors

Notes:

Absolute error

The difference between the measured value and True value

Absolute error $= (x_i - T)$

Relative error

Relative error =

= Absolute error / True value =

$= (x_i - T) / T$

Constant and proportionate errors

Notes:

Constant errors

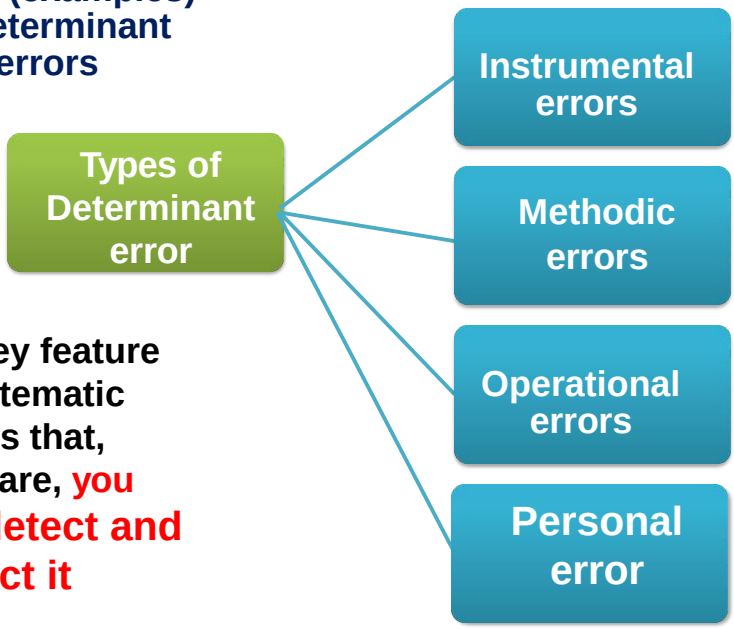
The error in which the absolute error remains constant and the relative error changes with the change in sample size

Proportionate errors

The error in which the magnitude of the absolute error changes with change in sample size but relative error remains constant

Types (examples) of determinant errors

Notes:



The key feature of systematic error is that, with care, you can detect and correct it

Instrumental errors

Notes:

- **Instrumental errors are introduced due to the use of defective instruments.**
- **Sometimes an instrument error may arise from the environmental factors on the instrument.**
- **Instrumental errors may largely be eliminated by periodically calibrating the instruments.**

Error is caused by uncertainty in the last digit of the measurement due to least count of the instrument or volumetric glass ware

- Example: counting /noting burette reading.
- Example: an error in volumetric analysis will be introduced, when a 20 ml pipette, which actually measures 20.1 ml, is used.

Error is caused by improper response: Optimum condition for the working of the Instrument. Instrument works in that condition only

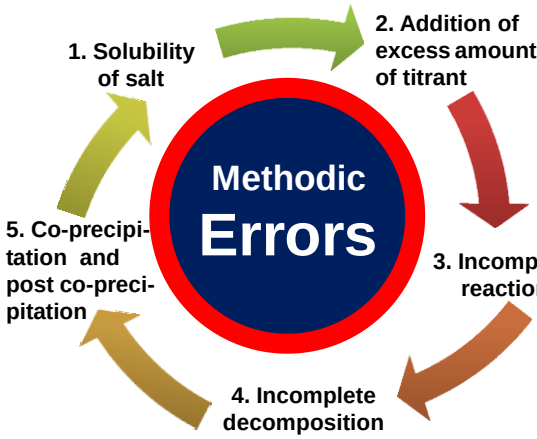
- Example: a pipette calibrated at 20°C, if used at 30°C will introduce error in volume.
- Example: Working of glass electrode to measure pH using pH meter. pH of solution 1-10 can be recorded properly. If the solution is having pH greater than this range, electrode system will give Improper response.

Methodical errors

Notes:

- These errors are caused by adopting defective experimental methods.
- Proper understanding of the theoretical background of the experiments is a necessity for avoiding methodical errors.

For example in volumetric analysis the use of an improper indicator leading to wrong results is an example for methodical error

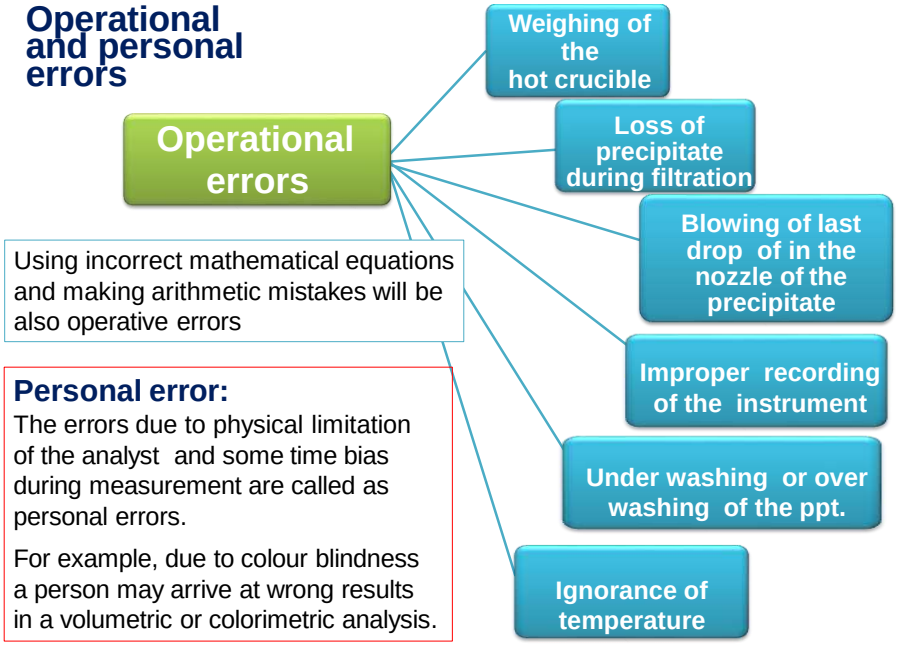


These errors appeared when using classical methods as these methods involve a number of steps.

$MnNH_4PO_4 \rightarrow Mn_2P_2O_7 + 2NH_3 + H_2O$

Operational and personal errors

Notes:



Using incorrect mathematical equations and making arithmetic mistakes will be also operative errors

Personal error:

The errors due to physical limitation of the analyst and some time bias during measurement are called as personal errors.

For example, due to colour blindness a person may arrive at wrong results in a volumetric or colorimetric analysis.

Indeterminate errors

Notes:

- These errors are also called accidental or random errors.
- They are always present, cannot be corrected, and are the ultimate limitation on the determination of a quantity.
- They arise from uncertainties in a measurement that are unknown and which cannot be controlled by the analyst.

For example:

- reading a scale on an instrument caused by the finite thickness of the lines on the scale;
- electrical noise;
- when pipetting out a liquid, the speed of draining, the angle of holding the pipette, the portion at which the pipette is held, etc, would introduce indeterminate error in the volume of the liquid pipette out.

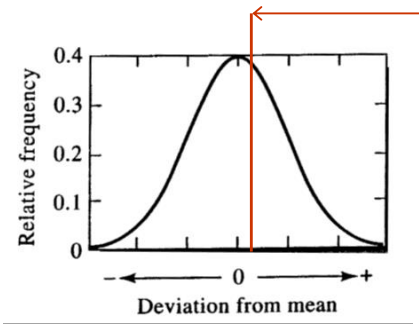
Effects of random and systematic errors

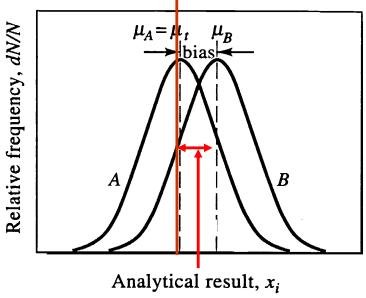
Notes:

Random (or Indeterminate) Error results in a scatter of results centered on the true value for repeated measurements on a single sample.

Systematic (or determinate) Error determines a shift between the measured and true values

True value





Random Error **Systematic Error**

3. Typical sources for errors in analytical chemistry
Methods of Weighing

Notes:

(i) Basic operational rules

- Chemicals should never be placed directly on the weighing pan
  - *corrode and damage the pan may affect accuracy*
  - *not able to recover all of the sample*
- Balance should be in arrested position when load/unload pan
- Half-arrested position when dialing weights
  - *dull knife edge and decrease balance sensitivity → accuracy*

(ii) Weight by difference:

- Useful for samples that change weight upon exposure to the atmosphere
  - *hygroscopic samples (readily absorb water from the air)*
- Weight of sample = (weight of sample + weight of container) – weight of container

(iii) Taring:

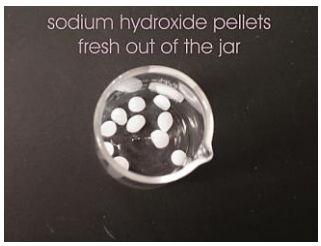
- Done on many modern electronic balances
- Container is set on balance before sample is added
- Container's weight is set automatically to read "0"

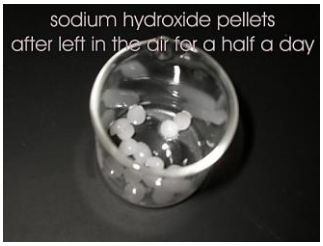
Errors in Weighing: Sources

Notes:

Any factor that changes the apparent mass of the sample

- Dirty or moist sample container:
  - also may contaminate sample;
  - important to dry sample before weighing.
- Sample not at room temperature:
  - avoid convection air currents (push/lift pan).
- Adsorption of water, etc. from air by sample;
- Vibrations or wind currents around balance;
- Non-level balance.



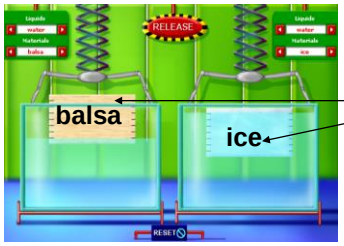


Errors in Weighing: Sources (continued)

Notes:

Any factor that changes the apparent mass of the sample

Buoyancy errors – failure to correct for weight difference due to displacement of air by the sample.



Different displacement of ice and balsa wood in water

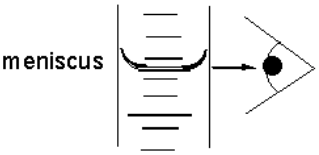
Correction for buoyancy to give true mass of sample: $$m = \frac{m'\left(1-\frac{d_a}{d_w}\right)}{\left(1-\frac{d_a}{d}\right)}$$

m = true mass of sample
m' = mass read from balance
d = density of sample
d_a = density of air (0.0012 g/ml at 1 atm & 25°C)
d_w = density of calibration weights (~ 8.0 g/ml)

Errors in volumes: Source

Notes:

(i) Always measure volume at <u>bottom</u> of a concave meniscus:
- always fill all volumetric flasks or transfer pipettes to calibration line



(ii) always read at the same eye level as the liquid

Eye level

15.46 mL

View from above

15.31 mL 1% error

(iii) <u>Don't</u> force out last drop from pipette!

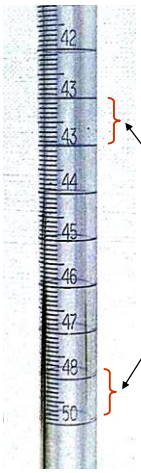
(iv) Remove air bubbles

Volume measurements: systematic errors

Notes:

Let us remember that systematic errors are:

1. An error appeared consistently in all results due to inappropriate methods or experimental techniques.
2. Results in all measurements exhibit a definite difference from the correct value.
3. This type of error can be discovered and corrected.



Example: The burette is incorrectly calibrated

Problem: Indeterminate errors

Notes:

Random error in a burette reading is about ± 0.02 mL
If initial reading is 45.06 ± 0.02 mL
Final reading is 12.67± 0.02 mL
What is the precision (±) of the delivered volume?
The errors in the IR and FR are absolute uncertainties

The relative uncertainty is 0.02mL/45.06mL *100 = 0.04%
The larger measurement, the smaller the relative uncertainty

4. Approaches to minimisation of errors
Error minimisation

Notes:

Detection of Determinate Method Errors is possible by:

- analysis of standard samples (SRS);
- independent analysis;
- blank determinations;
- variation in sample size.

(SRS) Standard Reference Samples

Error minimization

Notes:

Analyst has no control on random errors but systemic errors can be reduced by following methods.

Calibration of apparatus: By calibrating all the instruments, errors can be minimized and appropriate corrections are applied to the original measurements. *Operational and instrumental error can be minimized.*

Control determination: Standard substance is analysed in identical experimental condition and its result compared with the true value. *Deviation of the obtained result from the true or expected value will be measure of methodic and operational errors*

Blank determination: By omitting sample, a determination is carried out in identical condition to minimize the errors occurs due to impurities present in reagent. *Methodic and operational errors can be minimized*

Error minimisation (continued)

Notes:

Independent method of analysis: It is carried out to maintain accuracy of the result *(Methodic and operational errors can be different).*

For example, Iron (III) is first determined gravimetrically by precipitation method as iron (III) hydroxide and then determined titrimetrically by reduction to the iron (II) state.

Parallel determination: Instead of single determination, duplicate or triplicate determination is carried out to minimize the possibilities of accidental errors.

Standard edition: Sample is analysed alone then sample + standard substance analysed *(Methodical and operational errors will be same for two measurements).* This method is generally applied to physico-chemical procedures such as polarography and spectrophotometry (will be discussed later).

Internal standards: It is used in spectroscopic and chromatographic determination (will be discussed later).

5. Significant figures and some statistical parameters

Notes:

How many figures should be reported in experimental results?

- Data have to be reported with care keeping in mind reliability about the number of figures used.
- Each measurement is associated with error or uncertainty (except for simple counting).
- To evaluate the validity of a measurement, it is necessary to evaluate its error or uncertainty.

For example, if somebody uses a calculator, as many as six decimal numbers can be obtained when reporting a value.

However, reporting all these decimal numbers is meaningless because, as is generally true, there may be uncertainty about the first decimal itself.

Therefore, experimental data should be rounded off.

Notes:

Significant figure: definition

- The number of significant figures is the minimum number of digits needed to write a given value in scientific notation without loss of accuracy.
- most significant figure - the left-hand most digit, the digit which is known most exactly
- least significant figure - the right-hand most digit, the digit which is known most exactly

9.25×10^4 3 significant figs

9.250×10^4 4 significant figs

9.2500×10^4 5 significant figs

Which figures are significant?

Notes:

Rules for determining, which digits are significant, are as follows:

1. All non-zero numbers are significant.
2. Zeros between non-zero numbers are significant.
3. Zeros to the right of the non-zero number **and** to the right of the decimal point are significant.
4. Zeros before non-zero numbers are **not** significant.

Examples for Zeros

1) Leading zeros - never count: 0.0025 - 2 significant figures.
2) Captive zeros - always count: 1.008 - 4 significant figures.
3) Trailing zeros - count only if the number is written with a decimal point:
   100 - 1 significant figure;
   100. - 3 significant figures;
   120.0 - 4 significant figures.

Significant figure (continued)

Notes:

- The number of significant figures in a given number is found by counting the number figures from the left to right in the number beginning with the first non-zero digit and continuing until reaching the digit that contains the uncertainty.

Example: Each of the following has three significant figures:

646 0.317 9.22 0.00149 20.2

- When multiplication and division are carried out, it is assumed that the number of significant figures of the result is equal to the number of significant figures of the component quantity that contains the least number of significant figures

Example $\frac{11 \times 0.122}{10} = 0.1342 = 0.13$

Significant figure (continued)

Notes:

The last significant figure in any number is the first digit with any uncertainty:

i. the minimum uncertainty is ± 1 unit in the last significant figure
ii. if the uncertainty in the last significant figure is ≥ 10 units, then one less significant figure should be used.
iii. Example:

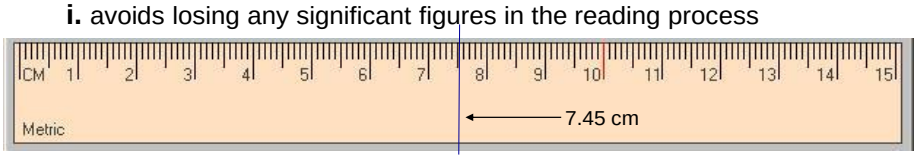
9.34 ± 0.02 **3 significant figures**

But

6.52 ± 0.12 should be 6.5 ± 0.1 **2 significant figures**

Whenever taking a reading from an instrument, graph, etc. always estimate the result to the nearest tenth of a division.

i. avoids losing any significant figures in the reading process



Once again: In experimental data, the first uncertain figure is the last significant figure.

Addition and Subtraction

Notes:

Addition and Subtraction

Use the following procedure:

Express all numbers using the same exponent

Align all numbers with respect to the decimal point

$$\begin{array}{rl} 1.25 & \times 10^{5} \\ 2.48 & \times 10^{4} \\ +\ 1.235 & \times 10^{4} \end{array} \Rightarrow \begin{array}{rl} 12.5 & \times 10^{4} \\ 2.48 & \times 10^{4} \\ +\ 1.235 & \times 10^{4} \end{array}$$

Add or subtract using all given digits

Round off the answer so that it has the same number of digits to the right of the decimal as the number with the fewest decimal places

$$\begin{array}{rl} 12.5 & \times 10^{4} \\ 2.48 & \times 10^{4} \\ +\ 1.235 & \times 10^{4} \\ \hline 16.215 & \times 10^{4} \end{array} = 16.2 \times 10^{4}$$

1 decimal point

Addition and Subtraction (continued)

Notes:

Addition and Subtraction

Use the following procedure:

- Round off the answer to the nearest digit in the least significant figure.
- Consider all digits beyond the least significant figure when rounding.
- If a number is exactly half-way between two digits, round to the nearest <u>even</u> digit.
  - minimizes round-off errors
- Examples:

3 sig. fig.:	12.534	➔	12.5
4 sig. fig.:	11.126	➔	11.13
4 sig. fig.:	101.250	➔	101.2
3 sig. fig.	93.350	➔	93.4

Multiplication and Division

Notes:

Multiplication and Division

Use the following procedure:

- For multiplication and division, the number of significant figures used in the answer is equal to the number in the value with the fewest significant figures.
- Examples:

$$\begin{array}{l} 3.261 \times 10^{-5} \\ \times\ 1.78 \\ \hline 5.80 \times 10^{-5} \end{array}$$

3 significant figures

$$\begin{array}{l} 34.60 \\ :\ 2.4287 \\ \hline 14.05 \end{array}$$

4 significant figures

Logarithms and Antilogarithms

Notes:

Logarithms and Antilogarithms

(i) the logarithm of a number "a" is the value "b", where:

$a = 10^b$ or $\text{Log}(a) = b$

(ii) example:

The logarithm of 100 is 2, since:

$100 = 10^2$

(iii) The antilogarithm of "b" is "a"

$a = 10^b$

(iv) the logarithm of "a" is expressed in two parts

$\text{Log}(339) = 2.530$

character mantissa

Logarithms and Antilogarithms (continued)

Notes:

Logarithms and Antilogarithms

(v) when taking the logarithm of a number, the number of significant figures in the resulting mantissa should be the same as the total number of significant figures in the original number "a"

(vi) Example:

$\text{Log}(5.403 \times 10^{-8}) = -7.2674$

4 sig. fig. 4 sig. fig.

(vii) when taking the antilogarithm of a number, the number of significant figures in the result should be the same as the total number of significant figures in the mantissa of the original logarithm "b"

(viii) Example:

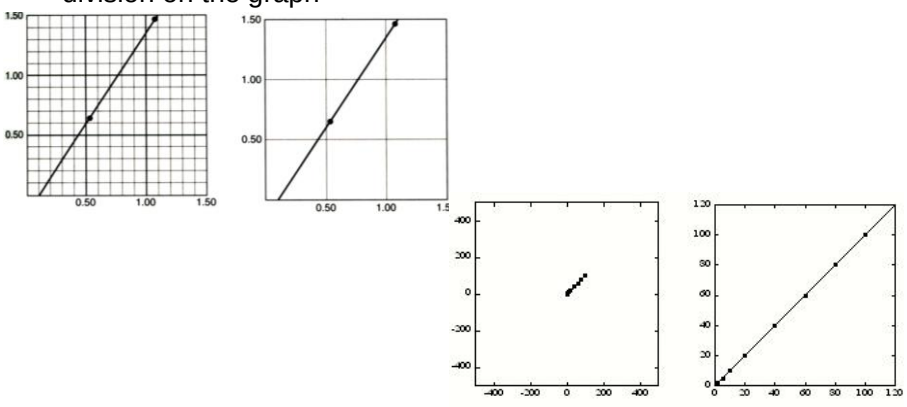
$\text{Antilog}(-3.42) = 3.8 \times 10^{-4}$

2 sig. fig. 2 sig. fig.

Graphs

Notes:

- use graph paper with enough rulings to accurately graph the results
- plan the graph coordinates so that the data is spread over as much of the graph as possible
- in reading graphs, estimate values to the nearest 1/10 of a division on the graph



Notes:

Problem

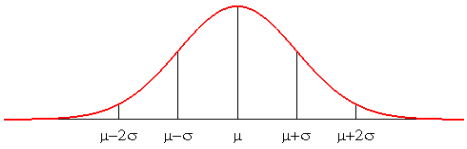
How many significant figures are in:

1) 12.548
2) 0.00335
3) 504.70
4) 4000
5) 0.10200

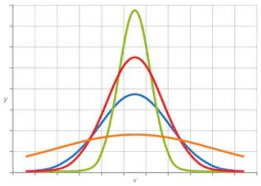
Normal error Curve

Notes:

- The normal error curve was first studied by Carl Friedrich Gauss as a curve for the distribution of errors. This normal distribution curve is a useful tool to measure the extent of indeterminate (random) error. It is given by the equation: $f(X) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}}$ *where σ is the standard deviation; x = value of the continuous random variable; μ = mean of the normal random variable; π=3.14.*
- In normal error curve, the frequency is plotted against mean deviation.
- When the frequency is maximum the error is nil.
- When the frequency decreases, the magnitude of the error increases.



- When σ is very large, the curve obtained is bell shaped.
- When σ is very small, then a sharp curve is obtained.
- When frequency increases, the σ will decrease → sharp curve → nil error.
- When frequency decreases the σ increase → bell shaped curve → increases



Normal error Curve

Notes:

- The normal error curve was first studied by Carl Friedrich Gauss as a curve for the distribution of errors.
- Normal distribution is common in nature.
- For example, the following random variables are well modelled by the normal distribution:
  - *measurement errors;*
  - *some characteristics of living organisms in the population.*
- The normal distribution curve is a useful tool to measure the extent of indeterminate (random) error.
- It is given by the equation: $y = \frac{1}{\sigma\sqrt{2\pi}} e^{-(x-\mu)^2/2\sigma^2}$
- *where σ is the standard deviation;*
  x = value of the continuous random variable;
  μ = mean of the normal random variable; π=3.14.

The normal distribution characterises population by taking samples.

The larger the number of samples, the closer the distribution becomes to normal

Mean and Standard deviation

Notes:

Estimate of mean value of population = μ

Estimate of mean value of samples = $\bar{x}$ Mean = $\bar{x} = \frac{\sum_i x_i}{n}$

The standard deviation is a measure of the amount of variation or dispersion of a set of values.

Degree of scatter of population is quantified by calculating the *standard deviation (std. dev.)*

- Std. dev. of population = σ
- Std. dev. of sample = s

$$s = \sqrt{\frac{\sum_i (x_i - \bar{x})^2}{n-1}}$$

- Characterize sample by calculating $\bar{x} \pm s$

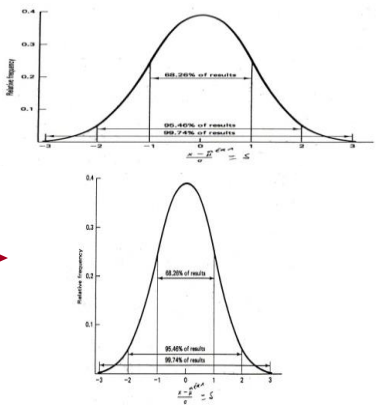
Standard deviation and the normal distribution

Notes:

A low standard deviation indicates that the values tend to be close to the mean (also called the expected value) of the set,

A high standard deviation indicates that the values are spread over a wider range.

- Standard deviation defines the shape of the normal distribution (particularly width)
- Larger std. dev. more scatter about the mean, worse precision. →
- Smaller std. dev. means less scatter about the mean, better precision. →

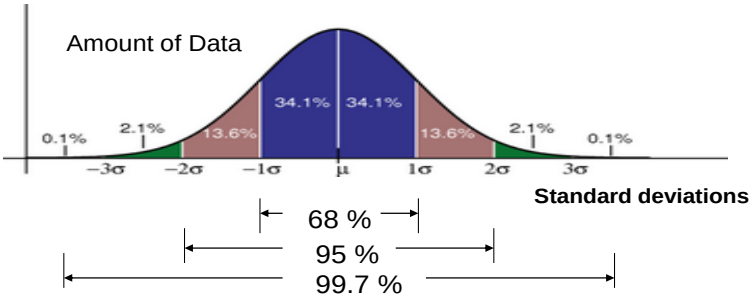


Standard deviation and the normal distribution

Notes:

There is a well-defined relationship between the std. dev. of a population and the normal distribution of the population.

(May also consider these percentages of area under the curve)



Total % of the data covered by distribution are shown above for 1, 2 and 3 sigma

Relative standard deviation, standard error and variance

Notes:

Relative standard deviation (rsd) or coefficient of variation (CV)

$$\text{rsd} = \left(\frac{s}{\bar{x}}\right)100$$

Standard error = $s_{\bar{x}} = \frac{s}{\sqrt{n}}$

Variance is used in many other statistical calculations and tests:

Variance = s^2

Standard deviation of set of samples should decrease if we take more measurements.
There are several quantitative ways to determine the sample size required to achieve a desired precision for various statistical applications.

Notes:

Some useful statistical tests

- Need to characterize or make judgments about data
- Tests that use the *Student's t distribution*
  - Confidence intervals
  - Comparing a measured result with a "known" value
  - Comparing replicate measurements (comparison of means of two sets of data)

Confidence interval (CI)

Notes:

- Quantifies how far the true mean (μ) lies from the measured mean, $\bar{x}$.
- Uses the mean and standard deviation of the sample.

$$\mu = \bar{x} \pm \frac{ts}{\sqrt{n}}$$

where coefficients *t* are from the *t*-tables and
n = number of measurements.
Degrees of freedom (df) = *n* - 1 for the confidence interval.

Interpreting:

what does confidence interval CI_{95} = 1.3 ± 0.2 mean?

- It means that there is a 95% probability that the true mean (μ) lies between the range 1.3 ± 0.2, or between 1.1 and 1.5
- Note that **CI** will decrease as n is increased.
- Useful for characterizing data that are regularly obtained; e.g., quality assurance, quality control

Testing a Hypothesis (Significance Tests)

Notes:

- Carry out measurements on an accurately known standard.
- Experimental value is different from the true value.
- Is the difference due to a systematic error (bias) in the method - or simply to random error?

Assume that there is *no* bias (**NULL HYPOTHESIS**), and calculate the probability that the experimental error is due to random errors.

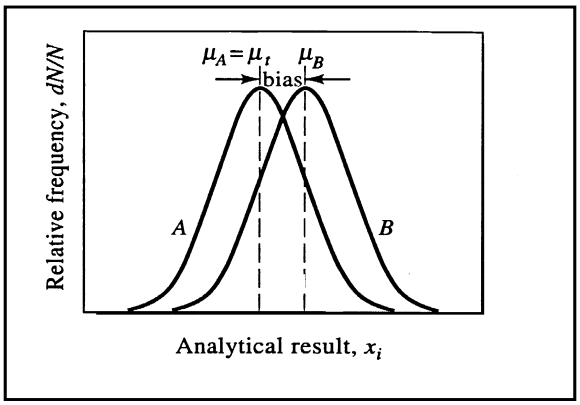


Figure shows (A) the curve for the true value ($m_A = m_t$) and (B) the experimental curve (m_B)

Comparing a measured result with a "known" value

Notes:

- This is another application of the *t* statistic
- "Known" value would typically be a certified value from a standard reference material (SRM)

$$t_{calc} = \frac{|known\ value - \bar{x}|}{s}\sqrt{n}$$

- Calculate t_{calc} and then compare it to tabulated value of t_{table} at appropriate df and CL , where df = n -1 for this test
- **If $|t_{calc}| < t_{table}$, results <u>are not</u> significantly different at a given CL.**
- **If $|t_{calc}| \geq t_{table}$, results <u>are</u> significantly different at a given CL.**

For **$|t_{calc}| < t_{table}$,** THE NULL HYPOTHESIS IS MAINTAINED and no BIAS at the 95 % confidence level.

Therefore, the difference between samples A and B is insignificant.

6. Methods of quantitative analysis

Notes:

Key quantification methods are as follows

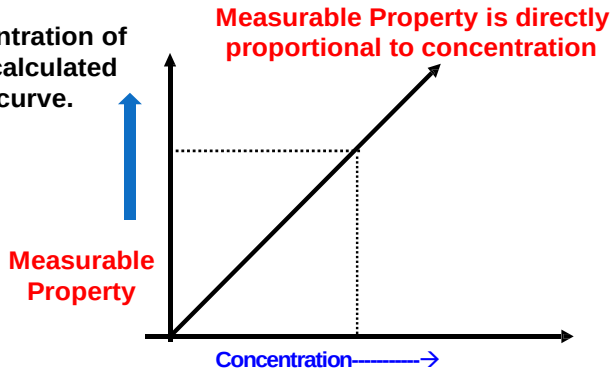
Quantitative Analysis

- **Calibration Curve method**
- **Method of Standard Addition**
- **Internal Standard Method**

Calibration Curve method

Notes:

- A calibration curve is used to determine the unknown concentration of an element in a solution.
- The instrument is calibrated using several solutions of known concentrations.
- The property to be measured of each known solution is measured and then a calibration curve of property measured versus concentration is plotted.
- The property of a sample solution is measured.
- **The unknown concentration of the element is then calculated from the calibration curve.**



Example: Calibration Curve method

Notes:

Optical density of 5 standard solutions of known concentrations was measured and then compared with the density of a sample solution of unknown concentration

Sr. No.	Concentration of $KMnO_4$	O.D.
1	5	0.02
2	10	0.04
3	15	0.06
4	20	0.08
5	25	0.10
6	Unknown	0.05

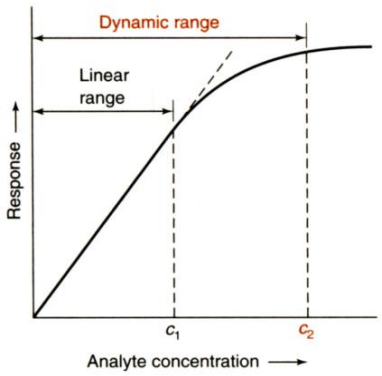
Plotting a calibration curve

Notes:

<u>Calibration curve</u>: shows a response of an analytical method to known quantities of analyte

Procedure:

a)Prepare known samples of analyte covering convenient range of concentrations.
b) Measure the response of the analytical procedure.
c)Subtract average response of blank
(no analyte).
a)Make graph of corrected response versus concentration.
b)Determine best straight line.



Using a calibration curve

Notes:

Prefer calibration with a linear response

- analytical signal proportional to the quantity of analyte

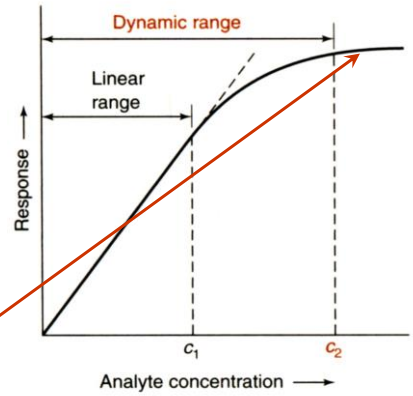
Linear range

- analyte concentration range over which the response is proportional to concentration

Dynamic range

- concentration range over which there is a measurable response to analyte

Outside the linear range, additional analyte does not result in an increase in response



Bad data points

Notes:

"Bad" Data Points may affect the results and should be removed from the consideration

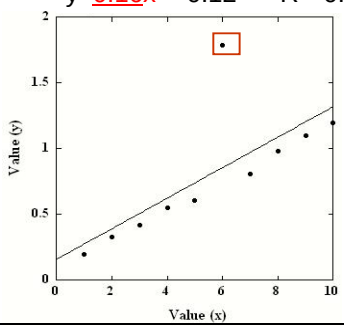
Identification of erroneous data point:

- compare points to the best-fit line;
- compare value to duplicate measures.

Omit "bad" points if much larger than averages and not reproducible.

- "bad" data points can distort the best-fit line and the accurate interpretation of data.

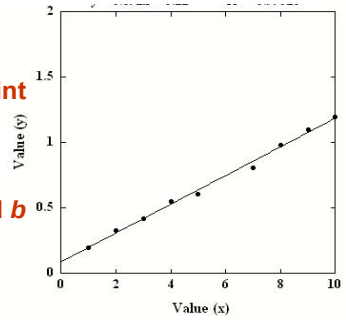
y=0.16x + 0.12 R^2=0.53261



Remove "bad" point

Improve fit and accuracy of *m* and *b*

y=0.091x + 0.11 R^2=0.99518

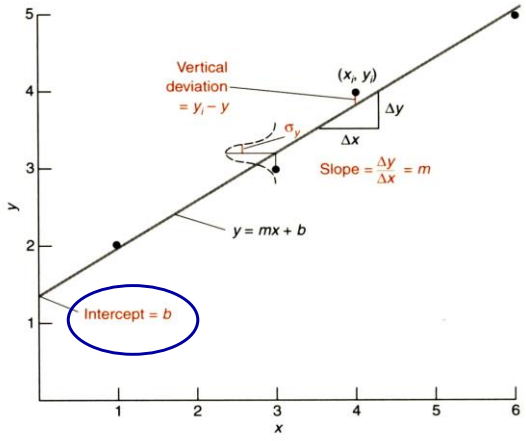


Finding the "Best" Straight Line

Notes:

Many analytical methods generate calibration curves that are linear or near linear in nature

Equation of Line: $y = mx + b$



x = independent variable
y = dependent variable
m = slope
b = y-intercept

$$slope = \frac{\Delta y}{\Delta x} = m$$

Determining the Best fit to the Experimental Data

Notes:

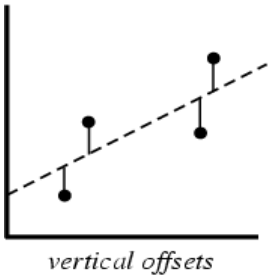
Method of Linear Least Squares is used to determine the best values for "m" (slope) and "b" (y-intercept) given a set of x and y values

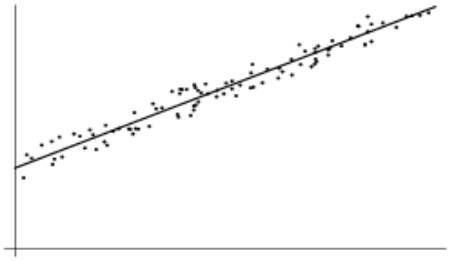
One need to minimize vertical deviation between points and line

$$d_i = (y_i - y) = (y_i - m(x_i) + b)$$

One need to use square of the deviations → deviation irrespective of sign

$$d_i^2 = (y_i - y)^2 = (y_i - m(x_i) + b)^2$$





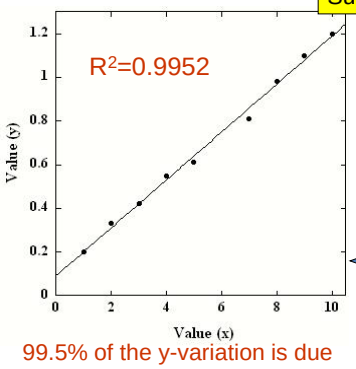
Goodness of the Fit

Notes:

R^2: compares the sums of the variations for the y-values to the best-fit line relative to the variations to a horizontal line.

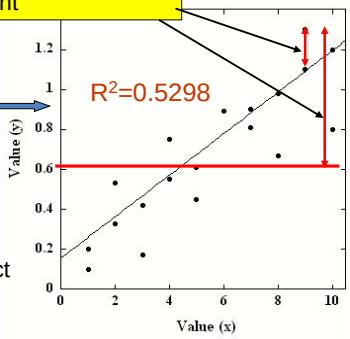
- R^2 x 100: percent of the variation of the y-variable that is explained by the variation of the x-variable.
- A perfect fit has an $R^2 = 1$; no relationship for $R^2 \approx 0$

R^2 based on these relative differences Summed for each point



Very weak to no relationship

Strong direct relationship



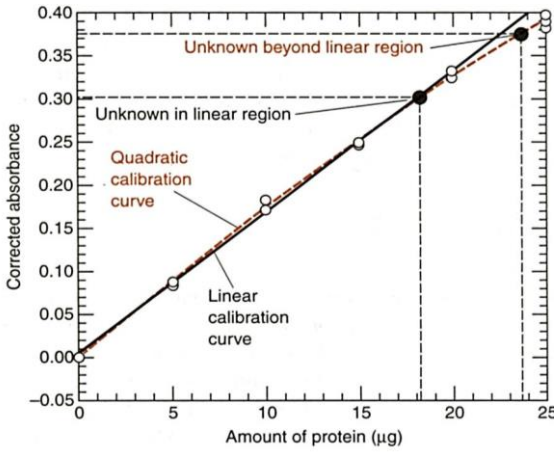
99.5% of the y-variation is due to the x-variation

53.0% of the y-variation is due to the x-variation. What is the other 47% caused by?

Determining Unknown Values from Calibration Curves

Notes:

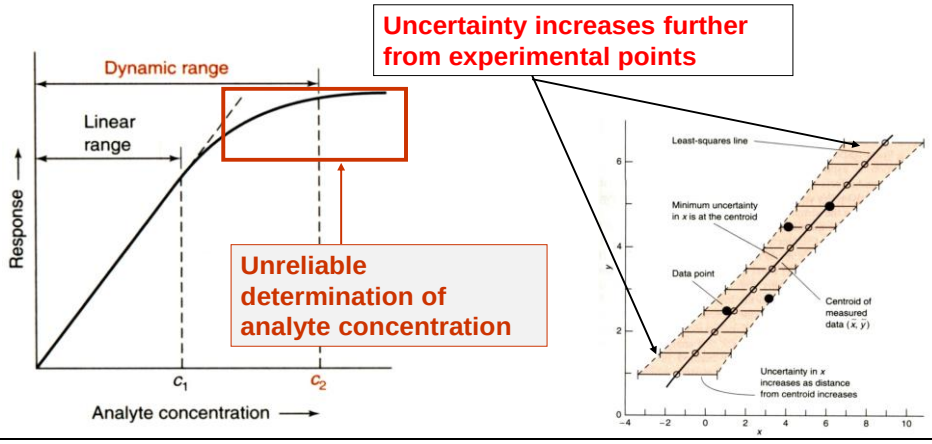
- Knowing the values of "m" and "b" allow the value of x to be determined once the experimentally y value is known.
- Know the standard deviation of m & b, the uncertainty of the determined x-value can also be calculated



Limitations in a Calibration Curve

Notes:

Key limitation in application of calibration curves are:
- Limited to linear range of curve;
- Limited to range of experimentally determined response for known analyte concentrations.



Limitations in a Calibration Curve (continued)

Notes:

Detection limit

- smallest quantity of an analyte that is significantly different from the blank

Signal detection limit: $y_{dl} = y_{blank} + 3s$ where S is standard deviation

- need to correct for blank signal

Corrected signal: $y_{cs} = y_{sample} - y_{blank}$

- minimum detectable concentration

Detection limit: $$C = \frac{3s}{m}$$

Where **C** is concentration
s – standard deviation
m – slope of calibration curve

Notes:

Problem (example)

Limitations in a Calibration Curve

Example:

- Low concentrations of Ni-EDTA near the detection limit gave the following counts in a mass spectral measurement: 175, 104, 164, 193, 131, 189, 155, 133, 151, 176.
- Ten measurements of a blank had a mean of 45 counts.
- A sample containing 1.00 mM Ni-EDTA gave 1,797 counts.
- Estimate the detection limit for Ni-EDTA

Method of Standard Addition

Notes:

The Method is useful:

- If sample composition is unknown
- Sample composition affects the results of analysis;
- To minimise the effect of matrix on the results of analysis.
- It is Very useful for complex mixtures because compensates for matrix effect (change in analytical signal caused by anything else than the analyte of interest)

Disadvantages:

It is impossible to take into account possible losses due to solubility or due to errors caused by the presence of other components with similar properties to the element of interest.

Possible influence of impurities in the reagents is controlled by conducting a "blank experiment" under the same conditions

Protocol of application of standard addition method

Notes:

Known quantities of an analyte are added to the unknown!!!

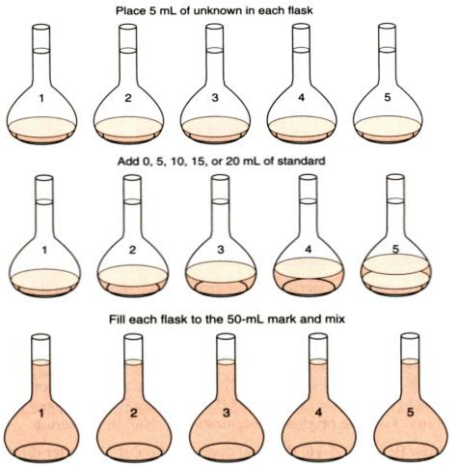
- known and unknown are the same analyte;
- increase in analytical signal is related to the total quantity of the analyte;
- requires a linear response to analyte.

Step by steps:

1. Place known volume of unknown sample in multiple flasks:

2. Add different (increasing) volumes of known standard to each unknown sample

3. Fill each flask to a constant, known volume

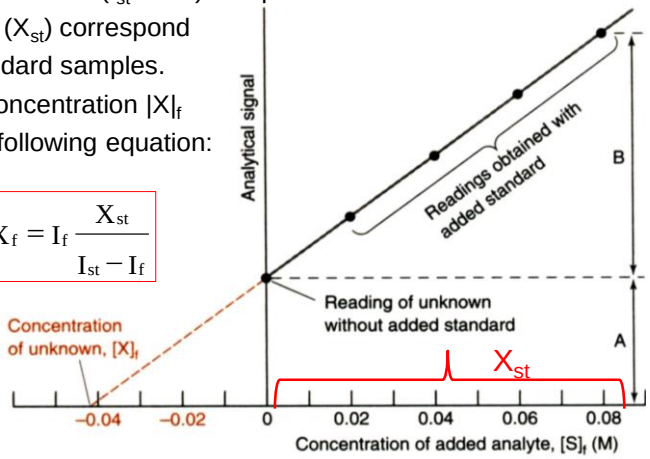


Determination of unknown concentration

Notes:

- Plot signals as a function of the added known analyte concentrations and determine the best-fit line.
- Continue the curve to the intersection with the axis OX at coordinate y=0.
- The values of A and (A+B) on the graph correspond to the signals from unknown (I_f=A) and standard (I_{st}=A+B) samples.
- The values of X_f and (X_{st}) correspond to unknown and standard samples.
- Then the unknown concentration $|X|_f$ is calculated by the following equation:

$$\frac{X_f}{X_f + X_{st}} = \frac{I_f}{I_{st}} \quad \text{and} \quad X_f = I_f \frac{X_{st}}{I_{st} - I_f}$$



Another variant of standard addition method

Notes:

- Solutions are prepared in the same way.
- In contrast to previous (graphic) variant of the standard addition method, only two flasks with solutions are needed for this determination:

  first – with only the sample under study without standard (test sample)

  second - with the studied sample plus standard (standard sample).
- Measure the intensity of the analytical signal of the test sample I_x.
- The signal intensity I_x is proportional to unknown concentration C_x

$$I_x = \text{const} \cdot C_x$$

- Measure the intensity of the analytical signal of the standard sample (I_{x+st}).
- The signal intensity (I_{x+st}) is proportional to the total concentration (C_{x+Cst})

$$I_{x+st} = \text{const} \cdot (C_x + C_{st})$$

Using two equations, one can obtain

$$C_x = C_{st} \frac{I_x}{I_{x+st} - I_x}$$

Problem (example for standard addition application)

Notes:

- Tooth enamel consists mainly of the mineral calcium hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$.
- Trace elements in teeth of archaeological specimens provide anthropologists with clues about diet and disease of ancient people.
- Researchers measured strontium in enamel from extracted wisdom teeth by atomic absorption spectroscopy.
- Solutions with a constant total volume of 10.0 mL contained 0.750 mg of dissolved tooth enamel plus variable concentrations of added Sr.
- Find the concentration of Sr.

Added Sr (ng/mL = ppb)	Signal (arbitrary units)
0	28.0
2.50	34.3
5.00	42.8
7.50	51.5
10.00	58.6

Internal Standard Method

Notes:

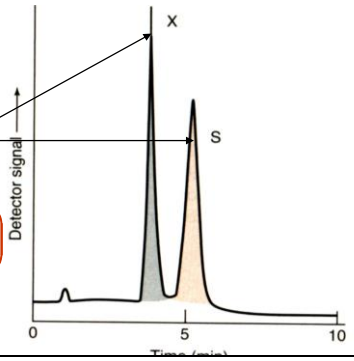
The method is useful for analysis:

- when quantity of sample analyzed or the instruments responses varies slightly from run to run.
- such responses are difficult to control.
- when sample loss occur during sample preparation.
- Widely used in chromatography

Area under curve proportional to concentration of unknown (x) and standard (s)

$$\frac{\text{Area of analyte signal}}{\text{Concentration of analyte}} = F\left(\frac{\text{area of standard signal}}{\text{Concentration of standard}}\right)$$

$$\frac{A_x}{[X]} = F\left(\frac{A_S}{[S]}\right)$$



Internal Standard Method

Notes:

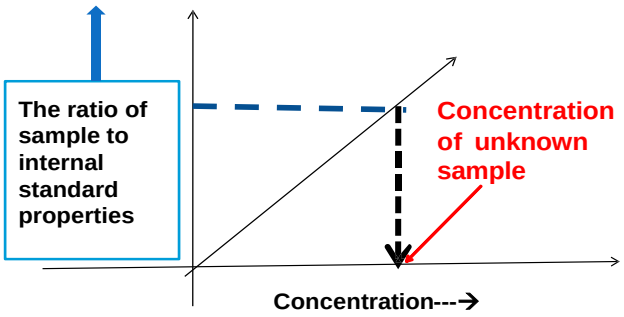
- A series of standard solution containing the same elements as that present in sample solution is prepared.
- A fixed quantity of suitable internal standard is then added to each of standard solutions, blank and sample solutions alike.
- The measurable property of each of above standard solutions and sample solutions are measured.

Sr. No.	Volume of sample solution	Concentration internal standard, ppm	O.D.
1	Blank	5	0.02
2	sample	5	0.06
3	5	5	0.08
4	10	5	0.10
5	15	5	0.12
6	20	5	0.14

Internal Standard Method (continued)

Notes:

- The measurable property for each of above standard **(Is) & (Ii)** and sample **(Ix & Ii)** solutions are measured at different wavelength;
- One wavelength corresponds to element and other - to the internal standard.
- These measurements are made against blank.
- The ratio of measured property of the standard solutions to that of internal standard **(Is/Ii)** are plotted against the concentration of standard solutions.
- This gives a straight line from this curve concentration of sample solution can be read by finding where the ratio **(Ix/Ii)** falls on concentration scale.



Tasks to Section 2

1. Give definitions of these terms: mean value, precision, accuracy, selectivity, sensitivity, dynamic range, the limit of linearity, the limit of detection.

2. What differences between such errors: random and systematic; absolute and relative; constant and proportionate; methodical and instrumental? How can errors be minimised?

3. How many figures should be reported in experimental results?

4. How many significant figures are in: a) 12.548; в) 0.00335; c) 504.70; d) 4000; e) 0.10200?

5. Find the average, standard deviation, and coefficient of variation for 721, 683, 734, and 755. If each of the four numbers is divided by 2, how will the mean, standard deviation, and coefficient of variation be affected?

6. Calculate confidence Interval: The carbohydrate content of a glycoprotein (a protein with sugars attached to it) is found to be 11.6, 10.9, 12.0, 11.7, and 11,5 wt% (g carbohydrate/100 g glycoprotein) in replicate analyses. Find 50% and 90% confidence intervals for the carbohydrate content.

7. The optical density of five standard solutions of known concentrations was measured and then compared with the density of a sample solution of unknown concentration. The optical density of the solution with unknown concentration was 0,05. Draw a calibration graph according to data in the table below. Determine the unknown concentration in a solution by using the calibration curve.

Section 3: Sample Collection, Handling and Preparation

Contents:

Introduction

It is essential to obtain a representative sample for analysis. Without this, the results can be meaningless or even grossly misleading.

It is necessary that the objectives of the analysis be transparent and that an appropriate sampling procedure is adopted.

If environmental samples of soil, water or atmosphere are collected, or a complex industrial process is controlled, a sampling strategy should be developed to optimize the value of the collected analytical information. Legislative requirements may also determine the sampling strategy, especially in the food and pharmaceutical industry sectors.

Sampling is particularly crucial for the analysis of heterogeneous material.

A representative sample is one of the original compositions of the material to be analyzed in the context of a particular analytical problem.

Section 3 pays special attention to the conditions of sample storage. A different time may elapse between sampling and analysis. Therefore, storage conditions should elude undesired loss of weight, contamination or other changes that could affect the analysis results.

Sometimes it is necessary to pre-treat the sample. That process often involves the separation or concentration of analytes and the removal of matrix components that may interfere with the analysis.

The samples usually need to be brought into a form suitable for measurements carried out under controlled conditions. Preparation of samples for analysis may include dissolution, grinding to a specific size, obtaining a particular shape, granulation, placement in a special holder for samples.

A small sample taken for analysis is called a laboratory sample.

If repeated tests or several different tests are required, the laboratory sample will be divided into parts of the sample, which must have the same composition.

Homogeneous materials (e.g. pure or mixed solvents and solutions, most gases) generally do not pose a particular problem for sampling. The composition of any small laboratory sample taken from a larger volume of such systems will represent their overall composition.

Heterogeneous materials should be homogenized to obtain a laboratory sample if a medium or bulk composition is required.

Notes:

Representative sample

Where analyte levels in different parts of the material are to be measured, they may need to be physically separated before laboratory samples are taken.

This is known as **selective sampling.**

Representative sample

Notes:

- surface waters such as streams, rivers, reservoirs and seawater, where the concentrations of trace metals or organic compounds in solution and in sediments or suspended particulate matter may each be of importance;
- materials stored in bulk, such as grain, edible oils, or industrial organic chemicals, where physical segregation (stratification) or other effects may lead to variations in chemical composition throughout the bulk;
- ores, minerals and alloys, where information about the distribution of a particular metal or compound is sought;
- laboratory, industrial or urban atmospheres where the concentrations of toxic vapors and fumes may be localized or vary with time.

Representative sample

Notes:

Obtaining a laboratory sample to establish an average analyte level in a highly heterogeneous material can be a lengthy procedure. For example, sampling a large shipment of an ore or mineral, where the economic cost needs to be determined by a very accurate assay, is typically approached in the following manner.

(i) Relatively large pieces are **randomly** selected from different parts of the shipment.

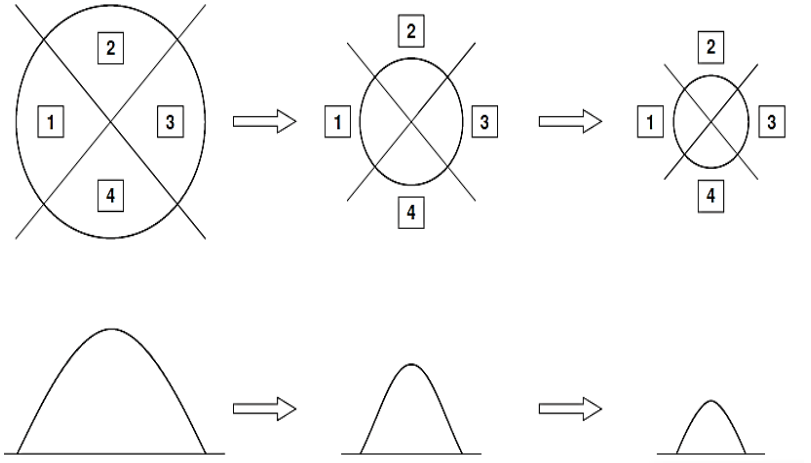
(ii) The pieces are crushed, ground to coarse granules and mixed.

(iii) A repeated **coning and quartering** process, with additional grinding to reduce particle size, is used until a laboratory-sized sample is obtained.

This involves creating a conical heap of the material, dividing it into four equal portions, discarding two diagonally opposite portions and forming a new conical heap from the remaining two quarters. The

Diagrammatic representation of coning and quartering (quarters 1 and 3, or 2 and 4 are discarded each time).

Notes:



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Representative sample

Notes:

- Repeated sampling over a period of time is a common requirement. Examples include the continuous monitoring of a process stream in a manufacturing sampling.
- Studies of seasonal variations in the levels of pesticide, herbicide and fertilizer residues in soils and surface waters, or the continuous monitoring of drinking water supplies are two further examples.

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Representative sample

Notes:

- Having obtained a representative sample, it **must** be **labeled** and stored under appropriate conditions.
- Sample identification through proper labeling, increasingly done by using bar codes and optical readers under computer control, is an essential feature of sample handling.

Sample storage

Notes:

- Samples often have to be collected from places remote from the analytical laboratory and several days or weeks may elapse before they are received by the laboratory and analyzed.
- Furthermore, the workload of many laboratories is such that incoming samples are stored for a period of time prior to analysis. In both instances, sample containers and storage conditions (e.g., temperature, humidity, light levels and exposure to the atmosphere) must be controlled such that no significant changes occur that could affect the validity of the analytical data.

The following effects during storage should be considered:

Notes:

- increases in temperature leading to the loss of volatile analytes, thermal or biological degradation, or increased chemical reactivity;
- decreases in temperature that lead to the formation of deposits or the precipitation of analytes with low solubility;
- changes in humidity that affect the moisture content of hygroscopic solids and liquids or induce hydrolysis reactions;
- UV radiation, particularly from direct sunlight, that induces photochemical reactions, photodecomposition or polymerization;
- air-induced oxidation;
- physical separation of the sample into layers of different density or changes in crystallinity.

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Sample storage

Notes:

- In addition, containers may leak or allow contaminants to enter.
- A particular problem associated with samples having very low (**trace** and **ultra-trace**) levels of analytes in solution is the possibility of losses by adsorption onto the walls of the container or contamination by substances being leached from the container by the sample solvent.
- Trace metals may be depleted by adsorption or ion-exchange processes if stored in glass containers, whilst sodium, potassium, boron and silicates can be leached from the glass into the sample solution. Plastic containers should always be used for such samples.

Sample pretreatment

Notes:

- Samples arriving in an analytical laboratory come in a very wide assortment of sizes, conditions and physical forms and can contain analytes from major constituents down to ultra-trace levels.
- They can have a variable moisture content and the matrix components of samples submitted for determinations of the same analyte(s) may also vary widely.
- A preliminary, or **pre-treatment**, is often used to **condition** them in readiness for the application of a specific method of analysis or to **pre-concentrate** analytes present at very low levels.

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Sample pretreatment

Notes:

- drying at 100°C to 120°C to eliminate the effect of a **variable moisture content**;
- weighing before and after drying enables the water content to be calculated or it can be established by thermogravimetric analysis;
- separating the analytes into groups with common characteristics by distillation, filtration, centrifugation, solvent or solid phase extraction;
- removing or reducing the level of **matrix components** that are known to cause **interference** with measurements of the analytes;
- concentrating the analytes if they are below the concentration range of the analytical method to be used by evaporation, distillation, co-precipitation, ion exchange, solvent or solid phase extraction or electrolysis.

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Sample preparation

Notes:

A laboratory sample generally needs to be prepared for analytical measurement by treatment with reagents that convert the analyte(s) into an appropriate chemical form for the selected technique and method, although in some instances it is examined directly **as received** or mounted in a sample holder for surface analysis.

If the material is readily soluble in aqueous or organic solvents, a simple dissolution step may suffice. However, many samples need first to be decomposed to release the analyte(s) and facilitate specific reactions in solution.

Notes:

Sample solutions may need to be diluted or concentrated by enrichment so that analytes are in an optimum concentration range for the method.

The stabilization of solutions with respect to pH, ionic strength and solvent composition, and the removal or **masking** of interfering matrix components not accounted for in any pre-treatment may also be necessary.

An **internal standard** for reference purposes in quantitative analysis is sometimes added before adjustment to the final prescribed volume.

Some methods for sample decomposition and dissolution

Notes:

Method of attack	Type of sample
Heated with concentrated mineral acids (HCl, HNO_3, aqua regia) or strong alkali, including microwave digestion	Geological, metallurgical
Fusion with flux (Na_2O_2, Na_2CO_3, $LiBO_2$, $KHSO_4$, KOH)	Geological, refractory materials
Heated with HF and H_2SO_4 or $HClO_4$	Silicates where SiO_2 is not the analyte
Acid leaching with HNO_3	Soils and sediments
Dry oxidation by heating in a furnace or wet oxidation by boiling with concentrated H_2SO_4 and HNO_3 or $HClO_4$	Organic materials with inorganic analytes

Notes:

Several steps are required to estimate change in soil organic carbon stocks within a project area over time:

1. Develop a sampling plan for the Project Area based on a soil sampling design;
   - A sampling design provides instructions on the spatial layout of sampling locations, the number of samples, and (in some cases) the timing of sampling and compositing or bulking of soil samples.
1. Sample collection;
2. Sample preparation;
3. Laboratory analysis;
4. Calculation of the organic carbon content of soil samples and soil organic carbon stocks; and
5. Calculation of the change in soil organic carbon stocks over time within each Carbon Estimation Area (CEA).

Sample collection

Notes:

As an example, consider the sample preparation of food. Foods are solid, liquid, powdered, containing dissolved gases, and the like. Different methods are used for food sampling, storage and preservation.

The adequacy and condition of the sample or specimen received for examination are of primary importance

- If samples are improperly collected: the laboratory results will be meaningless
- Sampling protocol should be clearly defined

Start with a description of primary food product

Sample collection

Notes:

Identity of the food

- Common/alternative name
- Scientific name (Genus, species, variety)
- Plant food (entire plant/part e.g. roots)
- Animal food (entire animal/part)
- State of maturity (ripe immature)
- Other details

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Sample collection

Notes:

- Need to know:
  - Number and size of sample to be collected
  - Distribution of samples
  - Stratification to be used
- Sample label should be permanently attached to the sample
  - Common name of food
  - Sample code number
  - Date of receipt in Lab.

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Sample collection

Notes:

- During sample collection:
  - Collection details
    - Date and time of collection
    - Name of collector
    - Place of origin
    - Sampling point/addresses (roadside stall, farm, market)
    - Condition of cultivation (feed regime, altitude, irrigation)
    - Purchase price
    - Graphical record (Photograph, visual record with scale)
    - Transport conditions (mode and conditions of transport)

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Notes:

- Description of sample collected: after sample collection
  - Food type (Legume, fruit juice, milk product)
  - Local use of foods (Famine. Festivals)
  - State of food sample (solid, semisolid, viscous, or liquid)
  - Process and preservation methods (canned smoked)
  - Preparation method (cooking)
  - Extent of preparation (raw, fully cooked, reheated)

Description of sample collected: after sample collection

Notes:

- Food type (Legume, fruit juice, milk product)
- Local use of foods
- State of food sample (solid, semisolid, viscous, or liquid)
- Process and preservation methods (canned, smoked)
- Preparation method (cooking)
- The extent of preparation (raw, fully cooked, reheated)
- Packing medium (brine, oil)
- Container or wrapping (can, glass)
- Contact surface (can, glass)
- Label or list of ingredients (estimated by inspection)
- Batch number
- Weight of food collected/individual items
- Number of items
- Weight of common measure or portion

Sample collection

Notes:

Deliver samples to the laboratory promptly with the original conditions maintained as nearly as possible

- If products are in bulk: storage procedures, choice of containers, modes of transport should be considered
- Use containers that are clean, dry, leak-proof, wide-mouthed, sterile, and of a size suitable for samples of the product.

Sample Transportation

Notes:

- Whenever possible, avoid glass containers, which may break
- For dry materials, use sterile metal boxes, cans, bags, or packets with suitable closures.
- Identify each sample unit (defined later) with a properly marked strip of masking tape.
- Transport frozen or refrigerated products in approved insulated containers of rigid construction

Sample Handling

Notes:

Aim: To protect the sample from changes in composition and contamination

Things to note: Weight and nature of edible/inedible matter (Prior to further processing (outer wilted leaves)

- Method of preparation (cooking or not, time, the temperature of preparation)
- Weight before/after cooking
- Ingredients added if any
- Method of mixing and reduction (grinding, homogenization)
- Types of storage (addition of preservatives, the temp of storage)
- Methods used of taking analytical samples
- Storage of analytical samples or further processing
- Name and signature of person completing a record
- Date of record
- Other details

Sample Preparation

Notes:

Preparation of analytical portions

- If the particle size or bulk is too large for analysis, it must be reduced in bulk or size for analysis
- Documentation of sample preparation is very important
- Separate edible/inedible portions, record descriptions and weigh all parts
- Measure portion sizes, weights, volumes, density etc.

Homogeneous foods

Notes:

Solids

- Friable: crumble and mix.
- Sticky: freeze and crush at low temperature.
- Hygroscopic: take portions rapidly into preweighed sealable containers for weighing.

Emulsions

- Take by weight rather than volume; warm and mix.

Liquids with suspended solids

- Homogenize, or sample during gentle mixing.

Notes:

- **Reduction by quartering**

Food lots of small items (flour, rice, legumes, small fruits, chopped mixed units).

- The bulk is tipped into a uniform pile on a clean, inert surface
- Turned over several times with a polythene or glass spatula.
- The pile is leveled and then divided into four equal segments.
- Two opposing segments are taken and the other two discarded.
- The remaining segments are mixed and further reduced in the same way

Reduction by quartering

Notes:

- Foods consisting of fairly large, separate, but similar portions, such as loaves of bread or joints of meat, should be quartered and sampled then processed for analysis.
- Segmented foods sampling e.g. packets of biscuits, cartons of eggs, batches of bread rolls.
- Take every fourth item to form a composite sample.
- For sliced loaves, take every fourth slice and one end slice, which then must be thoroughly crumbed before further reduction.

Examples of analytical sample preparations

Notes:

Nuts

- Batches of nuts should be ground separately with a pestle and mortar, then mixed together thoroughly in a bowl.
- An analytical portion should be taken for inorganic analyses and the remaining mixture should be homogenized mechanically for further analyses.

Eggs

- Fresh. Fresh eggs should be shelled and mixed briskly with a fork; after analytical portions are taken for inorganic analyses, the remainder is homogenized mechanically.
- *Dried. Dried eggs should be handled as flour.*

Examples of analytical sample preparations

Notes:

Fruit

- **Large fruits (e.g. pineapples or watermelons) and medium-sized ones (e.g. apples)** must be quartered.
- Small fruits (e.g. cherries) should be quartered by the method used for particulate foods.
- Quarters should be coarsely chopped and combined, and unhomogenized analytical portions should be taken for immediate vitamin C and inorganic analyses.
- The remaining mixture can then be homogenized to produce an analytical sample for other analyses.

Examples of analytical sample preparations

Notes:

- Meats and fish (raw, cooked and processed).
- The fat and muscle of some meats are more conveniently analysed separately and the results combined to produce the final values.
- The edible portion of each unit is chopped coarsely with a sharp knife (fish is flaked with a fork) and mixed thoroughly in a bowl with a spatula.
- A portion is removed, frozen and crushed in a polythene bag, and used for inorganic analyses.
- The remainder of the analytical sample is minced and mixed thoroughly again; portions are taken for further analyses.
- Care must be taken to avoid fat separation during mixing

Notes:

Examples of analytical sample preparations

- **Leafy vegetables and vegetable inflorescences.**
- **Small leafy vegetables** should be mixed together in a bowl, chopped coarsely and mixed again briefly.
- A large portion should be taken for inorganic analysis and another portion into metaphosphoric acid for vitamin C analysis.
- Large tight-leaved vegetables (e.g. cabbage, iceberg lettuce) must be quartered.

Notes:

Examples of analytical sample preparations

- All large leafy vegetables must be chopped coarsely and mixed, and this must be done very quickly
- After the mixing, analytical portions should be taken for analyses of vitamin C, vitamin A, carotenes, vitamin E and inorganic nutrients
- The remainder can be chopped further. Stalks are often difficult to reduce and may have to be chopped separately and reintegrated into the food sample.

Notes:

Examples of analytical sample preparations

Prepared composite foods and dishes. This is the form in which most foods are consumed**.**

- Items should be briefly homogenized and carefully mixed.
- It can be assumed that laboratory homogenization will not introduce any contamination greater than that arising during domestic or commercial food preparation.

Notes:

Examples of analytical sample preparations

- Care is required to blend in the individual pieces of muscle, fat, vegetables, etc., which may be found in mixed prepared foods.
- Portions for vitamin C assay are best taken from the mixed homogenate before it is rehomogenized.
- If the prepared foods are hot, speed is essential to prevent moisture loss.
- Total meals or diets can be handled in the same way.

Sample Preparation

Notes:

Some practical equipment requirements for handling and preparation of laboratory and analytical samples

General:

- Trays (for carrying foods)
- Chopping boards (polythene, wood)
- Oven thermometer, meat thermometer
- Waring blender
- Pestle and mortar
- Ball mill
- Hammermill

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Sample Storage

Notes:

- Keep ground samples in glass or plastic containers with air and water tight covers.
- Samples not analysed immediately should be left in cold storage to minimise spoilage and other chemical reactions.
- Samples for lipid analysis – store under nitrogen at low temperature to prevent oxidation and unsaturated lipids

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Notes:

- Light may initiate oxidation so store in dark containers.
- For lipid analysis, antioxidants may be added if they wont interfere with the analysis
- It is therefore desirable to store a number of identical analytical samples
- Minimize the number of staff involved in taking portions from them.

Notes:

Effects of sample storage and preparation on nutrient content and precautions required to minimize them

Effects	Potential Changes	Nutrients Affected	Precaution
Drying out	Loss of water	All nutrients	Design of protocol, Keep samples sealed, weigh food at start and during preservation
Absorption	Gain of water	All nutrients	Design of protocol, keep samples in sealed container
Microbial activity	Degradation/autolysis/synthesis	Loss of CHO, proteins, gain in thiamin, Vit B6	Storage at low temperature, pasteurization or addition of inhibitors
Oxidation	Destruction of unsaturated fatty acids, loss of vitamins	Alterations in profile of fats	Store at -30C in sealed containers under nitrogen. Add antioxidants, bacteriostatic agents
Acid	Hydrolysis	Loss of sucrose and higher oligosaccharides	Store at low temperatures Neutralize acids

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Effects of sample storage and preparation on nutrient content and precautions required to minimize them

Notes:

Effects	Potential Changes	Nutrients Affected	Precaution
Alkaline	Destruction	Loss of thiamine	Avoid alkaline conditions and SO2
Light	Photo degradation	Loss of riboflavin	Protect from light
Contamination during sampling	From cooking vessels, soil, dust	Increase inorganic nutrients	Design protocol to minimize contamination, gently rinse with distilled water
Contamination from metallic blades, glassware	Increase in inorganic nutrients	Increase in major trace elements	Select apparatus with care Clean all utensils Store in plastic bags
Separation	Separation of fats	Changes in compositional Alteration in fibre content	Avoid over vigorous mixing and thaw/freeze cycles

Notes:

Sources of errors in sampling

- It is essential that all those involved in the sampling process are familiar with the objectives of the work and are clear about their roles.

- This will identify aspects that are unclear or impracticable and require modification to avoid errors.

Notes:

Analytical

The following aspects shall be monitored, evaluated, implemented and maintained to ensure accuracy and precision of the test carried out:

- Quality of distilled water
- **calibration** of measuring and testing instruments including analysers, balances, incubators, centrifuges and semi-automatic pipettes, and **regular servicing and maintenance of equipment.**

Notes:

- use standard/calibrator which is traceable to national/international reference material.

- include quality control specimens in each procedure on a daily basis

Analytical errors may be

systematic

or

random

Notes:

All data relating to the laboratory's internal **quality control** (QC) practices and performance in external quality assessment schemes (scoring, ranks, etc.) should be recorded, reviewed and corrective actions implemented.

Stability of reagents

Laboratory personnel should be aware that the stability of all reagents kept at room temperature shall be reduced from the stated values if the temperature exceeds 35^0C.

Notes:

Use of calibration graphs

A fresh standard curve should be carried out whenever:

- the calibrator is changed
- new reagents are introduced
- problems with QC are encountered

Notes:

Post-Analytical

In order to avoid transcriptional errors in the results of the test, the reporting/signatory technicians shall verify the results entered manually or through on-line instrument interfaces before the results are reported or dispatched.

Post-analytical errors:

Transcription errors
Excessive delay in reporting values
Correct interpretation

Notes:

Rectification of lab errors

It is therefore essential to continually ask the following questions.

1. Is there an analytical error?
2. If so, what type of error is this?
3. What could have been the causes for this error?
4. How to rectify this error?

Notes:

The analytical process

1. Formulating the question:
Translate general question into specific question
Is this water safe to drink? What is the concentration of Arsenic in the water sample?

Source	Caffeine (mgs per serving	Serving size (oz)
Regular coffee	106-164	5
Decaffeinated coffee	2-5	5
Tea	21-50	5
Cocoa beverage	2-8	6
Baking chocolate	35	1
Sweet chocolate	20	1
Milk chocolate	6	1
soft drinks	36-57	12

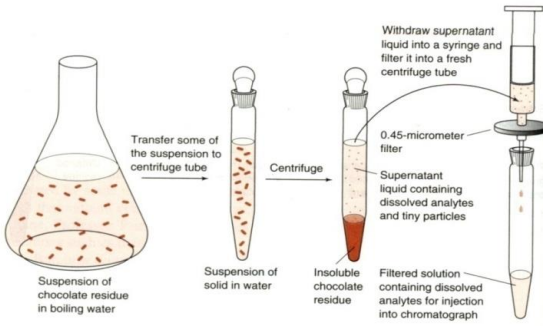
2. Selecting analytical procedures:
a) Choose procedure to measure
As in water
Uncertainty in measurement
Limit of detection
Destroy sample
Availability, time, cost
b) If necessary, develop new procedure
3. Sampling:
a) Select representative material to analyse
Do not use the entire sample
Consistency in sample collection

The analytical process

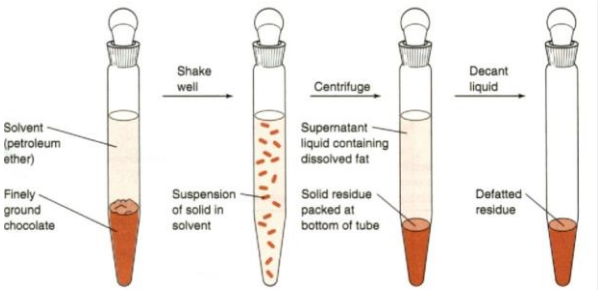
1. Sample preparation:

a) Convert sample into from suitable for chemical analysis

Dissolve sample
Concentrate sample



Remove species that interfere with analysis



Notes:

Sample preparation: Example

How do you prepare samples for Drug Discovery?

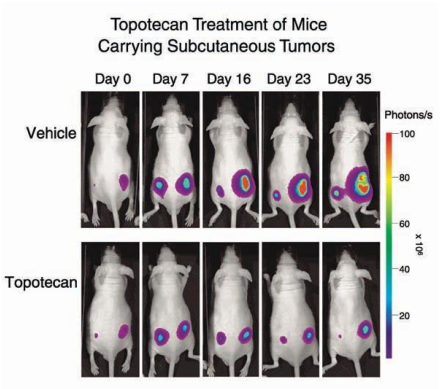
What we want to know:

- Is the drug active? Does it cure the disease/illness?
- How is the drug taken? (Pill, injection)
- How often does the drug need to be taken?
- Does the drug have side-effects?

How these Questions are Typically Addressed:

- Treat animal (rat, mice, etc) with drug
- Monitor drug duration in animal
- Monitor location of drug accumulation
- Monitor animal health

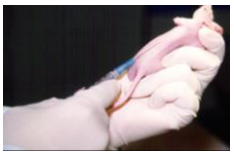
How do you treat the animal with the drug?
How do you monitor the drug concentration in the Animal?
How do you determine the drug location?
How do you determine the animals health?

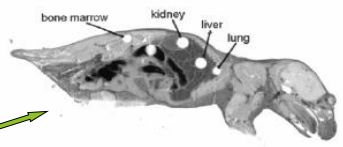


Tumor size is measured by fluorescence through the mouse skin using quantum dots as a function drug dosage

Notes:

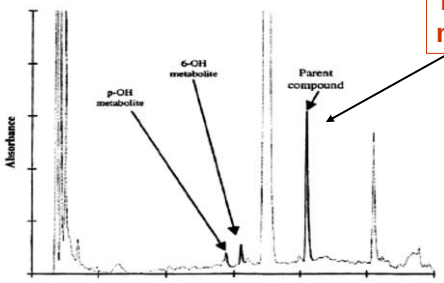
Inject mouse with drug





Cross-section of sacrificed mouse showing tissue removal

Tissue plug from mouse kidney



Chromatography indicates presence of drug an metabolites in tissue sample

	Parent compound (%)	Lipophilic metabolites (%)	Polar metabolites (%)	Total activity in PSL
1. Liver	9	8	80	27,000
2. Kidney	20	23	50	13,000
3. Lung	24	20	47	6,000
4. Blood	26	—	74	1,200

PSL, photo-stimulated luminescence.

Determine drug quantity and distribution

The analytical process

Analysis:

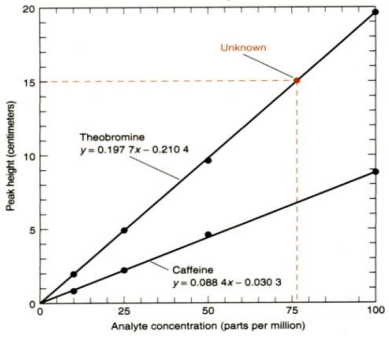
measure concentration of analyte in several identical **aliquots** (portions)

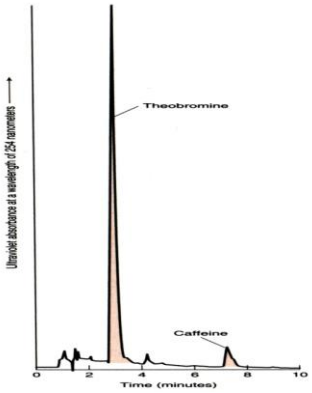
Replicate measurements → uncertainty in the analysis

- **Avoid large errors**
- **Reliability of measurement**

Calibration Curve

- **Measure response for known samples**





Report and Interpretation of Results

Drawing Conclusions

How the Report is used

Notes:

Notes:

Sampling for Molecular Systematics

Research in molecular systematics requires plasmid, cell or tissue samples in which proteins and nucleic acids are maintained in intact physically active state.

Materials are normally collected from field, therefore a proper planning is needed to ensure the good condition of the samples.

Notes:

Regulations governing acquisition of specimens

Collectors should become familiar with local state, national and international laws and regulations, and they should allow adequate lead time to obtain the necessary permits.

Scientific collecting permits/permissions usually are necessary for sampling natural populations and protected species.

Documentation of Samples

- Label samples and specimens so that no information is lost in wrapping, transport, storage, and entering of data into permanent records.
- Field collection data (location, habitat, behaviour, whether, date) is important.
- Prepare voucher specimens (herbarium, museum etc.) for the purpose of cross-reference.

Sources of Sample

Notes:

Fresh materials can be obtained from field.

Animal

blood, tissue (organ, muscle …), hair (follicle), bone, skin, egg etc.

Plant

leaf, flower (petal), inner bark tissue (cambium), twig, pollen, spore (fern) etc.

Notes:

Alternative sources

- ❑ Museum collection (animal samples)
- ❑ Herbaria (plant samples)
- ❑ Tissue/organ collection preserved in paraffin
- ❑ Protein extract from the isozyme analysis
- ❑ Tissue in microscopic slide
- ❑ Fossil/archeological material (degraded DNA)

Preservation of Samples

Notes:

Proper sample preservation in field is crucial for molecular systematic study.

Cryopreservation - use of liquid nitrogen

Alcohol or formalin - mainly for animal tissues where tissues are cut into small pieces and soaked in 95% ethanol

Buffer/salt solution – plant/animal tissues are cut into small pieces and soaked in DMSO (dimethyl sulfoxide; for animal) buffer or CTAB (cetyltrimethylammonium bromide; for plant) buffer

Notes:

Preservation of Samples

Silica gel – plant tissues are cut into small pieces and put into container containing silica gel

Other methods – leaf samples are wrapped with moist tissue paper before putting into plastic bag; add anti-clotting agent (EDTA, heparin) to blood plasma sample.

Tasks to Section 3

1. Give definitions of these terms: representative sample, sample storage, sample pretreatment, sample preparation, laboratory sample, homogenous materials, heterogeneous materials, internal quality control, and external quality assessment.
2. What are coning and quartering processes? Draw the scheme of coining and quartering processes for any powder sample.
3. Describe the rules for storing samples of different types.
4. Describe the factors that affect the samples during storage.
5. What stages of sample preparation do you know? Describe their purpose.
6. What is sample handling? Write the basic rules for sample storage.
7. What do you know about the impact of sample storage and preparation on sample content? Describe the security measures required to minimise the impact.
8. At the stage of pharmaceutical development of a new drug is carried out preclinical studies. To do this, conduct experiments on animals. Proper preservation of samples in this field is crucial for a systematic molecular study of the action of the drug.
9. Why is it essential again and again to ask oneself about the possibility of laboratory errors?
10. What are the types of errors in sample preparation?
11. How should the analyst keep samples to minimise errors?

Section 4: Chemical Equilibrium

Contents:

Introduction

A solution is a homogenous system consisting of two or more components: a solvent, a substance and products of their interaction. Solutions can be liquid, solid and gaseous. Usually, the solvent is a component that is in the same state as the resulting solution. In the case of dissolving sugar in water, the solvent is water, regardless of the amount of the substances. If both components are in the same physical state before dissolution (for example, alcohol and water), the component whose volume is more abundant in value is taken as the solvent.

The solute is(are) the substance(s) present in the smaller amount(s). The solution homogeneity is explained by the fact that the solute interacts with the solvent and decomposes into molecules or ions. These molecules cannot form an independent phase.

The stability of solutions is determined by the size of the particles. Usually, solutions are distinguished as real, colloidal, and coarse. Examples of unstable systems are suspensions (solids dissolved in liquid) and emulsions (liquid substances dissolved in liquid). These systems are inhomogeneous. Due to gravity, the distributed particles eventually settle to the vessel bottom or are exposed to the surface. Colloidal systems are characterized by higher stability.

The solutions have intrinsic properties of both chemical substances and mechanical mixtures. Modern solution theory considers dissolution a set of the following processes: solvation, ionization, diffusion. Some solutions mix in any ratio, such as, e.g. water and alcohol. Solids, most gases and liquids are soluble in water in some proportions. If the substance can no longer dissolve at a given temperature, such a solution is called saturated. A solution, in which the substance can still be dissolved under given conditions, is called unsaturated. These concepts are not related to the concepts of "concentrated" and "diluted" solution. There is a sufficient amount of low-soluble substances ($Ca(OH)_2$), whose saturated solutions have a low concentration of the dissolved substance.

The saturation of the solution is a measure of the solubility of the substance. The value of the solubility term is the ability of a substance to form homogeneous systems when mixed with another substance. Usually, the solubility of solids and liquids is expressed by the mass of the substance, which can be dissolved in 100 g of solvent at a given temperature. The solubility of gases is determined by the volume of gas that can be dissolved in 1 litre of solvent at a specific temperature. In this case, a quantitative indicator is used and is called the solubility coefficient. Solubility depends on the nature of the substance and the solvent. An empirical rule says that the like dissolves in the like. The best of the polar solvents is water.

Reactions in solution are faster than in the solid-state. Some substances form ions, which are species possessing a charge. These behave distinctly in solution. They may attract molecules of solvent, may associate together and may react with other species to form complexes or a precipitate.

Since concentrations of substances vary over a very wide range, they are often represented by the logarithmic pX notation. $pX = - \log(X)$, where X is the concentration or activity of an ion, or equilibrium constant.

The laws of thermodynamics govern the behaviour of all species in solution. Every reaction depends upon the thermodynamic properties of the species involved. Where the solvent association reaction or temperature change those properties, the behaviour will alter.

The use of solvents for analytical work is determined by their properties, as shown in *Table.*

Notes:

Solvent	Boiling point (°C)	Density, (g cm^{-3})	Dielectric constant, ε_r
Water	100	1.00	78.6
Ammonia	–34	0.68	22.0
Ethanol	78	0.79	24.3
n-hexane	69	0.66	1.88
Diethyl ether	34	0.71	4.33

Note: density at 25°C or at BP; dielectric constant = relative permittivity

Solvents with high dielectric constants, for example, water and ammonia, are referred to as **polar** and are **ionizing solvents**, promoting the formation and separation of ions in their solutions, whereas such as diethyl ether, tetrachloromethane and hexane are **nonpolar** and are **nonionizing solvents**.

There are also many solvents whose behavior is intermediate between these extremes.

Notes:

The action of solution changes the properties of both solute and solvent. The solute is made more mobile in solution, and its species may **solvate** by attraction to the solvent.

The solvent structure is also disrupted by the presence of species different in size, shape and polarity from the solvent molecules.

Ideally, the behavior should depend on the concentration C (in molarity, mole fraction or other units), but often this must be modified and the **activity *a*** used:

$$a = f \cdot C$$

Notes:

The coefficient of activity of substances and ions characterises the degree of deviation of the properties of a real solution from the properties of an ideal one, where there is no interaction.
The activity coefficient is a function of the concentration of

a solution, the nature of an electrolyte, the temperature and the ionic strength of a solution.

It can be said that activity is an imaginary concentration.
This value is denoted by the letter a and calculated by the formula: $a = f \cdot C$,
where f is the coefficient of activity, C is the molar concentration of a substance.

Notes:

The **ionic strength** of the solution (μ) is half the product of the concentrations of all ions in the solution (C_i) and the square of their charges (z_i):

$$\mu = \frac{1}{2}\left(C_1 z_1^{\,2} + C_2 z_2^{\,2} + \ldots + C_n z_n^{\,2}\right)$$

It is believed that, if the ionic strength of a solution is constant, the coefficients of activity of ions also remain constant and do not depend on the ion concentrations.

Notes:

Since there are no direct methods for determining the coefficients of activity, their values can be found by calculation. In particular, Debye-Hückel's formula can be used to calculate them:

$$\lg f_1 = -\frac{0.5 z^2 \sqrt{\mu}}{1 + \sqrt{\mu}}$$

If $\mu < 0{,}1$ then $\lg f_i = -0.5 z^2 \sqrt{\mu}$

Notes:

Example: Calculation of Ionic strength of a) 0,01 M $NaNO_3$; b) 0,010 M Na_2SO_4; and c) 0,020 M KBr

Solution:

(a) $\mu = \frac{1}{2}\{[Na^+] \cdot (+1)^2 + [NO_3^-] \cdot (-1)^2\}$
$= \frac{1}{2}\{0.10 \cdot 1 + 0.10 \cdot 1\} = 0.10\ \text{M}$

(b) $\mu = \frac{1}{2}\{[Na^+] \cdot (+1)^2 + [SO_4^{2-}] \cdot (-2)^2\}$
$= \frac{1}{2}\{(0.020 \cdot 1) + (0.010 \cdot 4)\} = 0.030\ \text{M}$

Note that $[Na^+] = 0.020$ M because there are two moles of Na^+ per mole of Na_2SO_4.

(c) $\mu = \frac{1}{2}\{[K^+] \cdot (+1)^2 + [Br^-] \cdot (-1)^2 + [Na^+] \cdot (+1)^2 + [SO_4^{2-}] \cdot (-2)^2\}$
$= \frac{1}{2}\{(0.020 \cdot 1) + (0.020 \cdot 1) + (0.020 \cdot 1) + (0.010 \cdot 4)\} = 0.050\ \text{M}$

Notes:

Example: Find the activity coefficient of Ca^{2+} in a solution of 3,3 mM $CaCl_2$.

Solution: The ionic strength is

$$\mu = \frac{1}{2}\{[Ca^{2+}] \cdot 2^2 + [Cl^-] \cdot (-1)^2\}$$

$$= \frac{1}{2}\{(0.003\,3) \cdot 4 + (0.006\,6) \cdot 1\} = 0.010\ \text{M}$$

In table on the next slide you may see activity coefficient for aqueous solution at 25^0C.
Ca^{2+} is listed under the charge ±2 and has a size of 600 pm.
Thus f=0,675 when ionic strength is equal to 0,010 M.

Notes:

Ion	Ion size (α, pm)	Ionic strength (μ, M) 0.001	0.005	0.01	0.05	0.1
Charge = ±1		*Activity coefficient (γ)*				
H^+	900	0.967	0.933	0.914	0.86	0.83
$(C_6H_5)_2CHCO_2^-$, $(C_3H_7)_4N^+$	800	0.966	0.931	0.912	0.85	0.82
$(O_2N)_3C_6H_2O^-$, $(C_3H_7)_3NH^+$, $CH_3OC_6H_4CO_2^-$	700	0.965	0.930	0.909	0.845	0.81
Li^+, $C_6H_5CO_2^-$, $HOC_6H_4CO_2^-$, $ClC_6H_4CO_2^-$, $C_6H_5CH_2CO_2^-$, $CH_2{=}CHCH_2CO_2^-$, $(CH_3)_2CHCH_2CO_2^-$, $(CH_3CH_2)_4N^+$, $(C_3H_7)_2NH_2^+$	600	0.965	0.929	0.907	0.835	0.80
$Cl_2CHCO_2^-$, $Cl_3CCO_2^-$, $(CH_3CH_2)_3NH^+$, $(C_3H_7)NH_3^+$	500	0.964	0.928	0.904	0.83	0.79
Na^+, $CdCl^+$, ClO_2^-, IO_3^-, HCO_3^-, $H_2PO_4^-$, HSO_3^-, $H_2AsO_4^-$, $Co(NH_3)_4(NO_2)_2^+$, $CH_3CO_2^-$, $ClCH_2CO_2^-$, $(CH_3)_4N^+$, $(CH_3CH_2)_2NH_2^+$, $H_2NCH_2CO_2^-$	450	0.964	0.928	0.902	0.82	0.775
$^+H_3NCH_2CO_2H$, $(CH_3)_3NH^+$, $CH_3CH_2NH_3^+$	400	0.964	0.927	0.901	0.815	0.77
OH^-, F^-, SCN^-, OCN^-, HS^-, ClO_3^-, ClO_4^-, BrO_3^-, IO_4^-, MnO_4^-, HCO_2^-, $H_2citrate^-$, $CH_3NH_3^+$, $(CH_3)_2NH_2^+$	350	0.964	0.926	0.900	0.81	0.76
K^+, Cl^-, Br^-, I^-, CN^-, NO_2^-, NO_3^-	300	0.964	0.925	0.899	0.805	0.755
Rb^+, Cs^+, NH_4^+, Tl^+, Ag^+	250	0.964	0.924	0.898	0.80	0.75
Charge = ±2		*Activity coefficient (γ)*				
Mg^{2+}, Be^{2+}	800	0.872	0.755	0.69	0.52	0.45
$CH_2(CH_2CH_2CO_2^-)_2$, $(CH_2CH_2CH_2CO_2^-)_2$	700	0.872	0.755	0.685	0.50	0.425
Ca^{2+}, Cu^{2+}, Zn^{2+}, Sn^{2+}, Mn^{2+}, Fe^{2+}, Ni^{2+}, Co^{2+}, $C_6H_4(CO_2^-)_2$, $H_2C(CH_2CO_2^-)_2$, $(CH_2CH_2CO_2^-)_2$	600	0.870	0.749	0.675	0.485	0.405
Sr^{2+}, Ba^{2+}, Cd^{2+}, Hg^{2+}, S^{2-}, $S_2O_4^{2-}$, WO_4^{2-}, $H_2C(CO_2^-)_2$, $(CH_2CO_2^-)_2$, $(CHOHCO_2^-)_2$	500	0.868	0.744	0.67	0.465	0.38
Pb^{2+}, CO_3^{2-}, SO_3^{2-}, MoO_4^{2-}, $Co(NH_3)_5Cl^{2+}$, $Fe(CN)_5NO^{2-}$, $C_2O_4^{2-}$, $Hcitrate^{2-}$	450	0.867	0.742	0.665	0.455	0.37
Hg_2^{2+}, SO_4^{2-}, $S_2O_3^{2-}$, $S_2O_6^{2-}$, $S_2O_8^{2-}$, SeO_4^{2-}, CrO_4^{2-}, HPO_4^{2-}	400	0.867	0.740	0.660	0.445	0.355
Charge = ±3		*Activity coefficient (γ)*				
Al^{3+}, Fe^{3+}, Cr^{3+}, Sc^{3+}, Y^{3+}, In^{3+}, lanthanides[a]	900	0.738	0.54	0.445	0.245	0.18
$citrate^{3-}$	500	0.728	0.51	0.405	0.18	0.115
PO_4^{3-}, $Fe(CN)_6^{3-}$, $Cr(NH_3)_6^{3+}$, $Co(NH_3)_6^{3+}$, $Co(NH_3)_5H_2O^{3+}$	400	0.725	0.505	0.395	0.16	0.095
Charge = ±4		*Activity coefficient (γ)*				
Th^{4+}, Zr^{4+}, Ce^{4+}, Sn^{4+}	1 100	0.588	0.35	0.255	0.10	0.065
$Fe(CN)_6^{4-}$	500	0.57	0.31	0.20	0.048	0.021

Notes:

Most reactions will eventually reach equilibrium. That is, the concentrations of reactants and products change no further, since the rates of the forward and reverse reactions are the same.

For the reaction $aA + bB \rightleftharpoons cC + dD$

we write the equilibrium constant:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where the lowercase superscript letters denote stoichiometry coefficients and each capital letter stands for a chemical species.

The symbol [A] stands for the concentration of A relative to its standard state (defined next).
By definition, a reaction is favored whenever K>1.

Notes:

For the ratios [A] (1 M) and [D] (1 bar) to be dimensionless, [A] *must* be expressed in moles per liter (M), and [D] *must* be expressed in bars. 1 bar = 10^5 Pa; 1 atm = 1.01325 bar

If C were a pure liquid or solid, the ratio [C] (concentration of C in its standard state) would be unity (1) because the standard state is the pure liquid or solid.

If C is a solvent, the concentration is so close to that of pure liquid C that the value of [C] is still essentially 1.

Manipulating Equilibrium Constants

Notes:

If two reactions are added, the new K is the product of the two individual K values:

$$HA \rightleftharpoons H^+ + A^- \qquad K_1 = \frac{[H^+][A^-]}{[HA]}$$

$$H^+ + C \rightleftharpoons CH^+ \qquad K_2 = \frac{[CH^+]}{[H^+][C]}$$

$$HA + C \rightleftharpoons A^- + CH^+ \qquad K_3 = \frac{[A^-][CH^+]}{[HA][C]}$$

$$K_3 = K_1K_2 = \frac{[H^+][A^-]}{[HA]} \cdot \frac{[CH^+]}{[H^+][C]} = \frac{[A^-][CH^+]}{[HA][C]}$$

Example: manipulating equilibrium constants

Notes:

Given the reactions and equilibrium constants:

$$H_2O \rightleftharpoons H^+ + OH^- \qquad K_w = 1.0 \times 10^{-14}$$

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \qquad K_{NH_3} = 1.8 \times 10^{-5}$$

Find the equilibrium constant for the reaction:

$$NH_4^+ \rightleftharpoons NH_3(aq) + H^+$$

Solution:

$$H_2O \rightleftharpoons H^+ + OH^- \qquad K_1 = K_w$$

$$NH_4^+ + OH^- \rightleftharpoons NH_3(aq) + H_2O \qquad K_2 = 1/K_{NH_3}$$

$$NH_4^+ \rightleftharpoons NH_3(aq) + H^+ \qquad K_3 = K_w * 1/K_{NH_3} = 5.6 \times 10^{-10}$$

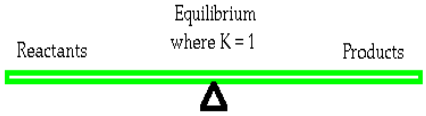
Chemical Equilibrium

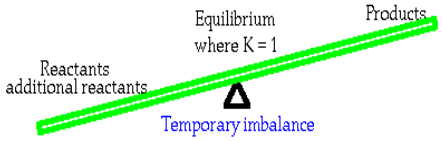
Notes:

Le Chatelier's Principal

What Happens When a System at Equilibrium is Perturbed?

Change concentration, temperature, pressure or add other chemicals

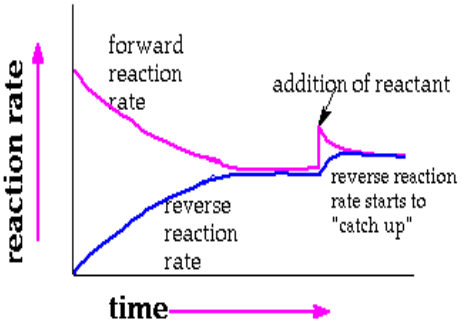




Equilibrium is re-established

Reaction accommodates the change in products, reactants, temperature, pressure, etc.

Rates of forward and reverse reactions re-equilibrate



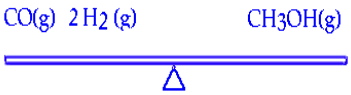
What Happens When a System at Equilibrium is Perturbed?

Notes:

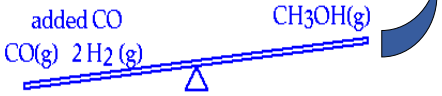
Le Chatelier's Principal: **the direction in which the system proceeds back to equilibrium is such that the change is partially offset.**

Consider this reaction: $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$

At equilibrium:



Add excess CO(g):



To return to equilibrium (balance), some (*not all*) CO and H_2 are converted to CH_3OH

If all added CO was converted to CH_3OH, then reaction would be unbalanced by the amount of product

---

Notes:

Example. Consider this reaction:

$$BrO_3^- + 2Cr^{+3} + 4H_2O \rightleftharpoons Br^- + Cr_2O_7^{-2} + 8H^+$$

$$K = \frac{[Br^-][Cr_2O_7^{2-}][H^+]^8}{[BrO_3^-][Cr^{3+}]^2} = 1 \times 10^{11} \text{ at } 25^oC$$

At one equilibrium state:

$$[H^+] = 5.0\,M \quad [Cr_2O_7^{2-}] = 0.10\,M \quad [Cr^{3+}] = 0.0030\,M$$

$$[Br^-] = 1.0\,M \quad [BrO_3^-] = 0.043\,M$$

Example. What happens when:

Notes:

$[Cr_2O_7^{2-}]$ *increased from* 0.10 M *to* 0.20 M

According to Le Chatelier's Principal, reaction should go back to left to off-set dichromate on right:

$$BrO_3^- + 2Cr^{+3} + 4H_2O \longleftarrow Br^- + Cr_2O_7^{-2} + 8H^+ \uparrow$$

Use reaction quotient (Q), Same form of equilibrium equation, but not at equilibrium:

$$Q = \frac{[Br^-][Cr_2O_7^{2-}][H^+]^8}{[BrO_3^-][Cr^{3+}]^2} = \frac{(1.0)(0.20)(5.0)^8}{(0.043)(0.0030)^2} = 2\times10^{11} > K$$

Notes:

Because Q > K, the reaction must go to the left to decrease numerator and increase denominator.

Continues until Q = K:

1. If the reaction is at equilibrium and products are added (or reactants removed), the reaction goes to the left

$$BrO_3^- + 2Cr^{+3} + 4H_2O \longleftarrow [Br^- + Cr_2O_7^{-2} + 8H^+] \uparrow$$

2. If the reaction is at equilibrium and reactants are added (or products removed), the reaction goes to the right

$$\uparrow [BrO_3^- + 2Cr^{+3} + 4H_2O] \longrightarrow Br^- + Cr_2O_7^{-2} + 8H^+$$

Notes:

The pX notation

The concentration of species in solution may range from very small to large. For example in a saturated aqueous solution of silver chloride, the concentration of silver ions is about 10-5 M, while for concentrated hydrochloric acid the concentration of hydrogen and chloride ions is about 10 M. For convenience, a logarithmic scale is often used:

$$pX = -\log(X)$$

where X is the concentration of the species, or a related quantity.

Thus, for the examples above, pAg = 5 in saturated aqueous silver chloride and pH = -1 in concentrated HCl.
Since equilibrium constants are derived from activities or concentrations as noted below, this notation is also used for them:

$$pK = -\log(K)$$

Notes:

There are many types of equilibria that occur in solution, but for the important analytical conditions of ionic equilibria in aqueous solution, **four examples are very important**.

Acid and base dissociation

Complexation equilibria

Solubility equilibria

Redox equilibria

Notes:

Acid and base dissociation

In aqueous solution, strong electrolytes (e.g., NaCl, HNO_3, NaOH) exist in their ionic forms all the time. However, weak electrolytes exhibit **dissociation equilibria**.
For **acetic acid,** for example:

$$HOOCCH_3 + H_2O \rightarrow H_3O^+ + CH_3COO$$

$$Ka = (a_H \cdot a_A)/(a_{HA} \cdot a_W) = 1.75 \cdot 10^{-5}$$

where HA, W, H and A represent each of the species in the above equilibrium.

In dilute solutions the activity of the water a_W is close to 1.

Notes:

For ammonia:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

$$K_b = (a_{NH4^+} \cdot a_{OH^-})/(a_{NH_3} \cdot a_W) = 1.76 \times 10^{-5}$$

Water behaves in similar way:

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

$$K_W = (a_{H_3O^+} \cdot a_{OH^-}) = 10^{-14}$$

Notes:

$$KA \leftrightarrow K^+ + A^-$$

Denote the concentrations of ions as [K^+] and [A^-], and the concentration of non-dissociated molecules through [KA]. Then we write the **equilibrium constant** as follows:

$$K = \frac{[K^+] \cdot [A^-]}{[KA]}$$

Notes:

The smaller the value of K_d, the weaker the electrolyte and vice versa, the more K_d, the better dissolves the dissolved substance.

The dissociation constant does not depend on the concentration of a solution but depends on the temperature. It has the dimension of concentration in moles per litre.

Weak electrolytes, which consist of more than two ions, dissociate stepwise.

Each degree of dissociation is characterised by a certain magnitude of the dissociation constant. These dissociation constants are stepped and denoted by

K_1, K_2, ... K_n

Notes:

$$H_3PO_4 \leftrightarrow H^+ + H_2PO_4^-, \quad K_1 = \frac{[H^+] \cdot [H_2PO_4^-]}{[H_3PO_4]} = 7.1 \cdot 10^{-3}$$

$$H_2PO_4^- \leftrightarrow H^+ + HPO_4^{2-}, \quad K_2 = \frac{[H^+] \cdot [HPO_4^{2-}]}{[H_2PO_4^-]} = 6.2 \cdot 10^{-8}$$

$$HPO_4^{2-} \leftrightarrow H^+ + PO_4^{3-}, \quad K_3 = \frac{[H^+] \cdot [PO_4^{3-}]}{[HPO_4^{2-}]} = 5 \cdot 10^{-13}$$

$$K_{sum} = K_1 K_2 K_3 = 7.1 \cdot 10^{-3} \cdot 6.2 \cdot 10^{-8} \cdot 5 \cdot 10^{-13} = 2.2 \cdot 10^{-22}$$

Notes:

Buffer is a mixture of a weak acid and its conjugate base. A buffered solution is one that resists changes in pH when acids or bases are added.

$HCOOH + HCOONa$
$CH_3COOH + CH_3COONa$
$NH_4OH + NH_4Cl$
$KH_2PO_4 + K_2HPO_4$
$K_3PO_4 + K_2HPO_4$

Buffer capacity β is a measure of the ability of a buffer to resist changes in pH. The larger the buffer capacity, the greater the resistance to pH change.

The definition of buffer capacity is $\beta = dC_b / d\text{pH} = -dC_a/d\text{pH}$, where C_a and C_b are the number of moles of strong acid or base per litre needed to produce a unit change in pH. Also called buffer intensity.

Notes:

pH Buffer can be calculated by using equation:

Weak acid and its salt

$$pH = pK_{acid} - \lg \frac{C_{acid}}{C_{salt}}$$

Weak base and its salt

$$pOH = pK_{base} - \lg \frac{C_{base}}{C_{salt}}$$

$$pH = 14 - pOH = 14 - pK_{base} + \lg \frac{C_{base}}{C_{salt}}$$

Notes:

1.Please, calculate the pH and α for 0,1 M solution of the HCN ($K_{HCN} = 7{,}2 \cdot 10^{-10}$)

2. α for 0,1M solution of NH_4OH is equal to 1,33%. Please, calculate concentration of the OH^- and dissociation constant K_b

3. Buffer consist of KH_2PO_4 and K_2HPO_4 in molar ratio 16:1. Please, calculate pH of the buffer.

Hydrolysis "Reaction with water"

Notes:

The reaction $B + H_2O \leftrightarrow BH^+ + OH^-$ is often called hydrolysis of a base.

The **degree of hydrolysis** (h) of salt is the ratio of the concentration of the salt subjected to the hydrolysis to its total concentration.

Similar to the degree of dissociation, the degree of hydrolysis can vary from 0 to 1, or from 0 to 100%.

Since hydrolysis is a reverse process, the mass action law can be used for its characterisation and calculation of the equilibrium constant — the **constant of hydrolysis (K_h).**

Notes:

To determine the relationship between K_h and h, for example, for a salt of a strong base and a weak acid, the ionic equation of its hydrolysis is written as follows:

$$CN^- + H_2O \leftrightarrow HCN + OH^-$$

If we denote the initial concentration of the salt in the solution through C (mol/L) and the degree of hydrolysis h, then:

$$[KCN]_0 = [CN^-]_0 = C$$

$$[CN^-]_0 = C \cdot h = [HCN] = [OH^-]$$

$$[CN^-] = C - C \cdot h$$

Notes:

The equation for calculating the hydrolysis constant can be written as follows:

$$K_h = \frac{C \cdot h \cdot C \cdot h \cdot}{C(1-h)} \quad \text{or} \quad K_h = \frac{C \cdot h^2}{1-h}$$

The equation is simplified if h <<1:

$$K_h \approx C \cdot h^2 \quad \text{and} \quad h \approx \sqrt{\frac{K_h}{C}}$$

Using equation, one can obtain:

$$h \approx \sqrt{\frac{K_{H_2O}}{C \cdot K_{d(acid)}}}$$

The calculation of K_h, h and pH of a salt solutions

Notes:

The hydrolysis constant of the salt formed by a strong base and a weak acid (CH_3COONa) is equal to the ratio of the ionic product of water and the dissociation constant of an acid.

$$K_h = \frac{K_{H_2O}}{K_{d(acid)}}$$

$$h = \sqrt{\frac{K_{H_2O}}{K_{d,\,acid} \cdot C_{salt}}} \qquad [H^+] = \sqrt{\frac{K_{H_2O} \cdot K_{d,\,acid}}{C_{salt}}}$$

$$pH = 7 + \frac{1}{2} pK_{d,\,acid} + \frac{1}{2} \lg C_{salt}$$

The calculation of K_h, h and pH of a salt solutions

Notes:

The hydrolysis constant of the salt formed by a weak base and a strong acid (NH_4Cl), is equal to

$$K_h = \frac{K_{H_2O}}{K_{b(base)}}$$

$$h_{ziòp} = \sqrt{\frac{K_{H_2O}}{K_{b,\,base} \quad C_{salt}}}$$

$$[H^+] = \sqrt{\frac{K_{H_2O} \cdot C_{salt}}{K_{b,\,base}}} = \sqrt{K_h \cdot C_{salt}}$$

$$pH = 7 - \frac{1}{2} pK_{b,\,base} - \frac{1}{2} \lg C_{salt}$$

Notes:

One can write for a salt formed by a weak base and a weak acid:

$$K_h = \frac{K_{H_2O}}{K_{d(base)} \cdot K_{d(acid)}}$$

$$h = \sqrt{\frac{K_w}{K_{acid} \cdot K_{base}}} \qquad [H^+] = \sqrt{\frac{K_w \cdot K_{base}}{K_{acid}}}$$

$$pH = 7 + \frac{1}{2} pK_{acid} - \frac{1}{2} pK_{base}$$

Notes:

The solution contains 4.8 gram ammonium acetate in 0.5 L. Please, calculate h and pH for this salt

0,05 M solution of the ammonium hydroxide contains 0,1 M ammonium chloride. Please, calculate [OH^-] in this solution

Name	Formula	K_b	pK_b
Ammonia	NH_3	1.8×10^{-5}	4.75

Name	Formula	K_{a1}	pK_{a1}
Acetic acid	H_3CO_2H	$1.75 \cdot 10^{-5}$	4.756

Notes:

Solubility equilibria

If a compound is practically insoluble in water, this is useful analytically because it provides a means of separating this compound from others that are soluble.

The technique of gravimetric analysis has been developed to give very accurate analyses of materials by weighing pure precipitates of insoluble compounds to give quantitative measurements of their concentration.

Notes:

For the quantitative determination of sulfate ions, SO_4^{2-}, the solution may be treated with a solution of a soluble barium salt such as barium chloride $BaCl_2$, when the following reaction occurs:

$$Ba^{2+} + SO_4^{2-} \rightleftharpoons BaSO_4\,(s)$$

Conversely, if solid barium sulfate is put into water:

$$BaSO_4\,(s) = Ba^{2+} + SO_4^{2-}$$

The solubility product, K_{sp}, is an equilibrium constant for this reaction

$$K_{sp} = a(Ba^{2+}) \,.\, a(SO_4^{2-}) = 1.2 \times 10^{-10}$$

bearing in mind that the pure, solid $BaSO_4$ has $a = 1$.
This means that a solution of barium sulfate in pure water has a concentration of sulfate ions of only $1.1 \cdot 10^{-5}$ M.
The concentration of the barium ions is the same.

Notes:

$$A_nB_m = nA + mB$$

$$K_{sb\ (AnBm)} = [A]^n\,[B]^m$$

[A] = nS and [B] = mS,
where S – molar solubility (mol/L)

$$K_{sb\ (AnBm)} = (nS)^n\,(mS)^m$$

$$S_{AnBm} = \frac{\sqrt[n+m]{K_{sb\ (AnBm)}}}{n^n m^m}$$

Notes:

If we place an insoluble compound such as $Pb(IO_3)_2$ in deionized water, the solid dissolves until the concentrations of Pb^{2+} and IO_3^- satisfy the solubility product for $Pb(IO_3)_2$. At equilibrium the solution is saturated with $Pb(IO_3)_2$, with simply means that no more solid can dissolve. How do we determine the equilibrium concentrations of Pb^{2+} and IO_3^-, and what is the molar solubility of $Pb(IO_3)_2$ in this this saturated solution?

We begin by writing the equilibrium reaction and the solubility product expression for $Pb(IO_3)_2$:

$$Pb(IO_3)_2(s) \rightleftharpoons Pb^{2+}(aq) + 2IO_3^-(aq)$$

As $Pb(IO_3)_2$ dissolves, two IO_3^- ions are produced for each ion of Pb^{2+}. If we assume that the change in the molar concentration of Pb^{2+} at equilibrium is **x**, then the change in the molar concentration of IO_3^- is **2x**.

The following table helps us keep track of the initial concentrations, the change in concentrations, and the equilibrium concentrations of Pb^{2+} and IO_3^-.

Notes:

Concentrations	$Pb(IO_3)_2(s)$	$\rightleftharpoons$	$Pb^{2+}(aq)$	+	$2IO_3^-(aq)$
Initial	solid		0		0
Change	solid		$+x$		$+2x$
Equilibrium	solid		x		$2x$

Substituting the equilibrium concentrations into equation and solving gives:

$$(x)(2x)^2 = 4x^3 = 2.5\times10^{-13}$$

$$x = 3.97\times10^{-5}$$

Concentrations	$Pb(IO_3)_2(s)$	$\rightleftharpoons$	$Pb^{2+}(aq)$	+	$2IO_3^-(aq)$
Initial	solid		0		0
Change	solid		$+x$		$+2x$
Equilibrium	solid		x		$2x$

Notes:

Substituting the equilibrium concentrations into equation and solving gives:

$$(x)(2x)^2 = 4x^3 = 2.5\times10^{-13}$$

$$x = 3.97\times10^{-5}$$

Substituting this value of x back into the equilibrium concentration expressions for Pb^{2+} and IO_3^- gives their concentrations as:

$$[Pb^{2+}] = x = 4.0\times10^{-5}\ M$$

$$[IO_3^-] = 2x = 7.9\times10^{-5}\ M$$

Because one mole of $Pb(IO_3)_2$ contains one mole of Pb^{2+}, the molar solubility of $Pb(IO_3)_2$ is equal to the concentration of Pb^{2+}, or 4.0×10^{-5} M.

Notes:

More complex problem

Calculating the solubility of $Pb(IO_3)_2$ in deionized water is a straightforward problem since the solid's dissolution is the only source of Pb^{2+} and IO_3^-. But what if we add $Pb(IO_3)_2$ to a solution of 0.10 M $Pb(IO_3)_2$, which provides a second source of Pb^{2+}? Before we set-up and solve this problem algebraically, think about the systems chemistry and decide whether the solubility of $Pb(IO_3)_2$ will increase, decrease or remain the same.

We begin by setting up a table to help us keep track of the concentrations of Pb^{2+} and IO_3^- as this system moves toward and reaches equilibrium.

Concentrations	$Pb(IO_3)_2(s)$	$\rightleftharpoons$	$Pb^{2+}(aq)$	+	$2IO_3^-(aq)$
Initial	solid		0.10		0
Change	solid		$+x$		$+2x$
Equilibrium	solid		$0.10+x$		$2x$

Notes:

Substituting the equilibrium concentrations into

$$(0.10+x)(2x)^2 = 2.5\times10^{-13}$$

and multiplying out the terms on the equation's left side leaves us with

$$4x^3 + 0.40x^2 = 2.5\times10^{-13}$$

This is a more difficult equation to solve than that for the solubility of $Pb(IO_3)_2$ in deionized water, and its solution is not immediately obvious.

Notes:

How might we solve equation if we do not have access to a computer?

One approach is to use our understanding of chemistry to simplify the problem. From Le Chatelier's principle we know that a large initial concentration of Pb^{2+} significantly decreases the solubility of $Pb(IO_3)_2$. One reasonable assumption is that the equilibrium concentration of Pb^{2+} is very close to its initial concentration. If this assumption is correct, then the following approximation is reasonable

$$[Pb^{2+}] = 0.10 + x \approx 0.10 \text{ M}$$

Substituting our approximation into equation and solving for x gives

$$(0.1)(2x)^2 = 2.5 \times 10^{-13}$$
$$0.4x^2 = 2.5 \times 10^{-13}$$
$$x = 7.91 \times 10^{-7}$$

Notes:

Before accepting this answer, we must verify that our approximation is reasonable. The difference between the calculated concentration of Pb^{2+}, 0.10+x M, and our assumption that it is 0.10 M is 7.9×10^{-7} M or 7.9×10^{-4}% of the assumed concentration. This is a negligible error.

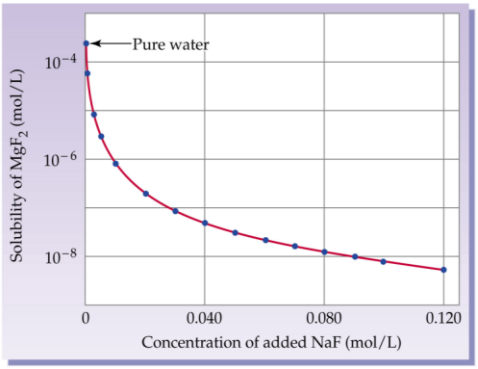
Accepting the result of our calculation, we find that the equilibrium concentrations of Pb^{2+} and IO_3^- are:

$$[Pb^{2+}] = 0.10 + x \approx 0.10 \text{ M}$$
$$[IO_3^-] = 2x = 1.6 \times 10^{-6} \text{ M}$$

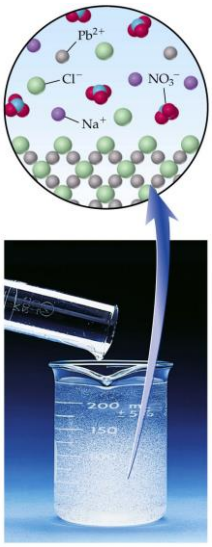
The molar solubility of $Pb(IO_3)_2$ is equal to the additional concentration of Pb^{2+} in solution, or 7.9×10^{-4}mol/L. As expected, $Pb(IO_3)_2$ is less soluble in the presence of a solution that already contains one of its ions. This is known as the **common ion effect.**

Notes:

Common ion effect – a salt will be less soluble if one of its constituent ions is already present in the solution.



Decrease in the solubility of MgF_2 by the addition of NaF



$PbCl_2$ precipitate because the ion product is greater than K_{sp}

Notes:

The solutions of 30 mL 0,003 mol/L K_2CrO_4 and 20ml 0,0002 mol/L $AgNO_3$ was mixed. How do you think a precipitate form?
K_{sb} (Ag_2CrO_4) = $8{,}8 \cdot 10^{-12}$

The concentration of ions from both of reagents will change after mixed. According to: $C_1/C_2 = V_2/V_1$ and
$C_1 = C_2 \cdot V_2/V_1$, so:

$C_1 = [K_2CrO_4] = 0.003 \cdot 30/\ 50 = 0.0018 = 1.8 \cdot 10^{-3}$ mol/L
$C_2 = [AgNO_3] = 0.0002 \cdot 20/\ 50 = 0.00008 = 8 \cdot 10^{-5}$ mol/L

$$K_2CrO_4 \leftrightarrow 2K^+ + CrO_4^{2-}$$
$$AgNO_3 \leftrightarrow Ag^+ + NO_3^-$$

$[Ag^+] = 8 \cdot 10^{-5}$ mol/L
$[CrO_4^{2-}] = 1.8 \cdot 10^{-3}$ mol/L

Notes:

$$Ag_2CrO_4 \rightleftharpoons 2\,Ag^+ + CrO_4^{2-}$$

$$K_{sb}\ (Ag_2CrO_4) = [Ag^+]^2\,[CrO_4^{2-}]$$

$$8{,}8 \cdot 10^{-12} = [Ag^+]^2\,[CrO_4^{2-}]$$

The conduct of the real concentrations of the ions is more then constant solubility for salt ($1.15 \cdot 10^{-11}$ is more then K_{sb}= $8.8 \cdot 10^{-12}$

$$K_{sb}\ (Ag_2CrO_4) < [Ag^+]^2 \cdot [CrO_4^{2-}]$$

The precipitate of silver chromate will be form

Notes:

Complexation equilibria

The reaction between an acceptor metal ion M and a **ligand** L to form a complex ML is characterized by an equilibrium constant.

$$M(aq) + L(aq) \rightleftharpoons ML(aq)$$

$$K_f = (a_{ML}) / (a_M \,.\, a_L)$$

For example, for the copper-EDTA complex at 25°C:

$$K_{st} = 6.3 \cdot 10^{18}$$

Notes:

The complexation reaction between Cd^{2+} and NH_3, for example, has the following equilibrium constant (K_f or K_{st}).

$$K_f = \frac{[Cd(NH_3)_4^{2+}]}{[Cd^{2+}][NH_3]^4} = 5.5 \times 10^7$$

$$Cd^{2+}(aq) + NH_3(aq) \rightleftharpoons Cd(NH_3)^{2+}(aq)$$

$$Cd(NH_3)^{2+}(aq) + NH_3(aq) \rightleftharpoons Cd(NH_3)_2^{2+}(aq)$$

$$Cd(NH_3)_2^{2+}(aq) + NH_3(aq) \rightleftharpoons Cd(NH_3)_3^{2+}(aq)$$

$$Cd(NH_3)_3^{2+}(aq) + NH_3(aq) \rightleftharpoons Cd(NH_3)_4^{2+}(aq)$$

Notes:

To avoid ambiguity, we divide formation constants into two categories. **Stepwise formation constants**, which we designate as K_i for the *i*th step, describe the successive addition of one ligand to the metal-ligand complex from the previous step. Thus, the equilibrium constants for reactions above are, respectively, K_1, K_2, K_3 and K_4.

Overall, or **cumulative formation constants**, which we designate as β_i, describe the addition of *i* ligands to the free metal ion. The equilibrium constant in equation is correctly identified as β_4, where

$$\beta_4 = K_1 \cdot K_2 \cdot K_3 \cdot K_4$$

In general

$$\beta_i = K_1 \cdot K_2 \cdot K_3 \cdot \ldots \cdot K_i$$

Redox equilibria

Notes:

When a species gains electrons during a reaction, it undergoes **reduction** and, conversely, when a species loses electrons it undergoes **oxidation**. In the total reaction, these processes occur simultaneously, for example:

$$Ce^{4+} + Fe^{2+} = Ce^{3+} + Fe^{3+}$$

The cerium is reduced from oxidation state 4 to 3, while the iron is oxidized from 2 to 3. Any general 'redox process' may be written:

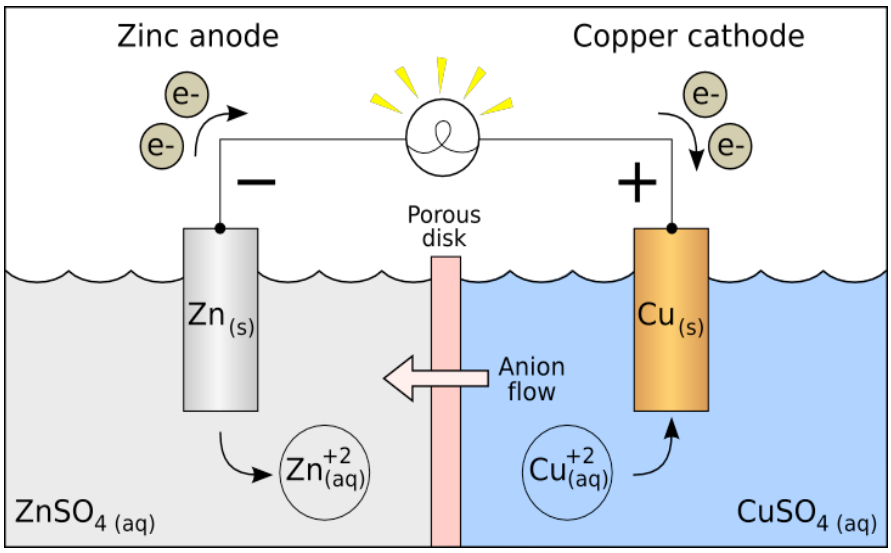
$$Ox1 + Red2 = Red1 + Ox2$$

The equilibrium constant of redox reactions is generally expressed in terms of the appropriate electrode potentials, but for the above reaction:

$$K = (a(Ce^{3+}) \,.\, a(Fe^{3+})) / (a(Ce^{4+}) \,.\, a(Fe^{2+})) = 2.2 \times 10^{12}$$

Danielle Cell: Copper Deposition / Zinc Dissolution

Notes:



Notes:

$$\Delta G^\circ = -nFE^\circ$$

ΔG – Gibb's free energy.
Negative values are more thermodynamically favorable

n – Represented in the book as v, is the coefficient in front of the electrons for the balanced **RedOx** reaction.

F – Faraday's constant, 96,480 J/mol·V or C/mol

E° – Standard potential of the reaction.

Notes:

$$aA + bB \longrightarrow cC + dD$$

$$Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$E_{cell} = E^\circ_{cell} - \frac{RT}{nF} \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

Notes:

$$E_{cell} = E^{\circ}_{cell} - \frac{RT}{nF} \ln \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

$$\underset{0.1\ M}{Zn_{(s)} + Sn^{+2}_{(aq)}} + 2e^- \longrightarrow \underset{0.5\ M}{Zn^{+2}_{(aq)}} + Sn_{(s)} + 2e^- \qquad E^{\circ}_{cell} = +0.62\ V$$

$$Q = \frac{0.5\ M}{0.1\ M}$$

$$E_{cell} = (0.62\ V) - \frac{(8.314\ J/mol \bullet K)(298\ K)}{2(96{,}480\ J/mol \bullet V)} \ln \frac{0.5\ M}{0.1\ M}$$

$$E_{cell} = 0.60\ V$$

Standard potentials

Notes:

A redox reactions **standard potential**, E^o, provides an alternative way of expressing its equilibrium constant and, therefore, its equilibrium position.

Because a reaction at equilibrium has a ΔG of zero, the potential, *E*, also must be zero at equilibrium. Substituting these values into equation and rearranging provides a relationship between E^o and *K*.

$$E^{\circ} = \frac{0.05916}{n} \log K$$

Notes:

We generally do not tabulate standard potentials for redox reactions. Instead, we calculate E^o using the standard potentials for the corresponding oxidation half-reaction and reduction half-reaction. By convention, standard potentials are provided for reduction half-reactions.

The standard potential for a redox reaction, E^o, *is*

$$\boldsymbol{E^o = E^o_{red} - E^o_{ox}}$$

where E^o_{red} *and* E^o_{ox} are the standard reduction potentials for the reduction half-reaction and the oxidation half-reaction.

Notes:

Because we cannot measure the potential tor a single half-reaction, we arbitrarily assign a standard reduction potential of zero to a reference halt- reaction and report all other reduction potentials relative to this reference. The reference halt-reaction is

$$2H_3O^+(aq) + 2e^- \rightleftharpoons 2H_2O(l) + H_2(g)$$

Reference books contain a lists of selected standard reduction potentials. The more positive the standard reduction potential, the more favorable the reduction reaction under standard state conditions.

Thus, under standard state conditions the reduction of Cu^{2+} to Cu (E^o = +0.3419 V) is more favorable than the reduction of Zn^{2+} to Zn (E^o = –0.7618 V).

Notes:

Standard Reduction Potentials at 25°C (298 K) for Many Common Half-reactions

Half-reaction	$\mathscr{E}°$ (V)	Half-reaction	$\mathscr{E}°$ (V)
$F_2 + 2e^- \rightarrow 2F^-$	2.87	$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$	0.40
$Ag^{2+} + e^- \rightarrow Ag^+$	1.99	$Cu^{2+} + 2e^- \rightarrow Cu$	0.34
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.82	$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.27
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.78	$AgCl + e^- \rightarrow Ag + Cl^-$	0.22
$Ce^{4+} + e^- \rightarrow Ce^{3+}$	1.70	$SO_4^{2-} + 4H^+ + 2e^- \rightarrow H_2SO_3 + H_2O$	0.20
$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.69	$Cu^{2+} + e^- \rightarrow Cu^+$	0.16
$MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2 + 2H_2O$	1.68	$2H^+ + 2e^- \rightarrow H_2$	0.00
$IO_4^- + 2H^+ + 2e^- \rightarrow IO_3^- + H_2O$	1.60	$Fe^{3+} + 3e^- \rightarrow Fe$	−0.036
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.51	$Pb^{2+} + 2e^- \rightarrow Pb$	−0.13
$Au^{3+} + 3e^- \rightarrow Au$	1.50	$Sn^{2+} + 2e^- \rightarrow Sn$	−0.14
$PbO_2 + 4H^+ + 2e^- \rightarrow Pb^{2+} + 2H_2O$	1.46	$Ni^{2+} + 2e^- \rightarrow Ni$	−0.23
$Cl_2 + 2e^- \rightarrow 2Cl^-$	1.36	$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.35
$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.33	$Cd^{2+} + 2e^- \rightarrow Cd$	−0.40
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.23	$Fe^{2+} + 2e^- \rightarrow Fe$	−0.44
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.21	$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.50
$IO_3^- + 6H^+ + 5e^- \rightarrow \frac{1}{2}I_2 + 3H_2O$	1.20	$Cr^{3+} + 3e^- \rightarrow Cr$	−0.73
$Br_2 + 2e^- \rightarrow 2Br^-$	1.09	$Zn^{2+} + 2e^- \rightarrow Zn$	−0.76
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	1.00	$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.83
$AuCl_4^- + 3e^- \rightarrow Au + 4Cl^-$	0.99	$Mn^{2+} + 2e^- \rightarrow Mn$	−1.18
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.96	$Al^{3+} + 3e^- \rightarrow Al$	−1.66
$ClO_2 + e^- \rightarrow ClO_2^-$	0.954	$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.91	$Mg^{2+} + 2e^- \rightarrow Mg$	−2.37
$Ag^+ + e^- \rightarrow Ag$	0.80	$La^{3+} + 3e^- \rightarrow La$	−2.37
$Hg_2^{2+} + 2e^- \rightarrow 2Hg$	0.80	$Na^+ + e^- \rightarrow Na$	−2.71
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77	$Ca^{2+} + 2e^- \rightarrow Ca$	−2.76
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.68	$Ba^{2+} + 2e^- \rightarrow Ba$	−2.90
$MnO_4^- + e^- \rightarrow MnO_4^{2-}$	0.56	$K^+ + e^- \rightarrow K$	−2.92
$I_2 + 2e^- \rightarrow 2I^-$	0.54	$Li^+ + e^- \rightarrow Li$	−3.05
$Cu^+ + e^- \rightarrow Cu$	0.52		

Notes:

Example 1: Calculate (a) the standard potential, (b) the equilibrium constant, and (c) the potential when $[Ag^+]$=0.020 M and $[Cd^{2+}]$=0.050 M, for the following reaction at 25°C.

$$Cd_{(s)} + 2Ag^+_{(aq)} \leftrightarrow 2Ag_{(s)} + Cd^{2+}_{(aq)}$$

In this reaction Cd is undergoing oxidation and Ag^+ is undergoing reduction. The standard cell potential, therefore, is

$$E° = E°_{Ag^+/Ag} - E°_{Cd^{2+}/Cd} = 0.7996 - (-0.4030) = 1.2026\ \text{V}$$

$$E° = 1.2026\ \text{V} = \frac{0.05916\ \text{V}}{2}\log K \qquad \log K = 40.6558$$

Solving for K gives the equilibrium constant as

$$K = 4.527 \times 10^{40}$$

To calculate the potential when $[Ag^+]$ is 0.020 M and $[Cd^{2+}]$ is 0.050 M, we use the appropriate relationship for the reaction quotient, Q, in

$$E = E° - \frac{0.05916\ \text{V}}{n}\log\frac{[Cd^{2+}]}{[Ag^+]^2} \qquad E = 1.2606\ \text{V} - \frac{0.05916\ \text{V}}{2}\log\frac{(0.050)}{(0.020)^2}$$

$$E = 1.14\text{V}$$

Summary

Notes:

For ionic equilibria in solution, which are widely used in analytical chemistry, a large equilibrium constant for the reaction indicates that it will proceed practically to completion. If the equilibrium constant is of the order of 10^{10}, then the ratio of products to reactants will be much greater than 1000 to 1. For example:

$$H^+ + OH^- = H_2O \qquad K = 10^{14}$$

$$C(aq) + A(aq) = CA(solid) \qquad K = 10^{10}$$

$$M(aq) + L(aq) = ML(complex) \qquad K = 10^{10}$$

$$Ox1 + Red2 = Red1 + Ox2 \qquad K = 10^{12}$$

Therefore, these reactions may be used for quantitative measurements, for example by volumetric or gravimetric techniques.

Notes

It should be noted that, in calculations involving solution equilibria, certain rules should always be considered.

- Electroneutrality. The concentrations of positive and negative charges must be equal. Sometimes, ions that do not react are omitted from the equations, although they must be present in the solution.

- Stoichiometry. The total amounts of all species containing an element must be constant, since no element can be created or destroyed.

- Equilibria. All possible equilibria, including those involving the solvent, must be taken into account.

Tasks to Section 4

1. Give definitions of these terms: solvent, activity, ionic strength, coefficients of activity of ions, equilibrium constant, pX, pH, buffer, hydrolysis, solubility, K_{sp}, common ion effect, central atom, ligand, stepwise and cumulative formation constant, redox reaction, standard potential

2. What is the ionic strength of 1 mM $CaCl_2$? Find the activity coefficient of Cl^- in $CaCl_2$?

5. Calculate the pH and α for 0,1 M solution of the HCN (K_{HCN} =7,2 10^{-10})

6. α for 0,1M solution of NH_4OH is equal to 1,33%. Calculate the concentration of the OH^- and dissociation constant K_b.

7. 0,1 normal solution of the NH_4OH contains 0,2 M NH_4Cl. Calculate [OH^-] and pH.

8. The buffer consists of KH_2PO_4 and K_2HPO_4 with molar ratio 16. Calculate the pH of the buffer.

9. The solution contains 10,5 gram NH_4CH_3COO in 0.25 L. Calculate h and pH of the salt.

10. Calculate the molar solubility for Hg_2Cl_2 in 0.10 M NaCl. Compare your answer to its molar solubility in deionized water.

11. The solutions of the 30 mL 0,003 mol/L K_2CrO_4 and 20 mL 0,0002 mol/L $AgNO_3$ was mixed. How do you think will a precipitate form? Ksb(Ag_2CrO_4)=8,8·10^{-12}

12. For the following reaction at 25 °C:

$$5Fe^{2+}_{(aq)} + MnO_4^-{}_{(aq)} + 8H^+_{(aq)} \leftrightarrow 5Fe^{3+}_{(aq)} + Mn^{2+}_{(aq)} + 4H_2O_{(l)}$$

Calculate (a) the standard potential, (b) the equilibrium constant, and (c) the potential under these conditions: [Fe^{2+}]=0.50M, [Fe^{3+}]=0.10M, [MnO_4^-]=0.025M, [Mn^{2+}]=0.015 M, and a pH of 7.00. See table before for standard state reduction potentials.

Section 5: Concentration. Preparing Solutions

Contents:

Introduction

The solubility depends on the nature of a substance and a solvent. The empirical rule says that similar dissolves in similar.

It can be explained from the standpoint of the nature of the chemical bonds. As a rule, ionic compounds (salts, alkalis) or substances, whose molecules are polar, are well soluble in polar solvents.

The best of polar solvents is water. Substances with a nonpolar molecular structure are well soluble in nonpolar or low-polar solvents, poorly in water.

The solubility of most solids increases with temperature. The mutual solubility of the liquids increases with increasing temperature until a temperature reaches, at which all liquids begin to mix in any proportions. The solubility of gases decreases with increasing temperature. The solubility of gases increases with increasing pressure and vice versa.

The composition of the solutions is determined by the content of the dissolved substance, which is characterised by its concentration or fraction.

The amount of dissolved substance contained in a certain amount of solution or solvent is called the concentration of the solution. Solutions with high concentrations of dissolved substances are called concentrated (conc), with small – diluted (dil). The boundaries between them are somewhat conditional. Quantitative characteristics are used for a complete characterisation of the composition of solutions. The unit of volume of solution or solvent is a cubic meter (m^3) or cubic decimetre (dm^3), which is equal to 1 litre (L).

All methods for expressing the contents of the dissolved substance are interconnected. The composition of solutions can be presented in any form with the use of mathematical calculations.

The molar concentration (C) is a physical quantity determined by the ratio of the number of moles of the dissolved substance to the volume of solution. This term extends to any kind of conditional particles (atoms, ions, molecules, parts of molecules, etc.). The molar concentration is expressed in moles per cubic decimetre or moles of the dissolved substance in a litre of solution. For example, C(HCl) = 0.1 mol/L. For some values of the molar concentration of solutions, the special terms and designations are used: 1.0000 mol/L (1 M) — molar, 0.1000 mol/L (0.1 M) – decimolar, 0.0100 mol/L (0.01 M) – centimolar.

The equivalent concentration or normality (C_f) is the number of equivalents of a substance contained in one litre of solution.

To calculate the equivalent concentration, one must mention the notion of chemical equivalents and their calculation methods. The index *f* is the equivalence factor. The molar mass of a substance must be multiplied by the equivalence factor to get the equivalent of a substance.

The **equivalence factor *f*** is for:

- **acids** – a unit divided by the number of hydrogen atoms involved in chemical reactions;
- **bases** – a unit divided by the number of hydroxyl groups involved in chemical reactions;
- **salts** – a unit divided by the product of the number of metal ions (cations) and the value of metal ion charge.

For **oxidation-reduction reactions**, the equivalence factor *f* of substances is defined as a unit divided by the number of electrons involved in the oxidation or reduction of particles.

The equinormal substances (the same in normality) interact with no residue. It is an illustration of the law of equivalents: the substances interact with each other in quantities proportional to their equivalents. The mathematical expression of the law makes it possible to calculate easily both the amount of substance entering into the interaction and the amounts required for the preparation of solutions: $\mathbf{C_{f1} \cdot V_1 = C_{f2} \cdot V_2}$.

The values of molar and normal concentrations are calculated to within four decimal places; these methods of expression of concentration are considered accurate and used for chemical analysis. The weight of substances for the preparation of solutions with a concentration expressed in moles per litre is necessarily weighed on the exact analytical scales.

Concentration

A measure of the amount of solute dissolved in the solution

Molarity (C or M)

Normality (C_f or N)

Molality (Cm or m)

Mole Fraction (x)

Percent by Mass (ω or %)

Ways of expressing the composition of solutions are shown in the Table.

	Value	Symbol	Equation	unit of measure: main	unit of measure: complementary
Fraction	Mass or percentage concentration	ω (omega)	$\omega = \frac{m_{sub}}{m}$ $\omega = \frac{m_{sub}}{m} \cdot 100$	Dimensionless, %	
Fraction	mol	χ (ksi)	$\chi = \frac{\nu_{sub}}{\nu_{sub} + \nu}$	dimensionless	
Fraction	bulk	φ (fi)	$\varphi = \frac{V_{sub}}{V}$	dimensionless	
Concentration	molar	c (si)	$C = \frac{\nu_{sub}}{V}$	mol/L	mol/dm³
Concentration	normal (normality, molar concentration of equivalents)	c_f (si–ef)	$C_f = \frac{1}{f} \cdot \frac{\nu_{sub}}{V}$	mol equivalent/L – equiv/L	mol equivalent/dm³ – equiv/dm³
Concentration	mas	ρ (ro)	$\rho = \frac{m_{sub}}{V}$	kg/L	kg/dm³
Concentration	molal	C_m (si–em)	$C_m = \frac{\nu_{sub}}{m_{solvent}}$	mol/kg	

Notes:

$$C = molarity = \frac{\text{moles of solute}}{\text{liters of solution}}$$

Notes:

This term extends to any kind of conditional particles (atoms, ions, molecules, parts of molecules, etc.)

The molar concentration is expressed in moles per cubic decimetre or **moles of the dissolved substance in a litre of solution,** for example, C(HCl) = 0.1 mol/L.

For some values of the molar concentration of solutions, the special terms and designations are used:

1.0000 mol/L (1 M) — molar,
0.1000 mol/L (0.1 M) — decimolar,
0.0100 mol/L (0.01 M) — centimolar.

Notes:

$$C = \textit{molarity} = \frac{\text{moles of solute}}{\text{liters of solution}}$$

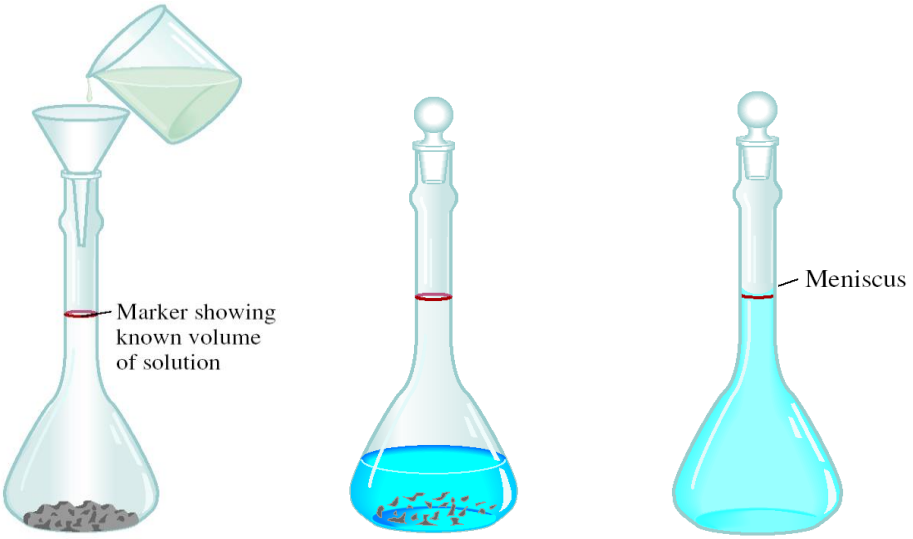
$$C = \frac{\nu_{sub}}{V}$$

? What mass of KI is required to make 500. mL of a 2.80 *M* KI solution?

volume of KI solution $\xrightarrow{C_{KI}}$ moles KI $\xrightarrow{\mathcal{M}_{KI}}$ grams KI

Notes:

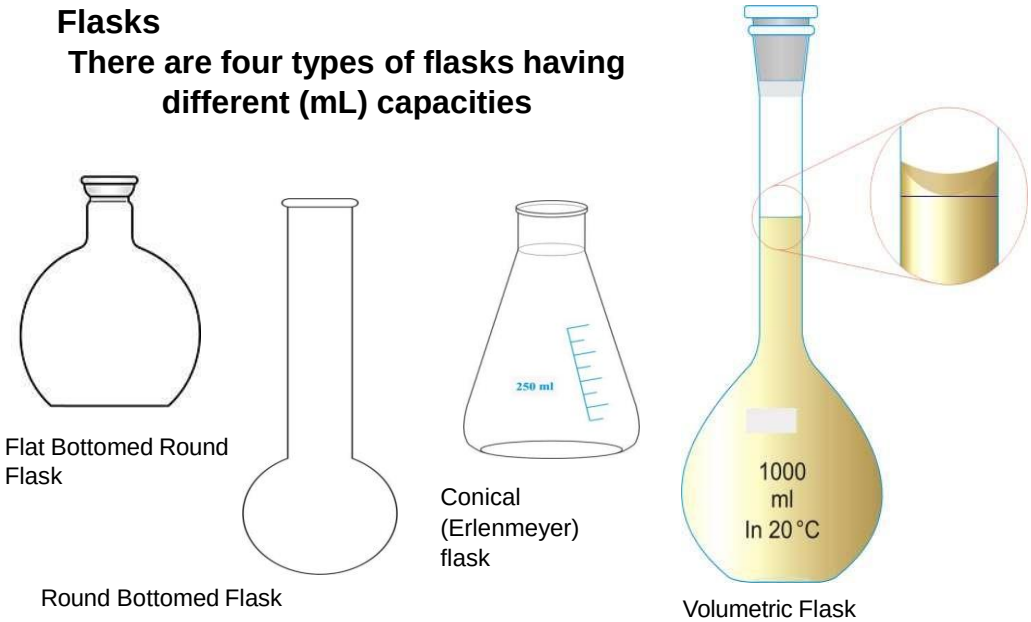
Preparing a solution of known concentration



Notes:

Flasks

There are four types of flasks having different (mL) capacities



Flat Bottomed Round Flask

Round Bottomed Flask

Conical (Erlenmeyer) flask

Volumetric Flask

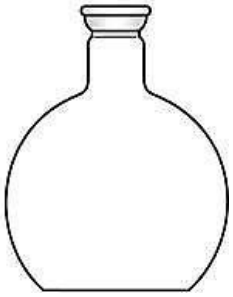
Notes:

Flat bottomed round flasks:

Flat-bottomed round flasks are convenient containers to heat liquids.

A gauze mat should be interposed between the flask and flame.

These flasks are widely used in the preparation of bacteriological culture media.



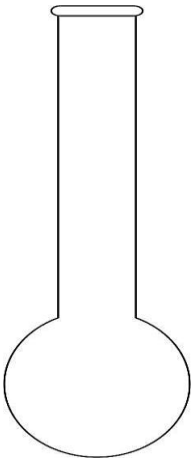
Notes:

Round bottomed flasks:

Round bottomed flasks can with stand higher temperatures than the flat-bottomed type

They may be heated in a necked flame, or in an electro-thermal mantle.

They can be used for boiling of different kinds of solutions and to make titration.



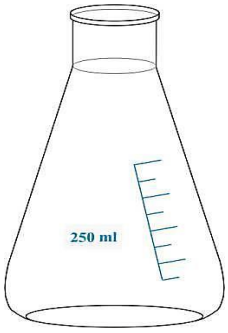
Notes:

Conical (Erlenmeyer) flasks:

Conical (Erlenmeyer) flasks are useful for titrations.

For boiling solutions when it is necessary to keep evaporation to a minimum.

Some have a side arm suitable for attachment to a vacuum pump.



Notes:

Volumetric flasks:

Volumetric flasks are flat - bottomed, pear-shaped vessels with long narrow necks, and are fitted with ground stoppers.

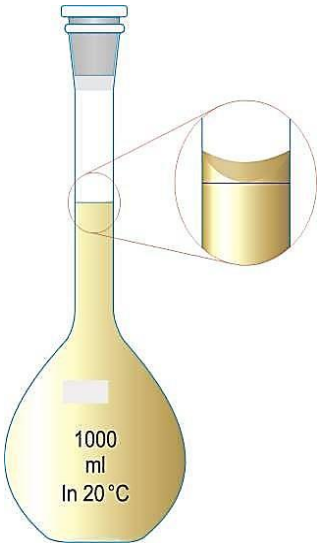
Most flasks are graduated to contain a certain volume, and these are marked with the letter “C”.

Those designed to deliver a given volume are marked with the letter “D”.

A horizontal line etched round the neck denotes the stated volume of water at given temperature, for example at 20°C.

They are used to prepare various kinds of solutions.

The neck is narrow so that slight errors in reading the meniscus results in relatively small volumetric differences (minimizes volumetric differences or errors)



Notes:

How do we present concentrations of solutions?

There are a number of different ways of expressing solute concentration that are commonly used. Some of these are listed below.

Molarity (C, M) = moles solute /litre of solution, mol/L or mmoles/mL

Normality (C_f, N) = moles equivalents of solute /litre of solution, mol·eqv/L or meq/mL

Formality (F)= is identical to molarity

Molality (C_m, m) = moles of solute /1000g solvent or moles of solute / mass solvent

Weight % (W_t, %, ω) = (mass of solute/ mass of solution)·100%

Mass per volume (mg/L) = mass of solute/ litre of solution

Parts per million (ppm) = (mass of solute/ mass of solution)·10^6

Mole fraction (χ) = moles of solute/ total moles

Notes:

The **equivalent concentration or normality** C_f is the number of equivalents of a substance contained in 1 litre of solution.

$$C_f = \textit{normality} = \frac{\text{moles of equivalents of solute}}{\text{liters of solution}}$$

$$C_f = \frac{1}{f} \cdot \frac{V_{sub}}{V}$$

Notes:

To calculate the equivalent concentration, one must mention the notion of chemical equivalents and their calculation methods.

The index **f** is the **equivalence factor**.

The molar mass of a substance must be multiplied by the equivalence factor to get the equivalent of a substance.

Notes:

The **equivalence factors** are:

for acids — a unit divided by the number of hydrogen atoms involved in chemical reactions;

for bases — a unit divided by the number of hydroxyl groups involved in chemical reactions;

for salts — a unit divided by the product of the number of metal ions (cations) and the value of metal ion charge.

Notes:

For oxidation-reduction reactions, the equivalence factor of substances is defined as a unit divided by the number of electrons involved in the oxidation or reduction of particles.

$$KMnO_4 + HCl_{(conc)} \rightarrow MnCl_2 + Cl_2 + KCl + H_2O$$

$$Mn^{+7} + 5\bar{e} \rightarrow Mn^{+2} \qquad f=1/5$$

$$2KMnO_4 + 3MnSO_4 + 2H_2O \rightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4$$

$$Mn^{+7} + 3\bar{e} \rightarrow Mn^{+4} \qquad f=1/3$$

Notes:

The features of the equinormal substances (the same in normality) is that they interact with no residue. This is an illustration of the law of equivalents: the substances interact with each other in quantities proportional to their equivalents.

The mathematical expression of the law makes it possible to calculate easily both the amount of substance entering into the interaction and the amounts required for the preparation of solutions:

$$C_{f_1} \cdot V_1 = C_{f_2} \cdot V_2.$$

Notes:

Dilution is the procedure for preparing a less concentrated solution from a more concentrated solution.

Moles of solute before dilution (i) = Moles of solute after dilution (n)

$C_i V_i = C_n V_n$

Notes:

Example: How would you prepare 60.0 mL of 0.200 *M* HNO_3 from a stock solution of 4.00 *M* HNO_3?

$$C_i V_i = C_n V_n$$

C_i = 4.00 *M* C_n = 0.200 *M* V_f = 0.0600 L V_i = ? L

$$V_i = \frac{C_f V_f}{C_i} = \frac{0.200\ M \times 0.0600\ \text{L}}{4.00\ M} = 0.00300\ \text{L} = 3.00\ \text{mL}$$

Dilute 3.00 mL of acid with water to a total volume of 60.0 mL.

Notes:

The values of molar and normal concentrations are calculated to within **four** decimal places; these methods of expression of concentration are considered accurate and used for chemical analysis.

The weight of substances for the preparation of solutions with a concentration expressed in moles per litre is necessarily weighed on the exact analytical scales.

Notes:

For some values of the equivalent concentration of solutions, special terms and designations are used:

1.0000 mol equivalent/L = 1.000 equiv/L — normal,

0.1000 equiv/L — decinormal,

0.0100 equiv/l – centinormal.

Notes:

The molal concentration, molality (C_m) is the number of moles of the dissolved substance in 1000 g of solvent. In the general form,

$$C_m = 1000v_{sub}/m$$

where is

v_{sub} is the number of moles of the dissolved substance;
m is the amount of solvent in grams

If you express the amount of solvent in kilograms, then the equation transforms into

$$C_m = v_{sub}/m$$

The **molar fraction** is the ratio of the number of moles of a certain substance to the sum of the moles of all substances contained in the solution.

The **mass fraction ω** (formerly referred to as a percentage concentration) is often used.

It is calculated as **the ratio of the mass of the dissolved substance to the mass of the solution**, or the number of grams of the dissolved substance contained in 100 g of solution.

Thus, a 9% solution of acetic acid corresponds to 100 g solution, which contains 9 grams of glacial acetic acid.

Notes:

The **mass concentration** is the ratio of the mass of the dissolved substance to the volume of solution (expressed in kilograms per decimetre cubic or kilograms per litre).

Mass concentration, expressed in grams per millilitre, is known as **titre.** This unit called the classical method of analysis — titrimetry.

The percentage concentration should be calculated to the nearest **second** decimal point. This way of expressing concentration is considered less accurate than others.

It is most often used to calculate the number of ingredients in different production processes.

Notes:

Example.

To make a 0.5-molar (0.5 *M*) solution, first add 0.5 mol of solute to a 1-L volumetric flask half filled with distilled water.

Notes:

Notes:

Swirl the flask carefully to dissolve the solute.

Fill the flask with water exactly to the 1-L mark

Notes:

Solution dilution

Solutions can also be prepared by **diluting** a more concentrated stock solution.

Concentrated solution + **Solvent** → **Dilute solution**

The initial molarity M_1 volume V_1 of a concentrated solution are related to the final molarity M_2 and volume V_2 of a dilute solution by equation:

$$M_1 \cdot V_1 = M_2 \cdot V_2$$

Note that the units for volume and concentration do not actually matter in this equation.

The total number of moles of solute remains unchanged upon dilution.

Notes:

Example. How many millilitres of aqueous 2.00 M $MgSO_4$ solution must be diluted with water to prepare 100.0 mL of aqueous 0.400 M $MgSO_4$?

To prepare 100 ml of 0.400 *M* $MgSO_4$ from a stock solution of 2.000 *M* $MgSO_4$, a student first measures 20 mL of the stock solution with a 20-mL pipet.

She then transfers the 20 mL to a 100-mL volumetric flask.

Finally she carefully adds water to the mark to make 100 mL of solution

Equivalent and Normal Solutions

Notes:

By definition, **a standard solution** is one whose strength is known.

1. amount of substance (moles) per unit volume - **moles/l** or **molar**
2. amount of reactive species (Equivalents) per unit volume - equivalents/l or normal

Think of N as meaning "equivalent in reactive strength"

$HCl \rightarrow H^+ + Cl^-$ 1M → 1 mole H^+ per litre

$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$ 1M → 2 mole H^+ per litre

Equal molarity does not give equal reactivity. However, one equivalent of each substance in a unit volume will give equivalence in reactivity.

Notes:

How can we calculate the equivalents and normal concentration?

- The equivalent weight of an element is equal to its atomic weight divided by the valence it assumes in compounds. The definition is based on the reaction type.
- The advantage is that the number of equivalents of reacting constituents is equal to the number of equivalents of product.
- The disadvantage is that a single substance can have several different equivalent weights because the substance is involved in different reactions
- One normal solution contains one equivalent weight of a substance per litre of solution.

Notes:

Example. Equivalents and Normal Concentration

- Oxygen has an atomic weight of 16.0 and always assumes valence 2 in compounds, so its equivalent weight is 8.0
- Iron (atomic weight 55.8) has an equivalent weight of 27.9 in ferrous compounds (valence 2) and 18.6 in ferric compounds (valence 3)

In general the normality is the molarity times n where n is either the ion charge or number of protons, hydroxyl ions or electrons transferred in a reaction

The normality of a solution is never less than the molarity.

Normal Solutions

Notes:

1 Normal Solution is a solution containing 1 Equivalent Weight of a substance per litre of volume.

For Acids

1N solution of HCl = M_{Wt}/n per litre = 36.5/1 per litre = 36.5g HCl per litre

1N solution of H_2SO_4 = M_{Wt}/n per litre = 98/2 per litre = 49g H_2SO_4 per litre

For Bases (Alkali)

n equals the number of moles of H^+ (HCl) that would react with 1 mole of the base.

$NaOH + H^+ \rightarrow Na^+ + H_2O$ n = 1

$Ca(OH)_2 + 2H^+ \rightarrow Ca^{2+} + 2H_2O$ n = 2

Equivalent weight of NaOH is M_{Wt}/n = 40/1 = 40 g/equiv

Equivalent weight of $Ca(OH)_2$ is M_{Wt}/n = 74/2 = 37 g/equiv

Notes:

Ionic Reactions (e.g. Precipitation Reactions) the value of n is based on the ion charge.

$Ca^{2+} + CO_3^{2-} \rightarrow CaCO_3(s)$ n = 2

Equivalent weight of $CaCO_3$ is M_{Wt}/n = 100/2

E_{Wt} = 50g per equivalent

$Al_2(SO_4)_3 \rightarrow 2Al^{3+} + 3SO_4^{2-}$ n = 6

Redox Reactions the Equivalent Weight is based on the change in the value of the Oxidation Number.

E_{Wt} = M_{Wt}/(number of electrons taking part in the half reaction)

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ E_{Wt} = 32/4 = 8 g per equiv

Example. The method uses potassium dichromate ($K_2Cr_2O_7$) to oxidise the chemical constituents in the sample.

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$ (half reaction)

n = 6 E_{Wt} = 294/6 =49 g/equiv

Notes:

The molar fraction is the ratio of the number of moles of a certain substance to the sum of the moles of all substances contained in the solution. Calculate the molar fraction of solute x_{solute} and solvent $x_{solvent}$ can by using the following equation

$$x_{solute} = \frac{\text{Moles of solute}}{\text{Moles of solution}}$$

$$x_{solvent} = \frac{\text{Moles of solvent}}{\text{Moles of solution}}$$

$$x_{solute} + x_{solvent} = 1$$

Notes:

The mass fraction ω (formerly referred to as a percentage concentration) is often used.

It is calculated as the ratio of the mass of the dissolved substance to the mass of the solution, or the number of grams of the dissolved substance contained in 100 g of solution.

Thus, a 9% solution of acetic acid corresponds to 100 g solution, which contains 9 grams of glacial acetic acid.

Notes:

The mass concentration is the ratio of the mass of the dissolved substance to the volume of solution (expressed in kilograms per decimetre cubic or kilograms per litre). Mass concentration, expressed in grams per millilitre, is known as titre. This unit called the classical method of analysis — **titrimetry**.

The **percentage** concentration should be calculated to the nearest **second decimal point**. This way of expressing concentration is considered less accurate than others. It is most often used to calculate the number of ingredients in different production processes.

Notes:

The concentration of a solution in percent can be expressed in two ways:

as the ratio of the volume of the solute to the volume of the solution or

as the ratio of the mass of the solute to the mass of the solution.

$$percent\_by\_volume(\%(v/v)) = \frac{volume_{solute}}{volume_{solution}} \cdot 100\%$$

Isopropyl alcohol (2-propanol) is sold as a 91% solution. This solution consist of 91 mL of isopropyl alcohol mixed with enough water to make 100 mL of solution.

Weight Percent

Notes:

ratio of the mass of the solute to the mass of the solution

$$weigh\_percent(w/w) = \frac{weight_{solute}}{weight_{solution}} \cdot 100\%$$

Example. Determine the mass % of a NaCl solution if 58.5 grams of NaCl was dissolved in 50 ml of water (assume the density of water to be 1 g/ml)

1. Convert ml of water to grams $(50\ \text{ml})\ \frac{1\ \text{g}}{1\ \text{ml}} = 50\ \text{grams water}$

2. Determine total mass of solution

Mass of solution = mass of solute + mass of solvent = 58.5 + 50 = 108.5 g

3. Apply the definition of mass percent

mass % = 58.5 (100) / 108.5 = 53.9% NaCl

Notes:

It is convenient to express exceedingly small concentrations, such as food contaminants and environmental pollutants, as parts per thousand (ppt), parts per million, parts per billion (ppb).

One part per million (1ppm) represents a convenient unit since it is the concentration of one milligram (1/1000 gram) of one substance distributed throughout one kilogram (1000 grams) of another, i.e. 1mg/kg

Parts per million and parts per billion

Notes:

Small concentration may be expressed as parts per million (ppm) or parts per billion (ppb):

$$ppm = \frac{mass_{solute}}{mass_{solution}} \cdot 10^6$$

$$ppb = \frac{mass_{solute}}{mass_{solution}} \cdot 10^9$$

Solution of 1 ppm is equivalent to a mass of 1 mg of solute in 1 kg of solution

Expression of Analytical Results

Notes:

Liquid Analyte

% (vol/vol) = (vol analyte/vol sample mL) x 10^2 %
pt (vol/vol) = (vol analyte/vol sample mL) x 10^3 ppt
ppm (vol/vol) = (vol analyte/vol sample mL) x 10^6 ppm
ppb (vol/vol) = (vol analyte/vol sample mL) x 10^9 ppb

Solid Samples:

% (wt/wt) = (wt analyte/wt sample)x 10^2 %
pt (wt/wt) = (wt analyte/wt sample)x 10^3 ppt
ppm (wt/wt) = (wt analyte/wt sample)x 10^6 ppm
ppb (wt/wt) = (wt analyte/wt sample)x 10^9 ppb

Liquid Samples

%(wt/vol) = (wt analyte/vol sample mL)x 10^2 %
pt(wt/vol) = (wt analyte/vol sample mL)x 10^3 ppt
ppm(wt/vol) = (wt analyte/vol sample mL)x 10^6 ppm
ppb(wt/vol) = (wt analyte/vol sample,mL)x 10^9 ppb

Notes:

Assuming the density of water to be 1 g/mL we approximate the density of a dilute aqueous solution to be 1 g/mL

$$1ppm = \frac{1\mu g}{1g} = \frac{1\mu g}{1g} \cdot \frac{1g}{1mL} = \frac{1\mu g}{1mL}$$

1 ppm = 1 µg/mL = 1 mg/L

1 ppb = 1 ng/mL = 1 µg/L

Notes:

Example. Traces of iodide ion in the diet help prevent the enlargement of the thyroid gland, i.e. goiter. To provide this dietary iodide KI is added to commercial table salt at about $7.6 \cdot 10^{-5}$ g of KI per gram of NaCl.

Convert this concentration into ppm.

The concentration is 7.6 x 10^{-5} g KI / 1g NaCl

We want to know how many grams of KI there are in 10^6 g of table salt.

$$\frac{7.6 \times 10^{-5}\ g\ KI}{1\ g\ NaCl} \times \frac{10^6}{10^6} = \frac{7.6 \times 10^1\ g\ KI}{1 \times 10^6\ g\ NaCl} = 76\ ppm\ KI$$

Density Calculations. How do we convert to Molarity?

Notes:

Density = mass solute /unit volume

Specific Gravity = D_{solute}/D_{H20}

D_{H2O} = 1.00000 g/mL at 4°C

D_{H2O} = 0.99821 g/mL at 20°C

Concentrations: Weight per volume (w/v)

Especially convenient when using aqueous (H_2O) solutions because:

Density of H_2O = 1 g/mL or 1kg/L

X ppm = X mg/kg or X mg/L

Remember: Molarity = moles/L

deci is 1/10 (10^{-1})

centi is 1/100 (10^{-2})

milli is 1/1000 (10^{-3})

Notes:

Example. Determine the ppm of a NaCl solution if 58.5 grams of NaCl was dissolved in 50.0 ml of water (assume the density of water to be 1 g/ml)

Convert ml of water to grams $(50\ \text{ml})\ \frac{1\ \text{g}}{1\ \text{ml}} = 50\ \text{grams water}$

Determine total mass of solution

Mass of solution = mass of solute + mass of solvent =

= 58.5 + 50.0 = 108.5 (g)

Apply the definition of ppm $58.5 \cdot (10^6) / 108.5$ =

$= 5.39 \cdot 10^5$ ppm NaCl

Notes:

Solution-diluent volume rations

The composition of a dilute solution is sometimes specified in terms of the volume of a more concentrated solution and the volume of solvent used in diluting it.

For example, usually 1:4 HCl solution meaning 4 volumes of water and 1 volume of concentrated hydrochloric acid.

Example. Calculating percent (volume/volume)

Notes:

What is the percent by volume of ethanol (C_2H_5OH or ethyl alcohol) in the final solution when 85 mL of ethanol is diluted to a volume of 250 mL with water?

We known:

Volume of ethanol = 85 mL

Volume of solution = 250 mL.

We unknown: ethanol (v/v) = ?%

$$Percent\_by\_volume(\%(v/v)) = \frac{volume_{solute}}{volume_{solution}} \cdot 100\%$$

$$\%(v/v) = \frac{85\ mL\ ethanol}{250\ mL} \cdot 100\% = 34\%\ ethanol\ (v/v)$$

Evaluate: Does the result make sense?

The volume of the solute is about one-third the volume of the solution, so the answer is reasonable. The answer is correctly expressed to two significant figures

Tasks to Section 5:

1. Give definitions of these terms: molarity (C or M), normality (C_f or N), equivalence factor *f*, molality (C_m or m), mole fraction (x), weight per cent (ω or %), volume per cent, weight/volume per cent, parts per million, titre, solute, solvent, solution.

2. A solution has a volume of 2.0 L and contains 36.0 g of glucose ($C_6H_{12}O_6$). If the molar mass of glucose is 180 g/mol, what is the molarity of the solution?

3. How many moles of solute are in 250 mL of 2.0 M $CaCl_2$? How many grams of $CaCl_2$ is this?

4. How many millilitres of a solution of 4.00 M KI are needed to prepare 250.0 mL of 0.760 M KI?

5. A bottle of the antiseptic hydrogen peroxide (H_2O_2) is labelled 3.0% (v/v). How many mL H_2O_2 are in a 400.0-mL bottle of this solution?

6. Calculate the molarity and molality of 48.42 % HNO_3 (density is 1.3 g/mL)

7. Calculate the formula mass of $CaSO_4$. What is the molarity of $CaSO_4$ in a solution containing 1.2 g of $CaSO_4$ in a volume of 50 mL? How many grams of $CaSO_4$ are in 50 mL of 0.086 M $CaSO_4$?

8. How many ppm of $C_{29}H_{60}$ are in 23 M $C_{29}H_{60}$?

9. Find the formula mass of anhydrous $CuSO_4$. How many grams should be dissolved in 250.0 mL to make a 16.0 mM solution?

10. Calculate how many mL of 71.63 % nitric acid (density is 1.42 g/mL) should be diluted to 0.250 L to make 3.00 M HNO_3?

11. Calculate the molarity and normality of H_2SO_4 using the density of 70.82 wt% H_2SO_4 (the density is 1.62 g/mL).

12. A solution with a final volume of 500.0 mL was prepared by dissolving 25.00 mL of methanol (CH_3OH, density is 0.791 4 g/mL) in chloroform.

(a) Calculate the molarity of methanol in the solution.

(b) The solution has a density of 1.454 g/mL. Find the molality of methanol.

13. The concentration of sugar (glucose, $C_6H_{12}O_6$) in human blood ranges from about 80 mg/100 mL before meals to 120 mg/100 mL after eating. Find the molarity of glucose in blood before and after eating.

14. What is the maximum volume of 0.25 M sodium hypochlorite solution (NaOCl, laundry bleach) that can be prepared by dilution of L of 0.80 M NaOCl?

Section 6: Qualitative Chemical Analysis

Contents:

Introduction

Qualitative analysis is the process of determining the identity of the constituents of a substance.

Qualitative analysis of compounds allows establishing the composition of both individual compounds and their mixtures. Aqueous solutions of salts, acids and bases are electrolytes and dissociate into ions. Therefore, a qualitative analysis of inorganic compounds is divided into an analysis of cations and anions.

The analysis of the ion mixture can be performed in different ways. There may be a small number of ions in the test sample, and they will not affect each other's determination. In this case, the ion is determined in separate portions of the solution. Specific or selective analytical reactions are used.

The reaction that allows determining the content of specific ions in solution in the presence of other ions without first isolating them is called specific. For example, a specific reaction to ammonium ions is their reaction with alkaline solutions when heated. The released ammonia is determined by the smell or colour change of wet litmus paper.

Nonspecific or selective is a reaction that can be used in the presence of a limited number of ions.

There are a few specific reactions. Selective or nonspecific reactions are most often used. These reactions require the use of methods that eliminate the effects of other substances present in the sample. Elimination of the effect of other ions is achieved by dividing the composition of the solution into components. The precipitate and the solution are most often separated. Then the ions that interfere with each other are in different phases. There are two methods of qualitative analysis: fractional and systematic.

In the fractional analysis, the composition of the substance is determined by specific reactions under certain conditions. The implementation of fractional analysis is carried out in two stages. The first, the effects of interfering components are eliminated by chemical reactions. Then reactions carry out to determine individual ions.

The systematic analysis is that a complex mixture of ions is divided into several simpler ones by the action of group chemical reagents. Then, within each of these groups, individual ions are detected by specific reactions.

Ions are divided into groups and then detected in a predetermined sequence.

Analysis of anions is most often performed by the fractional method.

In the analysis of cations, the presence of some ions interferes with the determination of others. There are a few specific reactions to individual cations.

Detection of cations is most often carried out using a systematic course of analysis. There are several methods of systematic analysis of cations, depending on the use of group reagents.

a) hydrogen sulphide method with the hydrogen sulphide and ammonium sulphide as group reagents;

b) ammonia-phosphate method - the group reagent is a mixture of $(NH_4)_2HPO_4 + NH_3$;

c) acid-base method - the group reagents are acids and bases.

As an example, in Section 5, acid-base method is used for the detection of cations. Analytical groups of cations for this method correspond to the groups of the periodic table of elements by DI Mendeleev.

There is no generally accepted classification of anions. In most cases, the anions are divided into three analytical groups depending on the solubility of the Barium and Argentum salts of the respective anions.

Notes:

Section 6. Qualitative Chemical Analysis

- Separation of the metal ions by selective precipitation
- Identification of metal cations in a solution
- Systematic analyses

Learning Objectives

To know how to separate metal ions by selective precipitation.

To understand how several common metal cations can be identified in a solution using selective precipitation.

Notes:

Aqueous solutions of salts, acids and bases are electrolytes. Qualitative analysis of inorganic compounds is divided into the **analysis of cations and anions.** Analysis of the mixture of ions can be carried out in fractional and systematic methods.

If there is a small number of ions in the sample to be analyzed, it is relatively easy to eliminate their interfering effects. In this case, a fractional analysis is used. For example, the content of anions is thus determined.

In the analysis of cations, the presence of some ions often interferes with the determination of others. There are a few specific reactions to determining the content of individual ions.

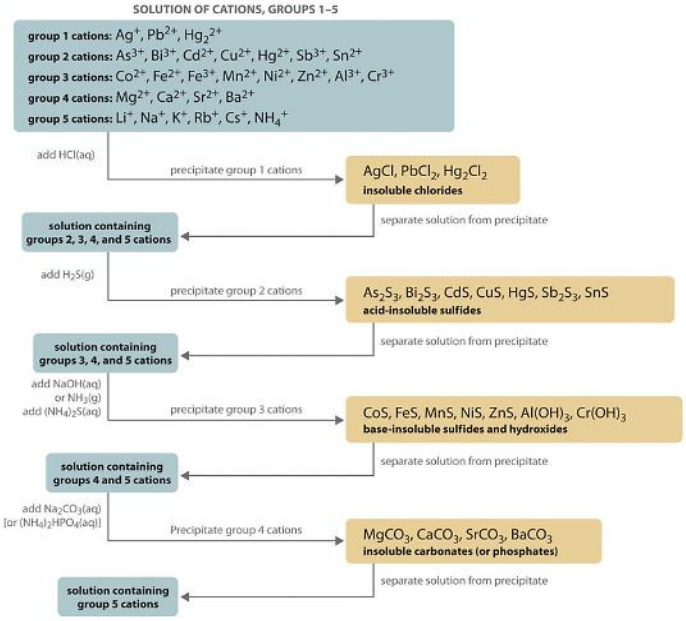
Notes:

Therefore, the detection of the content of cations is often carried out using a systematic analysis.

This procedure used to separate and identify more than 20 common metal cations from a single solution consists of selectively precipitating only a few kinds of metal ions at a time under given sets of conditions.

Consecutive precipitation steps become progressively less selective until almost all of the metal ions are precipitated, as illustrated in Figure on the next slide.

Steps in a typical qualitative analysis scheme for a solution that contains several metal ions



Notes:

Classification of the cations by sulphide methods

Groups	Cations	Basic group reagent	The solubility of the compounds
I	**Li^+; Na^+; K^+; NH_4^+**	**not available**	Sulphides, carbonates *, chlorides and hydroxides * are soluble in water
II	**Mg^{2+}; Ca^{2+}; Sr^{2+}; Ba^{2+}**	**$(NH_4)_2CO_3$ + NH_3+ NH_4Cl** pH =9,25	Carbonates are not soluble in water
III	**Ni^{2+}; Co^{2+}; Fe^{2+}; Fe^{3+}; Al^{3+}; Cr^{3+}; Mn^{2+}; Zn^{2+}**	**$(NH_4)_2S$ + NH_3+ NH_4Cl** pH =9,25	Sulphides are not soluble in water ** and ammonia, but are soluble in HCl
IV	**Cu^{2+}; Cd^{2+}; Bi^{3+}; Hg^{2+}; $As^{(3+;\,5+)}$; $Sb^{(3+;\,5+)}$; $Sn^{(2+;\,4+)}$**	**H_2S + HCl** pH =0,5	Sulphides are not soluble in water and HCl
V	**Ag^+; Pb^{2+}; Hg_2^{2+}**	**HCl**	Chlorides are not soluble in water and dilution acids

* – with the exception of **Mg^{2+}**.

** – sulphides of **Al^{3+}; Cr^{3+}** destroy by water

Notes:

Classification of the cations by ammonia-phosphate methods

Group	Cations	Basic group reagent	The solubility of the compounds
I	**Na^+; K^+; NH_4^+**	**not available**	Chlorides, nitrates, phosphates dissolve in water
II	**Li^+; Mg^{2+}; Ca^{2+}; Sr^{2+}; Ba^{2+}; Mn^{2+}; $Fe^{(2+;\,3+)}$; Al^{3+}; Cr^{3+}; Bi^{3+}**	**$(NH_4)_2HPO_4$ + NH_3** (conc)	Phosphates are insoluble in water and in excess ammonia
III	**Cu^{2+}; Cd^{2+}; Hg^{2+}; Ni^{2+}; Co^{2+}; Zn^{2+}**	**Na_2HPO_4+ NH_3** (conc)	Phosphates do not dissolve in water but dissolve in excess ammonia to form ammonia
IV	**$As^{(3+;\,5+)}$; $Sb^{(3+;\,5+)}$; $Sn^{(2+;\,4+)}$**	**HNO_3**	Oxidized to higher oxidation states, acid of Sb and Sn are not soluble in water
V	**Ag^+; Pb^{2+}; Hg_2^{2+}**	**HCl**	Chloride are not soluble in water and acids

Classification of the cations by acid-base methods

Groups	Cations	Basic group reagent	The solubility of the compounds	Compounds formed under the influence of a group reagent
I	Na^+; K^+; NH_4^+	not available	Chlorides, Sulphates, hydroxides are soluble in water	Solution contains: Na^+, K^+, NH_4^+
II	Ag^+; Pb^{2+}; Hg_2^{2+}	HCl	Chlorides are not soluble in water	Perspirations: AgCl, $PbCl_2$, Hg_2Cl_2
III	Ba^{2+}; Sr^{2+}; Ca^{2+}	H_2SO_4+C_2H_5OH	Sulphates are not soluble in water	Perspirations: $BaSO_4$, $SrSO_4$, $CaSO_4$
IV	Al^{3+}; Zn^{2+}; Cr^{3+}; $As^{(3+;\ 5+)}$; $Sn^{(2+;\ 4+)}$	Excess NaOH conc. + + 3% H_2O_2	Hydroxides are not soluble in water but dissolve in excess alkali	Solution contains: $[Al(OH)_4]^{1-}$ or $[Al(OH)_6]^{3-}$ $[Zn(OH)_4]^{2-}$ $[Cr(OH)_4]^{1-}$ or $[Cr(OH)_6]^{3-}$ $[Sn(OH)_4]^{2-}$ $[Sn(OH)_6]^{2-}$ AsO_3^{3-} ; AsO_4^{3-}
V	Mg^{2+}; Mn^{2+}; Bi^{3+}; $Fe^{(2+;\ 3+)}$; $Sb^{(3+;\ 5+)}$	Excess $NH_3 \cdot H_2O$ conc.	Hydroxides are not soluble in water, excess alkali and ammonia	Perspirations: $Fe(OH)_2$;
VI	Co^{2+}; Ni^{2+}; Cd^{2+}; Cu^{2+}; Hg^{2+}	Excess $NH_3 \cdot H_2O$ conc.	Hydroxides are not soluble in water, excess alkali, but are soluble in excess ammonia	Solution contains: $[Cu(NH_3)_4]^{2+}$; $[Co(NH_3)_6]^{2+}$; $[Ni(NH_3)_6]^{2+}$; $[Cd(NH_3)_4]^{2+}$; $[Hg(NH_3)_4]^{2+}$

Notes:

Notes:

The group reagent for each analytical group reacts with the ions of this group specifically.

Group reagents must satisfy certain **requirements**:

- react with ions quantitatively (residual concentration of half-life of interaction in solution should not exceed 10^{-6} mol/dm^3);
- the excess group reagent should not interfere with the determination of the ions remaining in the test sample;
- the precipitate obtained must be dissolved in certain reagents for further analysis.

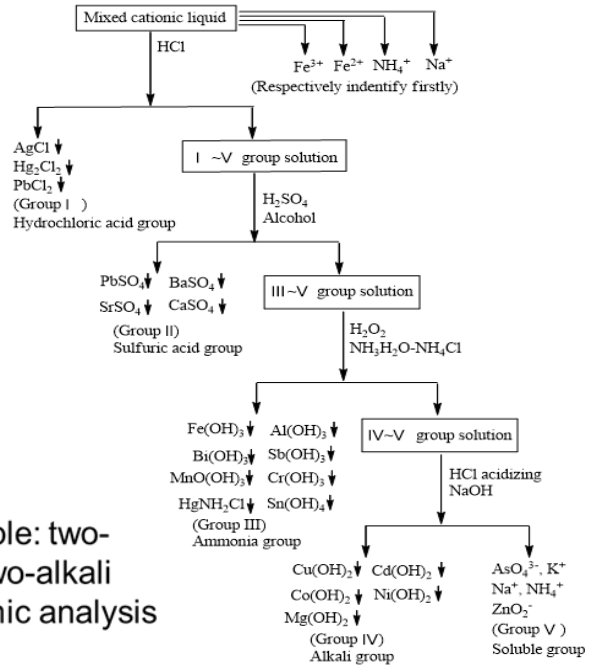
Notes:

For example, the two-acid-two-alkali systemic analysis is shown as follows:

Group Ⅰ Hydrochloric acid group: Ag^+, Pb^{2+}, Hg_2^{2+}
Group Ⅱ Sulfuric acid group: Ba^{2+}, Ca^{2+}, Pb^{2+}
Group Ⅲ Ammonia group: Fe^{3+}, Fe^{2+}, Al^{3+}, Mn^{2+}, Cr^{3+}, Bi^{3+}, Sb^{3+}, Hg^{2+}, Sn^{2+}
Group Ⅳ Alkali group: Cu^{2+}, Co^{2+}, Ni^{2+}, Mg^{2+}, Cd^{2+}
Group Ⅴ Soluble group: K^+, Na^+, NH_4^+, Zn^{2+}, As^{3+}

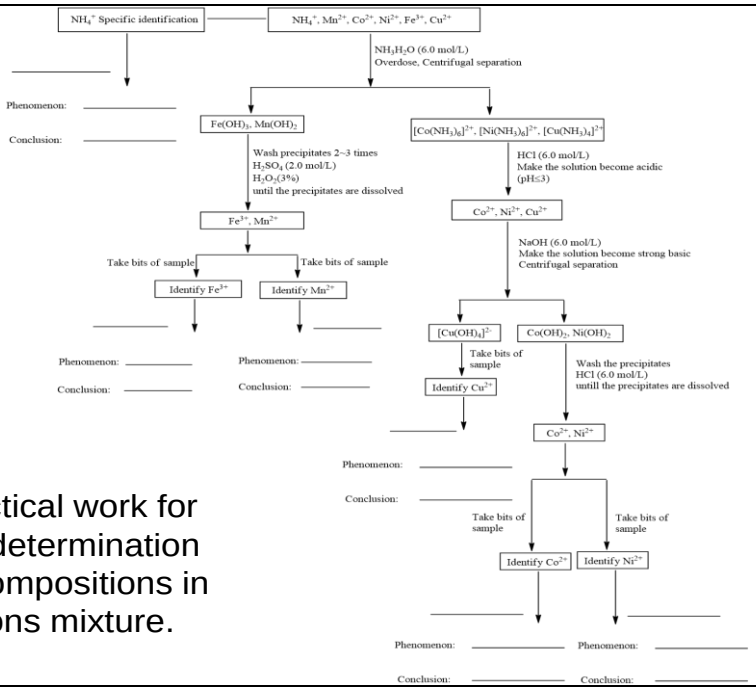
The next slide shows the example of practical work for the determination of compositions in cations mixture.

Notes:



Example: two-acid-two-alkali systemic analysis

Notes:



Practical work for the determination of compositions in cations mixture.

Notes:

Example: practical work for the determination of compositions in cations mixture

The **steps** of analysis:

1. Identification of the ammonia ion, NH_4^+

   This ion can be identified first before the system analysis. (Identifying by the test tube: take the unknown 15~20 drops of liquid, and identify it by the moist red litmus paper or pH test paper in the mouth of the test tube. Do not touch the liquid).

2. Identifying of the copper ion, Cu^{2+}

   If the liquid contains zinc (Zn^{2+}), cobalt (Co^{2+}) and nickel ions (Ni^{2+}), the colour of the precipitate, copper hexacyanoferrate ($Cu_2[Fe(CN)_6]$), may be transferred from the reddish-brown to the cameo brown.

Example: practical work for the determination of compositions in cations mixture

Notes:

3. Identifying the manganese ion, Mn^{2+}

The concentration of the Mn^{2+} must below. If the Mn^{2+} cannot be identified in several drops of the solution, the liquid can be diluted properly, and then perform the identification.

Otherwise, the generated permanganic acid radical reacts with the unoxidized Mn^{2+} to yield the manganese dioxide hydrate precipitate $MnO_2 \cdot nH_2O$. In addition, the hydrogen peroxide should be removed by heating due to its interference to the identification of the Mn^{2+}.

Example: practical work for the determination of compositions in cations mixture

Notes:

4. Identifying the cobalt ion, Co^{2+}

The ferric ions or cupric ions can interfere in the identification of the Co^{2+}. Add a small amount of thiourea $SC(NH_2)_2$ to mask the Cu^{2+}. The interference can be removed by the addition of the ammonium fluoride or sodium fluoride.

The Fluor ion plus ferric ion yield more stable ions $[FeF_6]^{3-}$, which will eliminate interference.

5. The precipitates must be washed completely

Example: practical work for the determination of compositions in anions mixture

Notes:

Common anions in aqueous solution are either single atom anions or polyatomic anions usually containing oxygen.

Only ten of the many known inorganic anions will be identified in this example:

chloride Cl^-; bromide Br^-; iodide I^-; sulfide S^{2-};
sulfite SO_3^{2-}; sulfate SO_4^{2-}; thiosulfate $S_2O_3^{2-}$;
nitrite NO_2^-; nitrate NO_3^-; phosphate PO_4^{3-}.

Some of these anions show oxidizing properties, some reducing properties. In most situations, there is no interference with one another among the anions in the course of identification. Many anions can be detected directly in the sample solution by the addition of a single test reagent, so the **specific anion test** is usually adopted.

Notes:

If specific anion tests are subject to interference from other ions, some anion-detection procedures require **a systematic removal** of the interferences before the use of the test reagent.

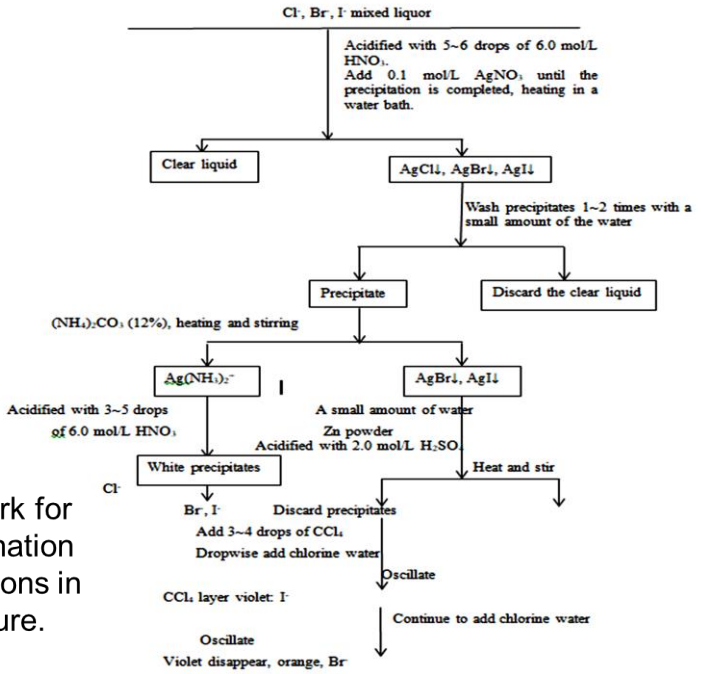
To characteristically identify an anion in a mixture, when some interference among the anions happen, **preliminary elimination**, or preliminary test, of the interferences is necessary and the proper method should be adopted.

For example, a test for the presence of SO_3^{2-} and $S_2O_3^{2-}$ requires the prior remove of S^{2-}.

Elimination method: Add the $PbCO_3$ solid into the anions mixed liquor, then the $PbCO_3$ precipitates are transformed into the PbS precipitates with less solubility. After centrifuging and separating, SO_3^{2-} and $S_2O_3^{2-}$ in clear liquid are identified respectively.

If Cl^-, Br^- and I^- ions are the coexistence, the separation and identification of the anions are outlined in the flow diagram. Follow the diagram as you read through the introduction and follow the experimental procedure.

Notes:



Practical work for the determination of compositions in anions mixture.

Notes:

Experimental procedures

1. The identifying reactions of the specific anions

Sulfide anion **S^{2-}**

Drop the Na_2S to the well plate and add 1% $Na_2[Fe(CN)_5NO]$. The appearance of the fuchsia colour confirms the presence of sulfide ion in the solution.

Sulfite anion **SO_3^{2-}**

Two drops of saturated $ZnSO_4$ are added to a well plate, and add one drop of 0.1 mol/L $K_4[Fe(CN)_6]$ and one drop of 1% $Na_2[Fe(CN)_5NO]$. Add one drop of $NH_3 \cdot H_2O$ until the solution is just neutral to pH paper. The red precipitate confirms the presence of sulfite ion in the solution.

Yellow-green precipitates adsorb the $Na_4[Fe(CN)_5(NOSO_3)]$ on the surface, which leads to the red colour.

Thiosulfate anion **$S_2O_3^{2-}$**

One drop of $Na_2S_2O_3$ is added to a well plate, then add two drops of $AgNO_3$. The colour of the precipitate changes from white to yellow, from yellow to brown, and finally to black, confirming the presence of $S_2O_3^{2-}$ ion in the test solution.

Sulfate anion **SO_4^{2-}**

Add 3~4 drops of Na_2SO_4 to a centrifuge test tube, and then add one drop of $BaCl_2$. After centrifugation, add several drops of 6.0 mol/L HCl to the precipitate. The presence of insoluble precipitate confirms the presence of the SO_4^{2-} ion in the solution.

Chloride anion **Cl^-**

1 drop of 2.0 mol/L HNO_3 is added into the 2 drops of 0.1 mol/L NaCl solution in a test tube. Add two drops of 0.1 mol/L $AgNO_3$ to the aqueous solution and centrifuge. A white precipitate indicates the likely presence of Cl^-. Discard the supernatant. To further confirm the presence of chloride ion in the test solution, the addition of several drops of aqueous ammonia quickly dissolves the precipitate if Cl^- is present. Reacidification of the solution with drops of 6.0 mol/L nitric acid re-forms the silver chloride precipitate.

Bromide ion **Br^-**

Two drops of 0.1 mol/L NaBr in a test tube are added one drop of 2.0 mol/L H_2SO_4 and 5~6 drops of CCl_4, then add the new chlorine water dropwise and agitate. Observe the colour of the CCl_4 layer, confirming the presence of Br^- ion in the test solution.

Iodide ion **I^-**

Two drops of 0.1mol/L KI in a test tube are added one drop of 2.0 mol/L H_2SO_4 and 5~6 drops of CCl_4, then add the new chlorine water dropwise and agitate. Observe the colour of the CCl_4 layer, confirming the presence of I^- ion in the test solution.

The yellow precipitate (AgI), which is insoluble in the diluted nitric acid, is produced by adding $AgNO_3$ solution. Add chloride water and starch reagent. Then the solution becomes blue.

Notes:

Nitrate ion **NO_3^-**

As all nitrate salts are soluble, no precipitate can be used for identification of the nitrate ion.

The nitrate ion is identified **by the brown ring test**.

The nitrate ion is reduced to nitric oxide by iron(II) ions in the presence of concentrated sulfuric acid. The nitric oxide combines with excess iron(II) ions, forming the brown $FeNO^{2+}$ ion at the interface of the aqueous layer and the concentrated sulfuric acid layer (where acidity is high) that underlies the aqueous layer. $FeNO^{2+}$ is more stable at low temperatures.

This test has many sources of interference:

① Sulfuric acid oxidizes bromide and iodide ions to bromine and iodine, and

② sulfites, sulfides, and other reducing agents interfere with the reduction of NO_3^- to NO.

A preparatory step of adding sodium hydroxide and silver sulfate removes these interfering anions, leaving only the nitrate ion in solution..

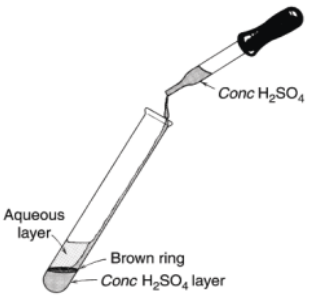
Notes:

Decant 1.0 mL of 0.1 mol/L KNO_3 into a small test tube and add 1~2 pellets of ferrous sulfate crystal and agitate.

Holding the test tube at a 45º angle with test tube tongs, add, with a dropping pipet, slowly and cautiously, down its side, about 15~20 drops of concentrated H_2SO_4.

Do not draw H_2SO_4 into the bulb of the dropping pipet. Do not agitate the solution. The more dense concentrated H_2SO_4 underlies the aqueous layer. Use extreme care to avoid mixing the concentrated H_2SO_4 with the solution.

Allow the mixture to stand for several minutes. A brown ring at the interface between the solution and the concentrated H_2SO_4 confirms the presence of the nitrate ion in the test solution.



Test of a brown ring

Nitrite ion **NO_2^-**

Decant one drop of 0.1 mol/L $NaNO_2$ into a small test tube and acidify (to pH paper) with 6.0 mol/L HAc. Add one drop of p-aminobenzene sulfonic acid and one drop of α-naphthylamine. The color of solution become red immediately, confirming the presence of NO_2^- ion in the solution.

Phosphate ion **PO_4^{3-}**

3~5 drops of 0.1mol/L sodium phosphate in a test tube is acidified with 10 drops of concentrated HNO_3 (Caution!) Add ~1ml of Ammonium molybdate. Shake and warm slightly in a warm water (~60℃) bath and let stand for 10~15 minutes. A slow formation of a yellow precipitate confirms the presence of phosphate ion in the test solution.

2. Separation and identification of the mixed halide anions **Cl^-, Br^-, I^-**

Add 3~4 drops of 0.1mol/L NaCl, 0.1mol/L NaBr, and 0.1mol/L KI solution into three centrifuge tubes, respectively, and perform the separation and identification anions with the method shown in the experiment principles.

Notes:

Tasks to Section 6:

1. Give definitions of these terms: qualitative analysis, specific and selective analytical reactions, fractional analysis, systematic analysis, group reagent, analytical groups of cations, analytical groups of anions.

2. What is the method of binding both ionic and extraneous ions called?

3. In two-acid-two-alkali systemic analysis method, why is a specific identification for NH_4^+ performed firstly?

4. Explain the effect of the presence of ions of different electrolytes on the solubility of the precipitate. Why use the action of ions of the same name.

5. Why are the precipitates in the test tube needed washing after the centrifugal separation? Explain how to wash them?

6. Explain how to wash the precipitates under the bottom of the centrifugal tube after centrifugation?

7. In the neutral or basic-mixing anion solution, the white precipitate would generate when the $BaCl_2$ solution is added. What are the possible anions of ten kinds of common anions?

8. To prepare for Practical work 1 write reactions to determine the content of each cation in the solution. Use the diagram and the description in Section 6.

9. When identifying the anions SO_4^{2-} and SO_3^{2-} it is necessary to eliminate the interference. When barium chloride is added to a mixture of such ions, white crystalline precipitates of barium sulphate and barium sulphite are formed. How to distinguish these sediments?

10. In identifying I^- with the chlorine water, why cannot the purple colour in the CCl_4 layer be observed if the chlorine water is added excessively?

11. The presence of the NO_2^- ion interferes with the identification of NO_3^-. Therefore, when determining the content of NO_3^- in the solution, it is necessary to get rid of NO_2^-. Explain how to do it?

12. Write the reactions to determine the content of each solution of the cation (a) or anion (b) in the solution. Use the diagram and description of Examples of practical work to determine the composition of the cationic or anionic mixture in Section 6.

Section 7: Basics of Titration. Titrimetric Methods

Contents:

Introduction

In titrimetric methods, the volume serves as an analytical signal. Titrimetry first appeared as an analytical method in the early eighteenth century. Analysts of that era did not well receive titrimetric methods. They could not provide accuracy that would be identical to the accuracy of gravimetric analysis.

Unlike gravimetric analyses, the development and adoption of titrimetry required a deeper understanding of stoichiometry, thermodynamics, and chemical equilibrium.

In titrimetric methods, we add a reagent, called the titrant, to a solution containing another reagent, called the titrand, and allow them to react.

The type of reaction provides us with a simple way to divide titrimetry into the following four categories:

– acid-base titrations, in which an acidic or basic titrant reacts with a titrand that is a base or an acid;
– complexometric titrations based on metal-ligand complexation;
– redox titrations, in which the titrant is an oxidizing or reducing agent;
– precipitation titrations, in which the titrant and titrand form a precipitate.

Despite the difference in chemistry, all titrations share several common features. During studying this section, you need to focus on the similarities between different titrimetric methods. You will find it easier to understand a new analytical method when you can see its relationship to other similar methods.

If a titration is to be accurate, we must combine the stoichiometrically equivalent amount of titrant and titrand. We call this stoichiometric mixture the equivalence point. A careful titration requires that we know the exact volume of titrant at the equivalence point. The product of the titrant's equivalence point volume and its molarity is equal to the moles of titrant reacting with the titrand.

If we know the stoichiometry of the titration reaction, then we can calculate the moles of titrand.

To find the endpoint of the titration, we need to trace a particular property of the reaction, which must change at the point of equivalence. For acid-based titrimetry, a simple method of finding the equivalence point is constant pH control using a pH meter electrode. Also, we can add to the solution an indicator that changes colour at pH 7.0.

The titration curve gives us an exact graphical representation of how the reaction property changes when we add titrant to the titrated solution. A careful study of this titration curve gives much information.

From an acid-base titration curve, we can deduce the quantities and pKa values of acidic and basic substances in a mixture. In pharmaceutical chemistry, the pKa and lipophilicity of a drug show how easily it will cross cell membranes.

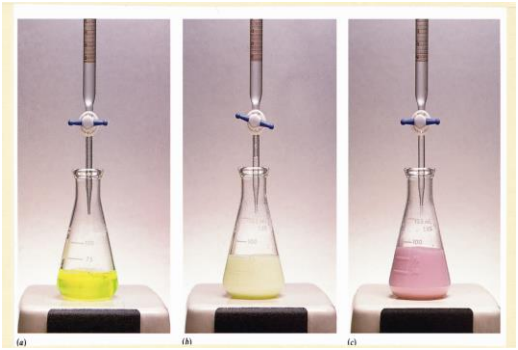
With pKa and pH, we can compute the charge of a polyprotic acid. Usually, the more highly charged a drug, the harder it is for that drug to cross a cell membrane.

In Section 7, we learn to plot the titration curves and to find endpoints with electrodes and indicators.

Notes:

Titrimetric methods include a large and powerful group of quantitative procedures based on measuring the amount of a reagent of known concentration that is consumed by the analyte.

Titrimetry is a term which includes a group of analytical methods based on determining the quantity of a reagent of known concentration that is required to react completely with the analyte.



Notes:

There are three main types of titrimetry:

Volumetric titrimetry is used to measure the volume of a solution of known concentration that is needed to react completely with the analyte.

Gravimetric titrimetry is like volumetric titrimetry, but the mass is measured instead of the volume.

Coulometric titrimetry is where the reagent is a constant direct electrical current of known magnitude that consumes the analyte; the time required to complete the electrochemical reaction is measured.

The benefits of these methods are that they are rapid, accurate, convenient, and readily available.

Notes:

Defining Terms

Titrimetry – determination of analyte by reaction with measured amount of standard reagent

Standard Solution (titrant) – reagent of known concentration

Titration – slow addition of titrant to analyte solution from a volumetric vessel (burette). This is performed by adding a standard solution from a burette or other liquid- dispensing device to a solution of the analyte until the point at which the reaction is believed to be complete.

Equivalence Point – reached when amount of added titrant is chemically equivalent to amount of analyte present in the sample.

End Point – the occurrence of an observable physical change indicating that the equivalence point is reached.

Defining terms

Notes:

Standardization – A process in which concentration of a volumetric solution is determined by using it to titrate a known mass of a primary standard. Process where the concentration of the titrant is determined exactly using a primary standard

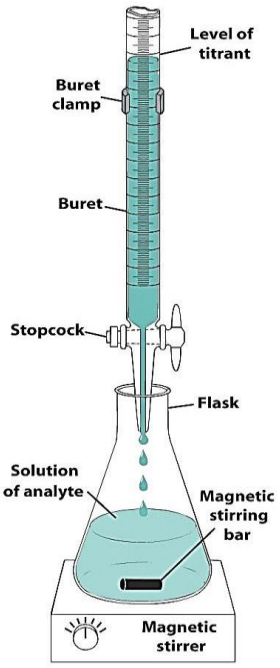
Primary standard – ultrapure reagent where the number of moles is known exactly so it can be used to accurately measure the titrant concentration, e.g.

$2HCl + Na_2CO_3 \rightarrow CO_2 + H_2O + 2NaCl$

Primary standard (MW = 105.99) 99.99% pure

Standard Solution – A reagent of a known concentration which is used in the titrimetric analysis.

Back-Titration – This is a process that is sometimes necessary in which an excess of the standard titrant is added, and the amount of the excess is determined by back titration with a second standard titrant. In this instance the equivalence point corresponds with the amount of initial titrant is chemically equivalent to the amount of analyte plus the amount of back-titrant.



Notes:

$aA + tT \rightarrow$ products

analyte titrant

$H_2SO_4 + 2\,NaOH \rightarrow 2H_2O + Na_2SO_4$

indicator – added compound that undergoes a color change at the eq. pt.

end point – end of titration when analyte moles are completely consumed and the indicator changes color

equivalence point – theoretical end of titration as calculated using stoichiometry,

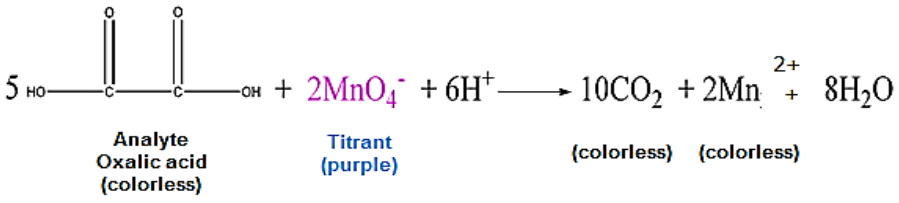
e.g. 1 mol H_2SO_4/2 mol NaOH

titration error – difference between the end point and the eq. pt. volumes

Notes:

Equivalence point

Quantity of added titrant is the exact amount necessary for stoichiometric reaction with the analyte is an **ideal theoretical result**



Equivalence point occurs when 2 moles of MnO_4^- is added to 5 moles of Oxalic acid

End point

Notes:

What we actually measure:

Marked by a sudden change in the physical property of the solution.

Change in color, pH, voltage, current, absorbance of light, presence/absence ppt.

$CuCl_2$ Titration with NaOH

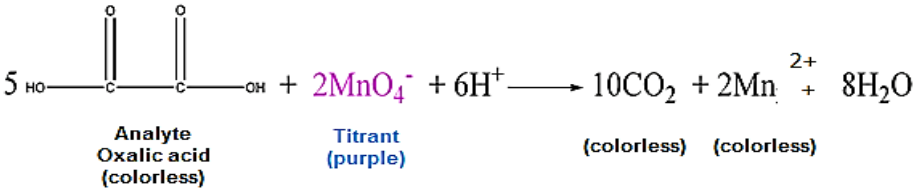
Before any addition of NaOH | **After the addition of 8 drops of NaOH** | **End Point**

Notes:

End point

Occurs from the addition of a slight *excess* of titrant

Endpoint <u>does not</u> equal equivalence point



After equivalence point occurs, excess MnO_4^- turns solution purple → Endpoint

Notes:

Titration Error: Difference between endpoint and equivalence point

Corrected by a blank titration repeat procedure without analyte

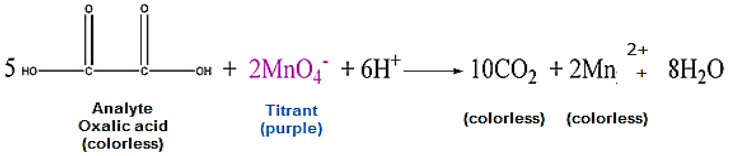
ii. Determine amount of titrant needed to observe change

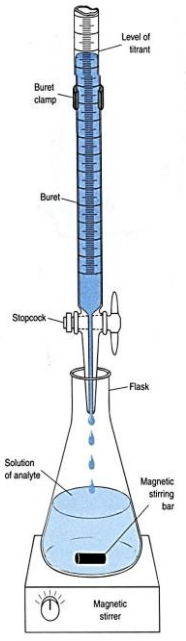
iii. Subtract blank volume from titration

Primary Standard

Accuracy of titration requires knowing precisely the quantity of titrant added.

99.9% pure or better → accurately measure concentration





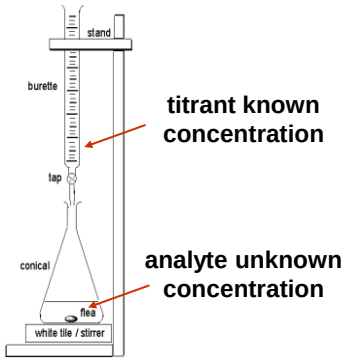
Standardization

Notes:

Required when a non-primary titrant is used

- Prepare titrant with approximately the desired concentration
- Use it to titrate a primary standard
- Determine the concentration of the titrant
- Reverse of the normal titration process!!!

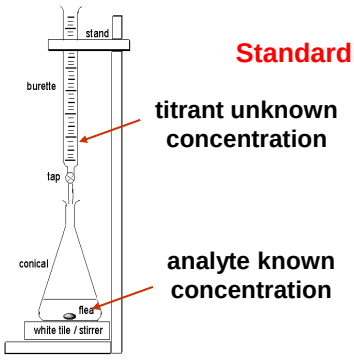
Titration



titrant known concentration

analyte unknown concentration

Standardization



titrant unknown concentration

analyte known concentration

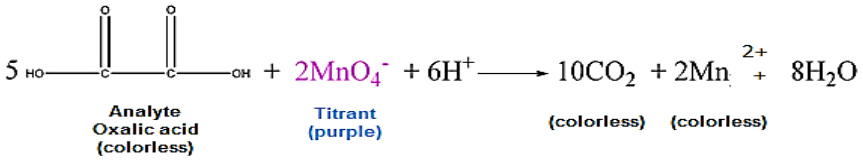
Back Titration

Notes:

Add *excess* of one standard reagent (known concentration)

Completely react <u>all</u> the analyte

Add enough MnO_4^- so all oxalic acid is converted to product



Titrate excess standard reagent to determine how much is left.

Titrate Fe^{2+} to determine the amount of MnO_4^- that did not react with oxalic acid

Differences is related to amount of analyte

Useful if better/easier to detect endpoint

Notes:

Basic principles of the volumetric analysis

Titration – What are the requirements?

1. Reaction must be stoichiometric
2. Reaction should be rapid
3. No side reactions
4. Marked change in some property of the solution when reaction is complete
5. Equivalence point
6. Reaction should be quantitative

Notes:

Primary Standards

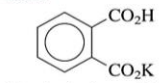
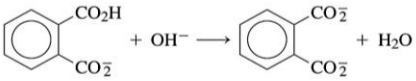
A **primary standard** is a highly purified compound that serves as a reference material in all volumetric and mass titrimetric properties. The accuracy depends on the properties of a compound and the important properties are:

1. High purity
2. Atmospheric stability
3. Absence of hydrate water
4. Readily available at a modest cost
5. Reasonable solution in the titration medium
6. Reasonably large molar mass

Compounds that meet or even approach these criteria are few, and only a few primary standards are available.

Notes:

Examples of primary standards

Compound	Formula mass	Notes
ACIDS		
 Potassium hydrogen phthalate	204.22	The pure solid is dried at 105°C and used to standardize base. A phenolphthalein end point is satisfactory. 
$KH(IO_3)_2$ Potassium hydrogen iodate	389.91	This is a strong acid, so any indicator with an end point between ~5 and ~9 is adequate.
BASES		
$H_2NC(CH_2OH)_3$ Tris(hydroxymethyl)aminomethane (also called tris or tham)	121.14	The pure solid is dried at 100°–103°C and titrated with strong acid. The end point is in the range pH 4.5–5. $H_2NC(CH_2OH)_3 + H^+ \longrightarrow H_3^+NC(CH_2OH)_3$
Na_2CO_3 Sodium carbonate	105.99	Primary standard grade Na_2CO_3 is titrated with acid to an end point of pH 4–5. Just before the end point, the solution is boiled to expel CO_2.
$Na_2B_4O_7 \cdot 10H_2O$ Borax	381.37	The recrystallized material is dried in a chamber containing an aqueous solution saturated with NaCl and sucrose. This procedure gives the decahydrate in pure form. The standard is titrated with acid to a methyl red end point. $"B_4O_7^{2-} \cdot 10H_2O" + 2H^+ \longrightarrow 4B(OH)_3 + 5H_2O$

Notes:

Standard Solutions

Standard solutions play a key role in titrimetric methods.

"Secondary Standard" – do not meet requirements for a primary standard but are available with sufficient purity and properties to be generally acceptable

Desirable properties of a Standard Solution:

- Prepared from primary standard
- Stable
- Reacts rapidly and completely with analyte
- Reacts selectively with analyte

Examples of Standard Materials

Notes:

Primary

Potassium Acid Phthalate

$KHC_8H_4O_4$

Benzoic Acid

C_6H_5COOH

Na_2CO_3 , $KH(IO_3)_2$

Arsenious Oxide (As_2O_3)

Sodium Oxalate ($Na_2C_2O_4$)

KI , $K_2Cr_2O_7$, Fe (pure)

Secondary

NaOH , KOH , $Ba(OH)_2$

HCl , HNO_3 , $HClO_4$

HSO_3NH_2

$KMnO_4$, $Na_2S_2O_3$

$Ce(HSO_4)_4$

Volumetric Analysis – Principles

Notes:

Standardization – involves establishing the concentration of a "standard solution"

Direct method:

dissolve carefully weighed quantity of primary standard; dilute to known volume

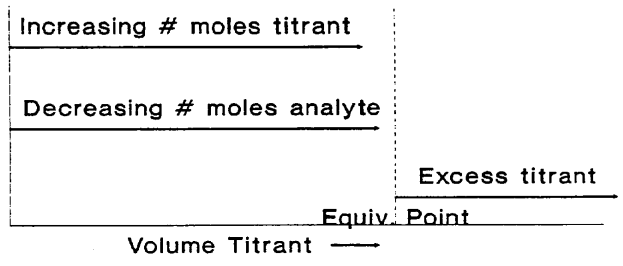
Indirect methods:

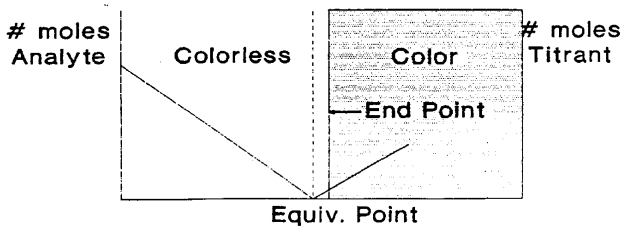
- Titrate weighed quantity of primary standard
- Titrate weighed quantity of secondary standard
- Titrate measured volume of other standard solution

Principles of volumetric analysis

Notes:

Titration Characteristics:





Notes:

Stoichiometric ratios (mole ratio)

$$V_c \cdot C_c = V_d \cdot C_d$$

What are stoichiometric ratios (mole ratios)?

$2\ HCl + Ba(OH)_2 \rightarrow 2\ HOH + Ba^{2+} + 2\ Cl^-$

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

Titration Types

Notes:

1. Acid-base

$HCl + NaOH \rightarrow H_2O + NaCl$

2. Redox

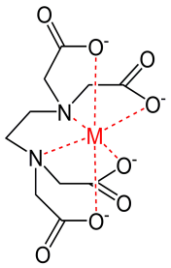
$5NaC_2O_4 + 2\ KMnO_4 + 6H^+ \rightarrow 10CO_2 + 2Mn^{2+} + 8H_2O$

3. Precipitation

$Ag^+ + X^- \rightarrow AgX\ (s)$

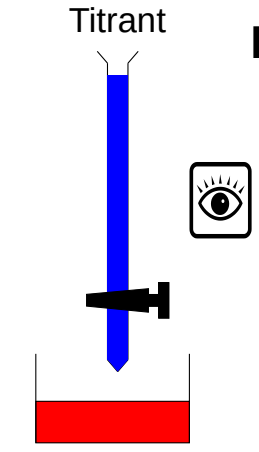
4. Complex formation (EDTA)

ethylenediaminetetraacetic acid



Notes:

Principle of a manual titration



- optical detection
- manual control
- manual addition

Burette and flask indicators
Phenolphthalein red (base) to colourless (acid)

Titration to an end-point

Amount of titrant = amount of analyte

Amount must be defined in a convenient form

Name	Colour		
	$[H^+] > [OH^-]$ **pH < 7**	$[H^+] = [OH^-]$ **pH = 7**	$[OH^-] > [H^+]$ **pH > 7**
litmus	**red**	**purple**	**blue**
phenolphthalein	**colourless**	**colourless**	**crimson**
methyl-orange	**pink**	**peach**	**yellow**

Notes:

Koltgof's multipurpose indicator

strong **weak** **weak** **strong**

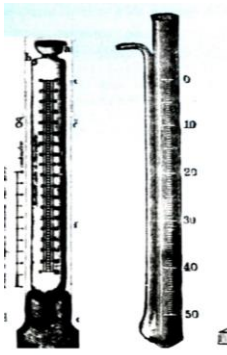
acid **neutral** **base**

Notes:

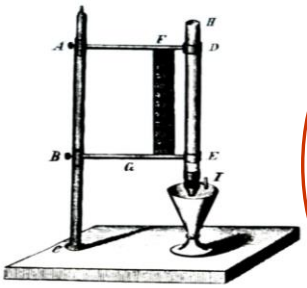
Titrations. Burette Evolution

Primary tool for titration

Gay-Lussac (1824)
Blow out liquid

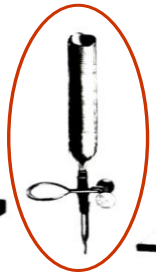


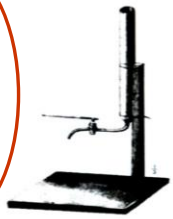
Descroizilles (1806)
Pour out liquid



Henry (1846)
Copper stopcock

Mohr (1855)
Compression clip
Used for 100 years





Mohr (1855)
Glass stopcock

Notes:

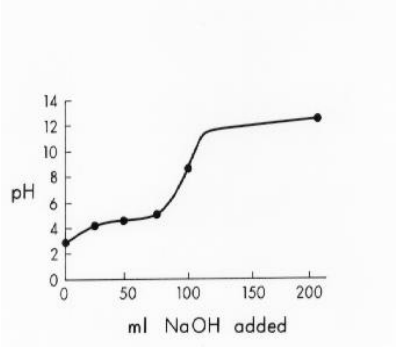
Titration steps

- sample preparation (homogeneity)
- titrant preparation
- titer determination
- burette/ sample size choice
- correct arrangement in titration vessel
- stirrer rate
- method parameters
- results calculation
- report

Titration Curves

Notes:

Example of a sigmoidal titration curve once calculations of data have been computed



A titration curve is a plot of pH vs. the amount of titrant added.

Typically the titrant is a strong and completely dissociated acid or base.

Such curves are useful for determining endpoints and dissociation constants of weak acids or bases.

Algebraic relationship

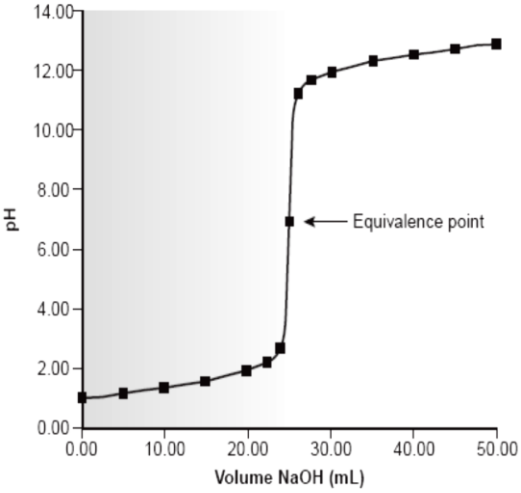
Notes:

At the equivalence point:

Equivalent A = Equivalent B

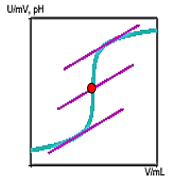
If the reaction is 1:1

Mol A = Mol B

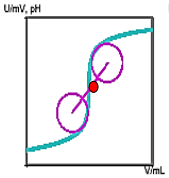


Equivalence point evaluation

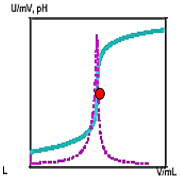
Notes:



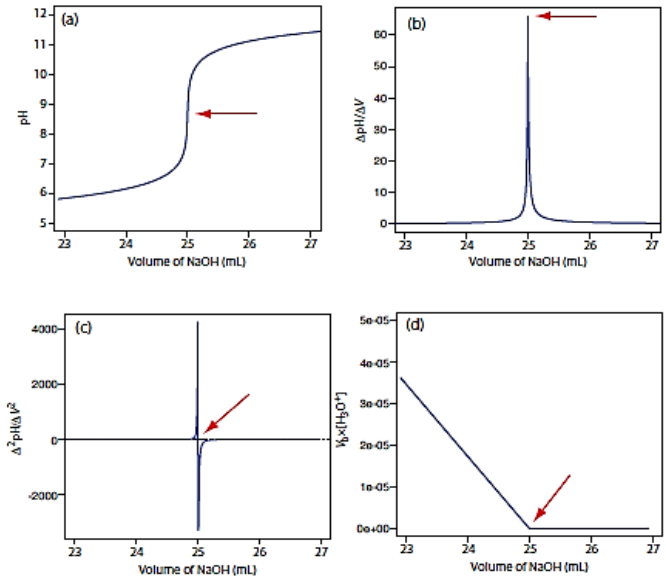
tangent method



circle method



derivative method



Acid & Bases

Notes:

Arrhenius: Acids are proton (H^+) sources and bases are hydroxide ion (OH^-) sources.

E.g. HCl is an acid and NaOH a base

Broensted-Lowry: Acids are proton sources and bases are proton acceptors.

E.g. HCl is an acid and NH_3 a base, these form the conjugate base Cl^- & NH_4^+

Lewis: Acids are electron pair acceptors and bases are electron pair donors.

E.g. $AlCl_3$ & $:NH_3$ to form $Cl_3Al:NH_3$

Acids and Bases

Notes:

Arrhenius

acids: generate H^+ in water

bases: generate OH^- in water

Broensted-Lowry

acids: H^+ donors

bases: H^+ acceptors

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{H_2O} \rightarrow Cl^- + H_3O^+$$

Conjugate acid-base pairs

Notes:

Conjugate base:

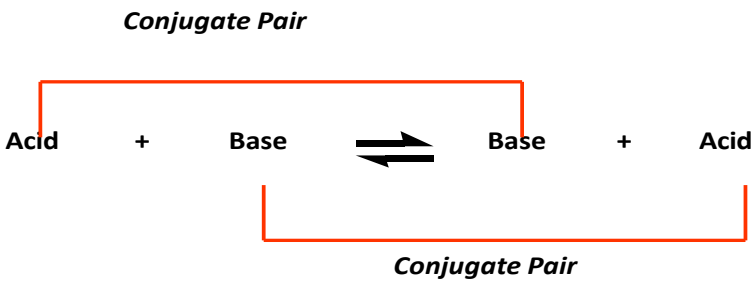
remains after H^+ is lost

acid: HCl conj. base: Cl^-

Conjugate acid:

remains after H^+ is gained

base: NH_3 conj. acid: NH_4^+



Notes:

Conjugate pairs in some acid-base reactions

	Acid	+	Base	⇌	Base	+	Acid
					Conjugate Pair		
Reaction 1	HF	+	H_2O	⇌	F^-	+	H_3O^+
Reaction 2	$HCOOH$	+	CN^-	⇌	$HCOO^-$	+	HCN
Reaction 3	NH_4^+	+	CO_3^{2-}	⇌	NH_3	+	HCO_3^-
Reaction 4	$H_2PO_4^-$	+	OH^-	⇌	HPO_4^{2-}	+	H_2O
Reaction 5	H_2SO_4	+	$N_2H_5^+$	⇌	HSO_4^-	+	$N_2H_6^{2+}$
Reaction 6	HPO_4^{2-}	+	SO_3^{2-}	⇌	PO_4^{3-}	+	HSO_3^-

Notes:

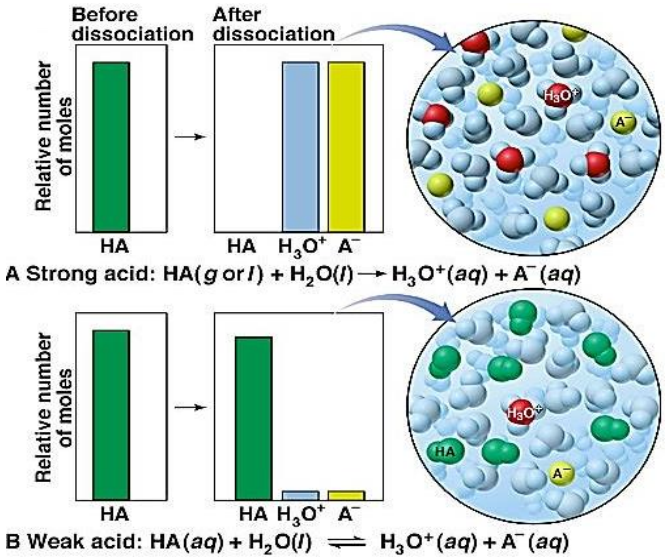
Strong and Weak Acids

Strong: **100%** dissociation
good H^+ donor
equilibrium lies far to right (HNO_3)
generates weak base (NO_3^-)

Weak: **<100%** dissociation
not-as-good H^+ donor
equilibrium lies far to left (CH_3COOH)
generates strong base (CH_3COO^-)

Notes:

Dissociation of strong vs weak acids



Acid-base equilibria

Notes:

For now, an acid is a proton (H^+) donor and a base is either a proton acceptor or a hydroxide (OH^-) donor. Water will be the solvent throughout this discussion.

Water dissociates to give <u>both</u> a proton and a hydroxide ion. This may be written several ways.

We choose to write it in the simplest, least correct, way more often

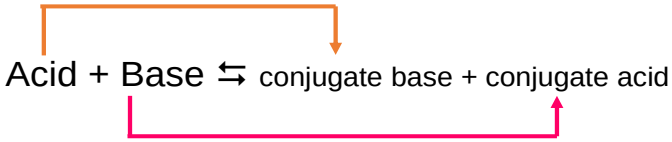
$$H_2O \leftrightarrows H^+ + OH^-$$

For any other type solution, the hydrogen or hydroxide ion concentrations will depend on BOTH the dissociation of water and ions contributed by other components of a solution.

For example, if we make a 0.20 M solution of nitric acid the hydrogen ion concentration would depend on the hydrogen ion from the nitric acid and from the dissociation of water.

Notes:

A standard acid/base reaction



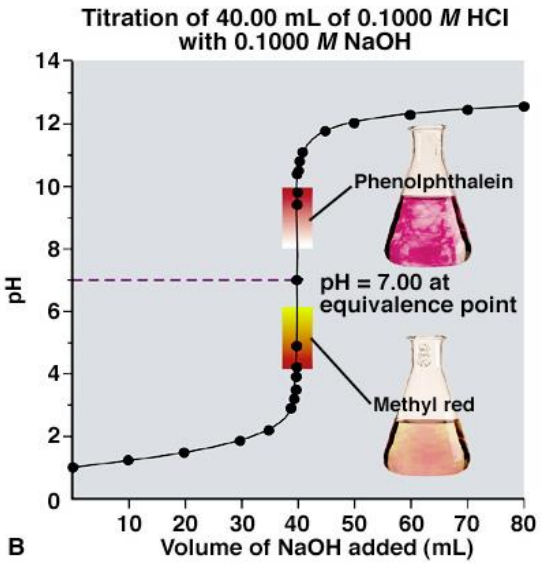
ex: $CH_3COOH + H_2O \leftrightarrows CH_3COO^- + H_3O^+$

$NH_3 + H_2O \leftrightarrows NH_4^+ + OH^-$

Notes:

Features of the strong acid - strong base titration curve

1. The pH starts out low, reflecting the high $[H_3O^+]$ of the strong acid and increases gradually as acid is neutralized by the added base.
2. Suddenly the pH rises steeply. This occurs in the immediate vicinity of the equivalence point. For this type of titration the pH is 7.0 at the equivalence point.
3. Beyond this steep portion, the pH increases slowly as more base is added.

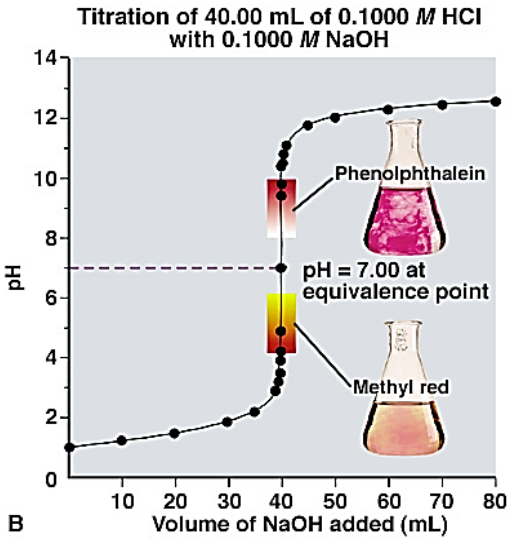


Strong acid-base titration curve

Notes:

Volume of NaOH added (mL)	pH
00.00	1.00
10.00	1.22
20.00	1.48
30.00	1.85
35.00	2.18
39.00	2.89
39.50	3.20
39.75	3.50
39.90	3.90
39.95	4.20
39.99	4.90
40.00	7.00
40.01	9.40
40.05	9.80
40.10	10.40
40.25	10.50
40.50	10.79
41.00	11.09
45.00	11.76
50.00	12.05
60.00	12.30
70.00	12.43
80.00	12.52

A



B

Selected primary standards for the standardization of strong acid and strong base titrants

Notes:

Primary Standard	Titration Reaction	Comment
Standardization of Acidic Titrants		
Na_2CO_3	$Na_2CO_3 + 2H_3O^+ \rightarrow H_2CO_3 + 2Na^+ + 2H_2O$	a
TRIS	$(HOCH_2)_3CNH_2 + H_3O^+ \rightarrow (HOCH_2)_3CNH_3^+ + H_2O$	b
$Na_2B_4O_7$	$Na_2B_4O_7 + 2H_3O^+ + 3H_2O \rightarrow 2Na^+ + 4H_3BO_3$	
Standardization of Basic Titrants		
$KHC_8H_4O_4$	$KHC_8H_4O_4 + OH^- \rightarrow K^+ + C_8H_4O_4^{2-} + H_2O$	c
C_6H_5COOH	$C_6H_5COOH + OH^- \rightarrow C_6H_5COO^- + H_2O$	d
$KH(IO_3)_2$	$KH(IO_3)_2 + OH^- \rightarrow K^+ + 2IO_3^- + H_2O$	

[a]The end point for this titration is improved by titrating to the second equivalence point, boiling the solution to expel CO_2, and retitrating to the second equivalence point. In this case the reaction is

$$Na_2CO_3 + 2H_3O^+ \rightarrow CO_2 + 2Na^+ + 3H_2O$$

[b]TRIS stands for *tris*-(hydroxymethyl)aminomethane.

[c]$KHC_8H_4O_4$ is also known as potassium hydrogen phthalate, or KHP.

[d]Due to its poor solubility in water, benzoic acid is dissolved in a small amount of ethanol before being diluted with water.

Notes:

Sample calculation: Strong acid - strong base titration curve

Problem. Consider the titration of 40.0 mL of 0.100 M HCl with 0.100 M NaOH.

Region 1. Before the equivalence point, after adding 20.0 mL of 0.100 M NaOH. (Half way to the equivalence point.)

Initial moles of H_3O^+ - Moles of OH^- added

$$[H_3O^+] = \frac{\text{amount (mol) of } H_3O^+ \text{ remaining}}{\text{original volume of acid} + \text{volume of added base}}$$

Sample calculation: Strong acid - strong base titration curve

Notes:

Region 2. At the equivalence point, after adding 40.0 mL of 0.100 M NaOH.

Initial moles of H_3O^+ = 0.0400 L x 0.100 M = 0.00400 M H_3O^+

- Moles of OH^- added = 0.0400 L x 0.100 M =0.00400 mol OH^-

$$[H_3O^+] = \frac{\text{amount (mol) of } H_3O^+ \text{ remaining}}{\text{original volume of acid} + \text{volume of added base}}$$

Region 3. After the equivalence point, after adding 50.0 mL of 0.100 M NaOH. (Now calculate excess OH^-)

Total moles of OH^- = 0.0500 L x 0.100 M = 0.00500 mol OH^- -Moles of H_3O^+ consumed = 0.0400 L x 0.100 M =0.00400 mol

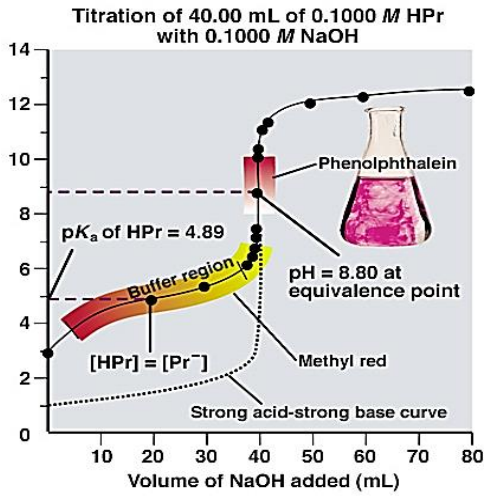
$$[OH^-] = \frac{\text{amount (mol) of } OH^- \text{ remaining}}{\text{original volume of acid} + \text{volume of added base}}$$

Notes:

The four major differences between a strong acid - strong base titration curve and a weak acid-strong base titration curve

HPr = Propionic Acid

1. The initial pH is higher.
2. A gradually rising portion of the curve, called the buffer region, appears before the steep rise to the equivalence point.
3. The pH at the equivalence point is greater than 7.00.
4. The steep rise interval is less pronounced.



TITRATION CURVES for weak acids or base

Notes:

- At the beginning, the solution contains only a weak acid or a weak base, and the pH is calculated from the concentration of that and its dissociation constant.
- After various increment of titrant have been added, the solution consists of a series of buffers. The pH of each buffer can be calculated from the analytical concentration of the conjugate base or acid and the residual concentration of the weak acid or base.
- At equivalence point, the solution contains only the conjugate of the weak acid or base being titrated, and the pH is calculated from the concentration of this product
- Beyond the equivalence point, the excess of strong acid or base titrate represses the acidic or basic character of the reaction product to such an extent that the pH is governed largely by the concentration of the excess titrant.

Notes:

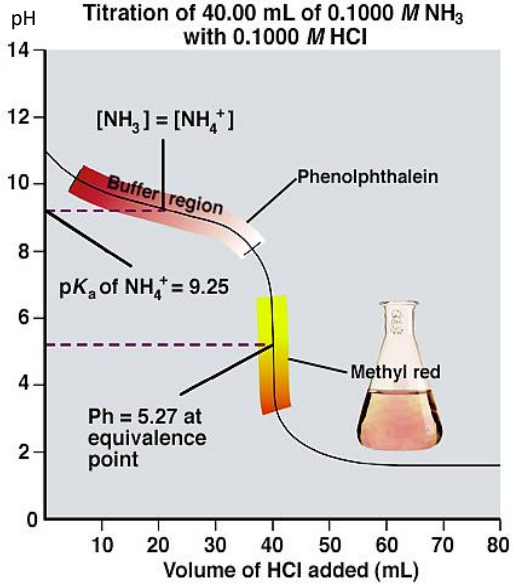
Finding the End Point with a visual indicator.

One interesting group of weak acids and bases are derivatives of organic dyes. Because such compounds have at least one conjugate acid-base species that is highly coloured, their titration results in a change in both pH and colour.

This change in colour can serve as a useful means for determining the end point of a titration, provided that it occurs at the titration's equivalence point.

Weak base – strong acid titration curve

Notes:



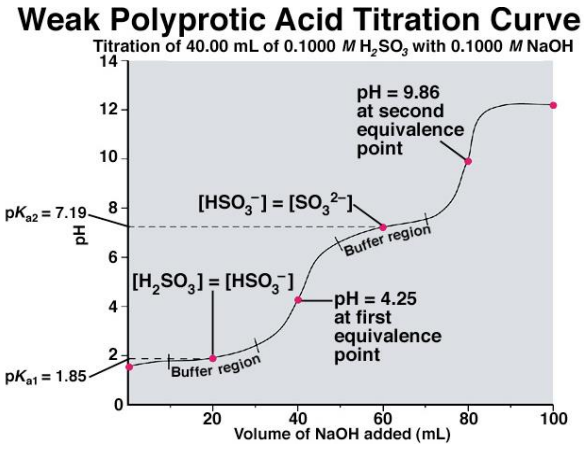
Notes:

Features of the titration of a polyprotic acid with a strong base

1.The loss of each mole of H^+ shows up as separate equivalence point (but only if the two pK_as are separated by more than 3 pK units).

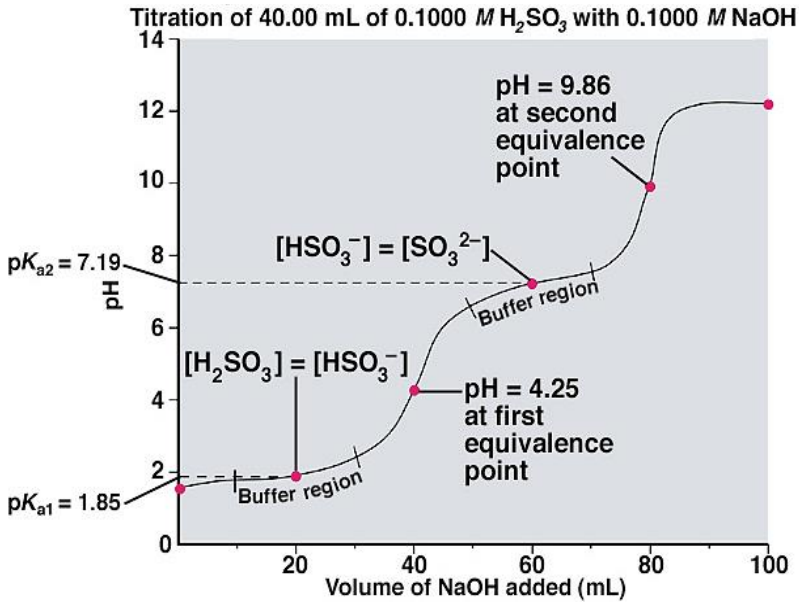
2.The pH at the midpoint of the buffer region is equal to the pK_a of that acid species.

3.The same volume of added base is required to remove each mole of H^+



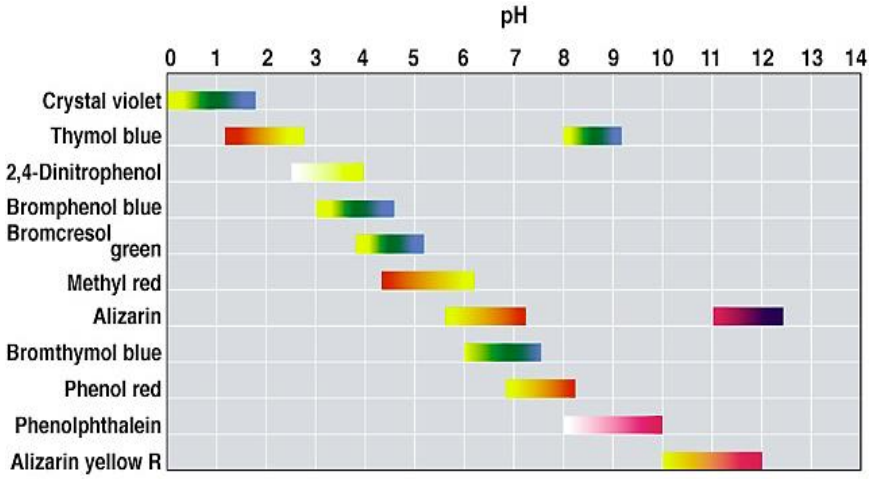
Weak polyprotic acid titration curve

Notes:



Notes:

pH range of acid-base indicators



Acid-base indicators and the measurement of pH

Notes:

- Definition: A weak organic acid, HIn that has a different color than its conjugate base, In^-, with the color change occurring over a specific and r**el**atively narrow pH range.
- Typically, one or both forms are intensely colored, so only a tiny amount of indicator is needed, far too little to perturb the pH of the solution.
- Since the indicator molecule is a weak acid, the ratio of the two forms governed by the $[H_3O^+]$ of the test solution:

$$HIn(aq) + H_2O(l) = H_3O^+(aq) + In^-(aq) \qquad K_a \text{ of } HIn = \frac{[H_3O^+][In^-]}{[HIn]}$$

Therefore: $$\frac{[HIn]}{[In^-]} = \frac{[H_3O^+]}{[K_a]}$$

Titration calculations

Notes:

Example: Calculating the Molarity of standard solutions

Describe the preparation of a 5.0 L of 0.10 M Na_2CO_3 (105.99 g/mol) from the primary standard solution.

Amount Na_2CO_3 = *n* Na_2CO_3 (mol) = Volume solution x *c* Na_2CO_3 (mol/ L)
= 5 L x $\underline{0.1 \text{ mol } Na_2CO_3}$ = 0.5 mol Na_2CO_3 / L

Mass Na_2CO_3 = *m*Na_2CO_3=0.5 mol Na_2CO_3 x $\underline{105.99 \text{ g } Na_2CO_3}$ =
=53 g Na_2CO_3

The solution is prepared by dissolving 53 g of Na_2CO_3 in water and diluting to 5 L

How to deal with titration data

Notes:

The following two examples show the two types of volumetric calculations.

The first involves computing the molarity of solutions that have been standardized against either a primary standard or another standard solution.

The second example involves calculating the amount of analyte in a sample of titration data.

Example: Molarity of solutions that have been standardized.

A 50mL volume of HCl solution required 29.71mL of 0.01963 M $Ba(OH)_2$ to reach an end point with bromocresol green indicator.

Calculate the normality of the HCl.

Notes:

Method of a separate samples

$m_{(A)} = (C_{eq(B)} \cdot V_{(B)} \cdot M_{eq(A)}) / 1000$

Method pipet

$m_{(A)} = (C_{eq(B)} \cdot V_{(B)} \cdot M_{eq(A)} \cdot V_f) / (V_{al(A)} \cdot 1000)$,

where

$C_{eq(B)}$ or $N_{(B)}$ – normality of a titrants solution, mol·eq/L
$V_{(B)}$ – volume of a titrants solution, mL
$M_{eq(A)}$ or $E_{eq(A)}$ – mass of the 1 mol substance, g/mol
V_f – volume volumetric flask, mL
$V_{al(A)}$ – volume aliquot of a substances solution, mL

Notes:

The problem. Calculate the weight of KOH contained in 250.0 ml of solution if 21.35 ml of 0.05316 normal sulfate acid solution is consumed for a titration of 25.0 ml of the solution mentioned above.

The solution.

The product of $N(H_2SO_4)$ x $V(H_2SO_4)$ yields the number of milliequivalents of sulfuric acid that reacts with KOH in a volume of 25.0 ml. This volume contains the same quantity of milliequivalents of KOH. If we multiply them by the mass of the equivalent, then we get the mass of alkali in this volume.

$$m_{KOH} = N(H_2SO_4) \times V(H_2SO_4) \times EKOH \ \ (mg)$$

$$m_{KOH} = \frac{N(H_2SO_4) \times V(H_2SO_4) \times EKOH}{1000} \ \text{(g)}$$

In a volume of 250 ml the mass of KOH will be 250/25 times greater.

In other words, taking into account the dilution, the mass of alkali in the flask is equal to:

$$m_{KOH} = \frac{N(H_2SO_4) \times V(H_2SO_4) \times EKOH \times V_{flask}}{V_a \times 1000}$$

$$m_{KOH} = \frac{21.35 \times 0.05316 \times 56.1 \times 250}{25 \times 1000} = 0.6367 \text{ g}$$

Tasks to Section 7:

1. Give definitions of these terms: titrimetric method, titration, equivalence point, endpoint, titration curve, direct titration, back titration, acid-base titration, p-function, volumetric titrimetry, gravimetric titrimetry, coulometric titrimetry, standard solution, primary standard, titration error.

2. Distinguish the terms endpoint and equivalence point.

3. Why does an acid-base titration curve (pH versus volume of titrant) have an abrupt change at the equivalence point?

4. Sketch the general appearance of the curve for the titration of a weak acid with a strong base. Explain (in words) what chemistry governs the pH in each of the four distinct regions of the curve.

5. Why is it not practical to titrate an acid or a base that is too weak or too dilute?

6. You have a standard solution of 0.01 M Na+. How would you prepare three diluted standard solutions, each of 50 mL in volume, that contain 0.005 M, 0.002 M, and 0.001 M Na^+, respectively, using this standard?

7. The solution contains 0,1 normal ammonium hydroxide and 0,2 molar ammonium chloride. Calculate $[OH^-]$ and pH of the solution.

8. The water solution contains 10,5 gram of ammonium acetate in 0.25 L. Calculate h and pH of the solution.

9. Calculate the pH at each of the following points in the titration of 50.00 mL of 0.0100 M NaOH with 0.100 M HCl. Volume of acid added: 0.00, 1.00, 2.00, 3.00, 4.00, 4.50, 4.90, 4.99, 5.00, 5.01, 5.10, 5.50, 6.00, 8.00, and 10.00 mL. Make a graph of pH versus volume of HCl added.

10. Calculate the pH at each point listed for the titration of 50.0 mL of 0.050 0 M formic acid with 0.050 0 M KOH. The points to calculate are Vb 0.0, 10.0, 20.0, 25.0, 30.0, 40.0, 45.0, 48.0, 49.0, 49.5, 50.0, 50.5, 51.0, 52.0, 55.0, and 60.0 mL. Draw a graph of pH versus Vb.

11. Consider the titration of 50.0 mL of 0.050 0 M malonic acid with 0.100 M NaOH. Calculate the pH at each point listed and sketch the titration curve: Vb 0.0, 8.0, 12.5, 19.3, 25.0, 37.5, 50.0, and 56.3 mL.

12. Finding the endpoint from pH measurements. Here are data points around the second apparent endpoint:

Vb (L)	pH	Vb (L)	pH
107.0	6.92	117.0	7.89
110.0	7.12	118.0	8.10
113.0	7.36	119.0	8.34
114.0	7.46	120.0	8.59
115.0	7.57	121.0	8.79
116.0	7.71	122.0	8.95

Section 8: Complexometric and Redox Titration

Contents:

Introduction

Practical analytical application of the method of complexometric titration developed slowly. Many metals and ligands form many metal-ligand complexes. It is challenging to develop a selective complexometric method. The earliest examples of complexometric titration are the determination of cyanide and chloride ions using solutions containing Ag^{+} and Hg^{2+}.

Liebig titration for cyanide ions was successful because cyanide and Argentum ions form a single stable complex. Interaction gives a single endpoint that is easy to identify. Other metal-ligand complexes, for example between Cadmium and Iodide ions, are not analytically useful. They form several metal-ligand complexes of variable composition. Therefore, the endpoint of the titration is very difficult to determine.

In the early 20th century, Schwarzenbach has been used amino carboxylic acids as ligands. Now the ethylenediaminetetraacetic acid or EDTA is the most widely used of these new ligands. EDTA is a merciful abbreviation for ethylenediaminetetraacetic acid. This compound forms strong 1:1 complexes with most metal ions, binding through four oxygen and two nitrogen atoms.

EDTA finds wide use in quantitative analysis. Using EDTA allows obtaining an identifiable endpoint of the titration quickly. Application of EDTA as a ligand has made complexometric titrimetry a practical analytical method.

EDTA plays a larger role as a strong metal-binding agent in industrial processes and products such as detergents, cleaning agents, and food additives that prevent metal-catalysed oxidation of food.

A redox titration is based on an oxidation-reduction reaction between analyte and titrant.

In addition to the many common analytes in chemistry, biology, and environmental and materials science that can be measured by redox titrations, exotic oxidation states of elements in uncommon materials such as superconductors and laser materials are measured by redox titrations. For example, chromium added to laser crystals to increase their efficiency is found in the common oxidation states +3 and +6, and the unusual +4 state. A redox titration is a good way to unravel the nature of this complex mixture of chromium ions.

This chapter introduces the theory of redox titrations and discusses some common reagents. A few of the oxidants and reductants can be used as titrants. Most reductants used as titrants react with O_2 and, therefore, require protection from the air.

The number of redox titrimetric methods increased in the mid-1800s with the introduction of MnO_4^{-}, $Cr_2O_7^{2-}$, and I_2 as oxidizing titrants, and of Fe^{2+} and $S_2O_3^{2-}$ as reducing titrants. Even with the availability of these new titrants, redox titrimetry was slow to develop due to the lack of suitable indicators. A titrant can serve as its own indicator if its oxidized and reduced forms differ significantly in colour. For example, the intensely purple MnO_4^{-} ion serves as its own indicator since its reduced form, Mn^{2+}, is almost colourless. Other titrants require a separate indicator. The first such indicator, diphenylamine, was introduced in the 1920s. Other redox indicators soon followed, increasing the applicability of redox titrimetry

Although other analytical methods have replaced many quantitative applications of redox titrimetry, a few essential applications continue to be relevant. In this section, we review the general application of redox titrimetry with an emphasis on environmental, pharmaceutical, and industrial applications. We begin with a brief discussion of selecting and characterizing redox titrants, and methods for controlling the titrant's oxidation state.

Complexometric titrations

Notes:

Complexometry: is the type of volumetric analysis involving the formation of complexes which are slightly ionized in solution, like weak electrolyte and sparingly soluble salt.

Complex is formed by the reaction of metal ion **(M^{n+})** with either an anion e.g. **$[Ag(CN)_2]^-$** or neutral molecule, e.g. **$[Ag(NH_3)_2]^+$**

The metal ion is known as **Central metal atom.**

The anion or neutral molecule is known as **Ligand.**

Notes:

A **coordination complex** is the product of a Lewis acid-base reaction in which neutral molecules or anions (called ligands and mark L) bond to a central metal atom (or ion) by **coordinate** covalent bonds.

$$\underbrace{K_3}_{\text{Counter ion}}\underbrace{[Fe(CN)_6]}_{\text{Coordinate sphere}}$$

Notes:

$$K_4[Fe(CN)_6] \overset{aq}{\Leftrightarrow} 4K^+ + [Fe(CN)_6]^{4-}$$

Central metal atom ↓ Ligand ↓

$$K_4[\underbrace{Fe(CN)_6}_{\text{Coordination sphere (entity)}}] \leftarrow \text{Coordination number}$$

↑ Counter ion

Notes:

$$M^+ + L \rightleftharpoons ML$$
$$Ag^+ + 2\,CN^- \rightleftharpoons [Ag(CN)_2]^-$$
$$Cu^{2+} + 4\,CN^- \rightleftharpoons [Cu(CN)_4]^{2-}$$
$$Ag^+ + 2\,NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$$
$$Cu^{2+} + 4\,NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$$

Central metal atom acts as Lewis acid (electron acceptor)

Ligand acts as Lewis base (electron donor)

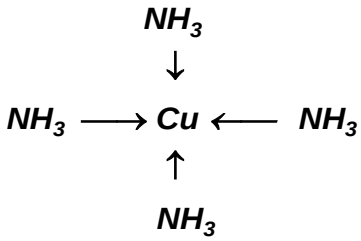
Coordinate bond (dative) = The bond is formed between central metal atom (ion) (**acceptor**) and the Ligand (**donor**)

Notes:

Dative bond is similar to covalent bond (that is formed by two electrons)

But in dative bond the electrons pair are donated from one atom to the other. The atom gives electron pair is known as donor, while the atom accept electron pair is known as acceptor.

The bond is represented by an arrow **(⟶)** from donor to acceptor.



Notes:

The number, indicating how many ligands are coordinated around the central atom, is called

the coordination number (c.n.).

The coordination number is often twice as much as the oxidation degree of the complexing agent.

For example, if the oxidation degree of the complexing agent is +1, then c. n. = 2

$\overset{+1}{[Ag(NH_3)_2]^+}$ $\overset{+2}{[Zn(OH)_4]^{2-}}$, $\overset{+3}{[Co(NO_2)_6]^{3-}}$

Characters of coordination number

Notes:

2 Ag^{+}

4 Ni^{2+} , Cu^{2+}

6 Fe^{3+} , Cr^{3+}

The charge of a complex is the algebraic sum of the charges of the central ion and ligand

$$[Ag(CN)_2]^{-} \Rightarrow Ag^{+} + 2\,CN^{-}$$

$$[Fe(CN)_6]^{3-} \Rightarrow Fe^{3+} + 6\,CN^{-}$$

The higher the valence of metal ion the more stable the complex. Ferricyanide is more stable than Ferrocyanide

Classification of ligands according to the number of sites of attachment to the metal ion

Notes:

Unidentate (Monodentate) Ligand or **"Simple Ligand"**

The ligand attached to metal at one site e.g. H_2O, NH_3, CN^-, Cl^-, I^-, Br^- **(i.e.** forming one coordinate bond, or capable of donating one unshared pair of electrons)

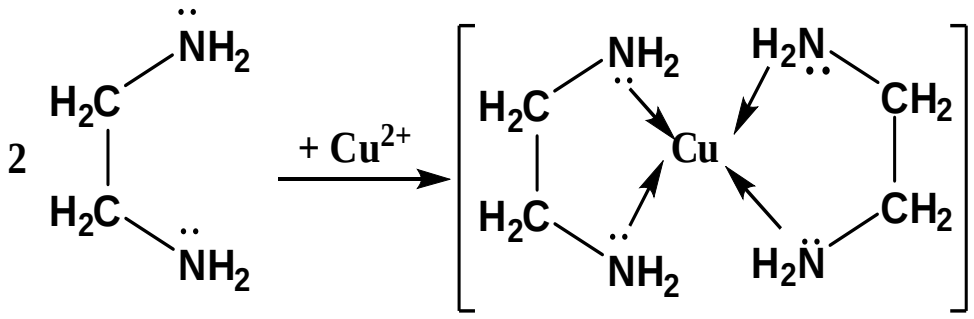
$$H_3N: \rightarrow Ag \leftarrow :NH_3$$

$$Cu^{2+} + 4NH_3 \leftrightarrow \left[\begin{array}{ccc} & :NH_3 & \\ & \downarrow & \\ H_3N: \rightarrow & Cu & \leftarrow :NH_3 \\ & \uparrow & \\ & :NH_3 & \end{array}\right]^{2+}$$

Bidentate Ligand

Notes:

The ligand attached to metal at two sites.

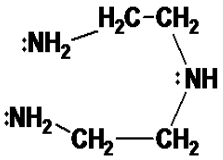


Ethylene diamine

Tridentate Ligand:

Notes:

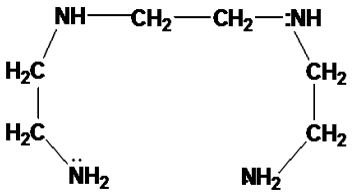
The Ligand attached to metal at 3 sites



Diethylene triamine

Tetradentate Ligand:

The Ligand attached to metal at 4 sites



Triethylene tetramine

Chelation

Notes:

Chelate: It is a complex formed between the ligand containing two or more donor groups and metal to form ring structure. (heterocyclic rings or chelate rings).

Chelating agents: organic molecules containing two or more donor groups which combine with metal to form complex having ring structure.

Chelates are usually insoluble in water but soluble in organic solvent.

Sequestering agent: Ligands which form water soluble chelates e.g. EDTA.

Factors affecting stability of complex

Notes:

Effect of central metal ion:

Ionic size (metal radius):

The smaller an ion (small radius of metal) the greater its electrical field ⟶ more stable complex

Ionic charge (metal charge):

Metal of higher charge give more stable complexes.

Ferricyanide [hexacyanoferrate III] is more stable than Ferrocyanide [hexocyanoferrate II].

Electronegativity:

The higher acidity (electronegativity) of metal (M^{n+}) the higher stability of complex.

Metal which has incomplete outer shell (has high acidity) have more tendency to accept electrons ⇨ more stable complex.

e.g. Ca^{2+} , Ni^{2+} , Zn^{2+} , Mn^{2+} , Cu^{2+}

Effect of Ligand:

Notes:

Basic character:

The higher the basicity (strong base is good electron donor) the higher the ability of ligand to form complex.

e.g. ligand contain electron donating atom.

$N > O > S > I^- > Br^- > Cl^- > F^-$

The extent of chelation:

Multidentate ligands form more stable complexes than monodentate.

Steric effect:

Large, bulky ligand form less stable complexes than smaller ones due to steric effect.

e.g. ethylene diamine complexes are more stable than those of the corresponding tetramethyl ethylene diamine.

COMPLEXOMETRIC TITRATION

Notes:

Complexometric titration is a form of volumetric analysis in which the formation of a colored complex is used to indicate the end point of a titration.

Complexometric titrations are particularly useful for the determination of a mixture of different **metal ions** in solution.

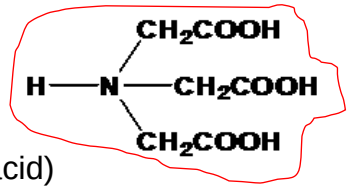
An indicator capable of producing an unambiguous color change is usually used to detect the end point of the titration.

Complexones

Notes:

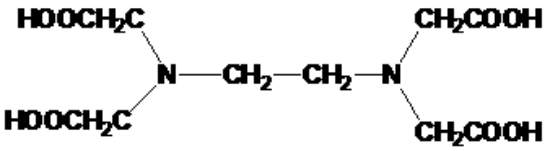
Amino polycarboxylic acid compounds used as complexing agents for many metal ions.

Complexone I: H_3Y



Nitrilo triacetic acid
(ammonia triacetic acid)

Complexone II: H_4Y



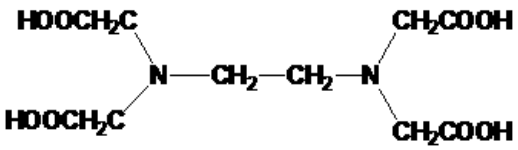
Ethylemediamine tetra acetic acid

Complexones

Notes:

Complexone II

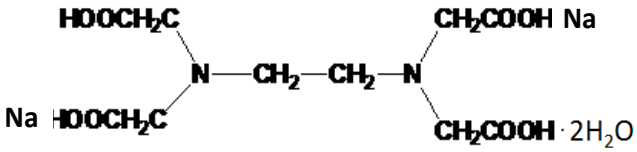
H_4Y



Ethylene diamine tetra acetic acid

Complexone III

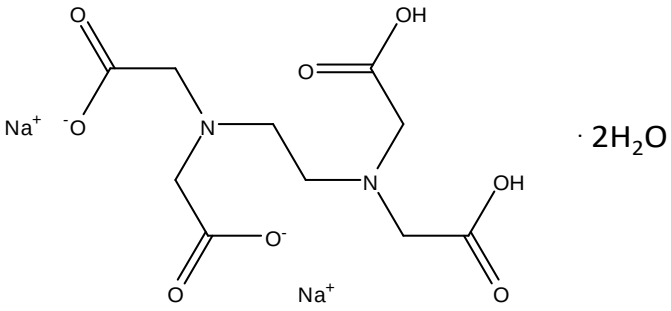
$Na_2H_2Y \cdot 2H_2O$



Sodium ethylene diamine tetra acetate

Complexone III: $Na_2H_2Y \cdot 2H_2O$

Notes:



Titration involving **EDTA** known as complexometric titration

EDTA is a hexadentate ligand, containing 4 oxygen and 2 nitrogen donor.

Notes:

It reacts with most cations (divalent, trivalent, tetravalent) forming freely stable complexes.

The formed complexes contain the metal and ***EDTA*** in the ratio of 1:1 irrespective to the charge of the metal ion.

The general reactions for the formation of metal – ***EDTA*** complexes are as follows:

$$M^{2+} + H_2Y^{2-} \rightleftharpoons MY^{2-} + 2H^+$$
$$M^{3+} + H_2Y^{2-} \rightleftharpoons MY^{-} + 2H^+$$
$$M^{4+} + H_2Y^{2-} \rightleftharpoons MY^{o} + 2H^+$$

$$M^{n+} + H_2Y^{2-} \rightleftharpoons (MY)^{n-4} + 2H^+$$

The basic form of EDTA (Y^{4-}) reacts with most metal ions to form a 1:1 complex

Notes:

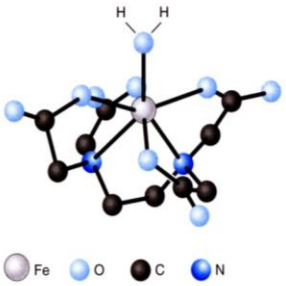


Table 12-2 Formation constants for metal-EDTA complexes

Ion	log K_f	Ion	log K_f	Ion	log K_f
Li^+	2.95	V^{3+}	25.9[a]	Tl^{3+}	35.3
Na^+	1.86	Cr^{3+}	23.4[a]	Bi^{3+}	27.8[a]
K^+	0.8	Mn^{3+}	25.2	Ce^{3+}	15.93
Be^{2+}	9.7	Fe^{3+}	25.1	Pr^{3+}	16.30
Mg^{2+}	8.79	Co^{3+}	41.4	Nd^{3+}	16.51
Ca^{2+}	10.65	Zr^{4+}	29.3	Pm^{3+}	16.9
Sr^{2+}	8.72	Hf^{4+}	29.5	Sm^{3+}	17.06
Ba^{2+}	7.88	VO^{2+}	18.7	Eu^{3+}	17.25
Ra^{2+}	7.4	VO_2^+	15.5	Gd^{3+}	17.35
Sc^{3+}	23.1[a]	Ag^+	7.20	Tb^{3+}	17.87
Y^{3+}	18.08	Tl^+	6.41	Dy^{3+}	18.30
La^{3+}	15.36	Pd^{2+}	25.6[a]	Ho^{3+}	18.56
V^{2+}	12.7[a]	Zn^{2+}	16.5	Er^{3+}	18.89
Cr^{2+}	13.6[a]	Cd^{2+}	16.5	Tm^{3+}	19.32
Mn^{2+}	13.89	Hg^{2+}	21.5	Yb^{3+}	19.49
Fe^{2+}	14.30	Sn^{2+}	18.3[b]	Lu^{3+}	19.74
Co^{2+}	16.45	Pb^{2+}	18.0	Th^{4+}	23.2
Ni^{2+}	18.4	Al^{3+}	16.4	U^{4+}	25.7
Cu^{2+}	18.78	Ga^{3+}	21.7		
Ti^{3+}	21.3	In^{3+}	24.9		

Notes:

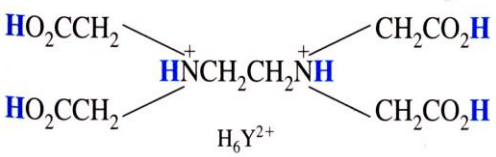
EDTA Ethylenediaminetetraacetic acid

One of the most common chelating agents used for complexometric titrations in analytical chemistry.

EDTA has *6* Nitrogen and Oxygen atoms in its structure giving it *6* free electron pairs that it can donate to metal ions.

High K_f values

***6* acid-base sites in its structure**



$pK_1 = 0.0$ (CO_2H) $\quad pK_4 = 2.69$ (CO_2H)

$pK_2 = 1.5$ (CO_2H) $\quad pK_5 = 6.13$ (NH^+)

$pK_3 = 2.00$ (CO_2H) $\quad pK_6 = 10.37$ (NH^+)

pK applies at 25°C and $\mu = 0.1$ M, except pK_1 applies at $\mu = 1$ M

Notes:

EDTA Complexes

The basic form of EDTA (Y^{4-}) reacts with most metal ions to form a 1:1 complex. **Other forms of EDTA will also chelate metal ions**

$$M^{n+} + Y^{4-} \rightleftharpoons MY^{n-4} \qquad K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y^{4-}]}$$

Recall: the concentration of Y^{4-} and the total concentration of EDTA is solution [EDTA] are related as follows:

This reaction only involves Y^{4-}, but not the other forms of EDTA

$$[Y^{4-}] = \alpha_{Y^{4-}}[EDTA]$$

where a_{Y4-} is dependent on pH

EDTA Complexes

Notes:

Substitute $[Y^{4-}]$ into K_f equation

$$[Y^{4-}] = \alpha_{Y^{4-}}[EDTA] \qquad K_f = \frac{[MY^{n-4}]}{[M^{n+}][Y^{4-}]}$$

$$K_f = \frac{[MY^{n-4}]}{[M^{n+}]\alpha_{Y^{4-}}[EDTA]}$$

where [EDTA] is the total concentration of EDTA added to the solution not bound to metal ions

If pH is fixed by a buffer, then a_{Y4-} is a constant that can be combined with K_f

Conditional or effective formation constant: (*at a given pH*)

$$K_f' = K = K_f \alpha_{Y^{4-}} = \frac{[MY^{n-4}]}{[M^{n+}][EDTA]}$$

EDTA Titration Curves

Notes:

$$M^{n+} + EDTA \rightleftharpoons MY^{n-4} \qquad K_f' = K_f \alpha_{Y^{4-}}$$

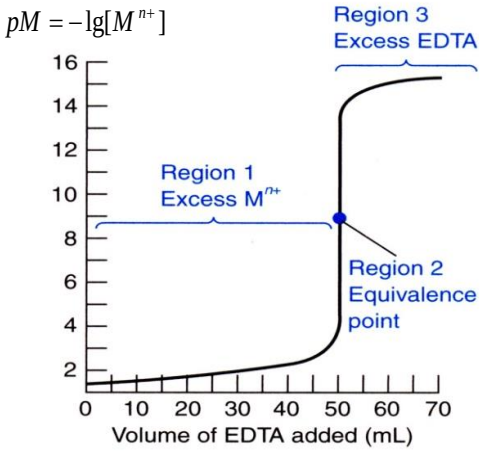
The titration of a metal ion with EDTA is similar to the titration of a strong acid (M^+) with a weak base (EDTA)

The Titration Curve has three distinct regions:

Before the equivalence point (excess M^{n+})

At the equivalence point $[EDTA]=[M^{n+}]$

After the equivalence point (excess EDTA)



Auxiliary Complexing Agents

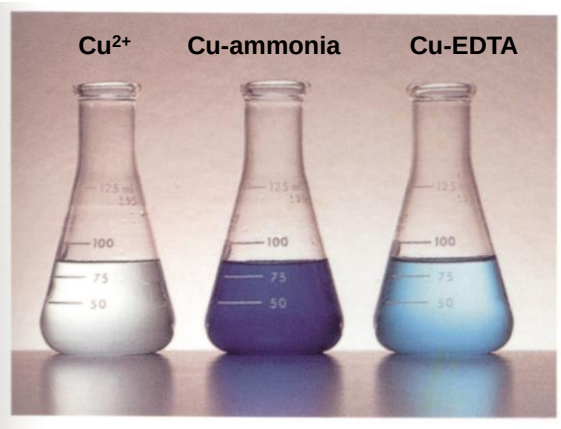
Notes:

Illustration: Titration of Cu^{2+} with EDTA

Addition of Ammonia Buffer results in a dark blue solution

Cu(II)-ammonia complex is formed

Addition of EDTA displaces ammonia with corresponding color change



pH Limitation

Notes:

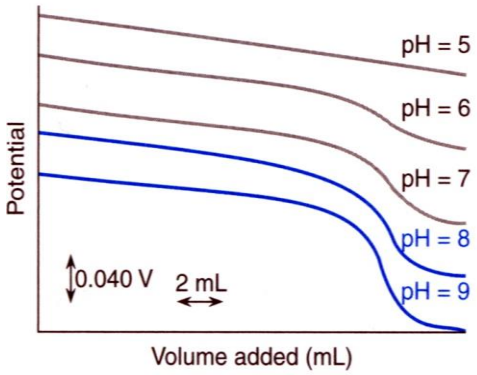
Note that the metal – EDTA complex becomes less stable as pH decreases

K_f decreases

$K_f[Fe^{3+}] = 5.4 \times 10^{-7}$ at pH 2.0

$K_f[Fe^{3+}] = 1.4 \times 10^{-12}$ at pH 8.0

In order to get a "complete" titration ($K_f \geq 10^6$), EDTA requires a certain minimum pH for the titration of each metal ion



End Point becomes less distinct as pH is lowered, limiting the utility of EDTA as a titrant

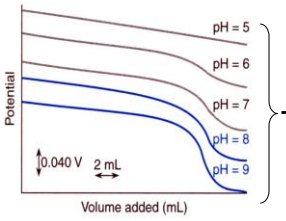
EDTA Titrations

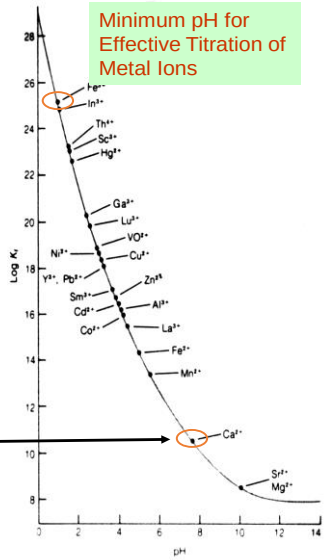
Notes:

pH Limitation

By adjusting the pH of an EDTA titration:

one type of metal ion (e.g. Fe^{3+}) can be titrated without interference from others (e.g. Ca^{2+})





Determination of EDTA Titration End Point

Notes:

Four Methods:

1. Metal ion indicator
2. Mercury electrode
3. pH electrode
4. Ion-selective electrode

} Potential Measurements

Metal ion indicator is a compound that changes colour when it binds to a metal ion

Similar to pH indicator, which changes colour with pH or as the compound binds H^+

For an EDTA titration, the indicator must bind the metal ion less strongly than EDTA

Needs to release metal ion to EDTA

End Point indicated by a color change from red to blue

$$\underset{\text{red}}{MgIn} + \underset{\text{colorless}}{EDTA} \longrightarrow \underset{\text{colorless}}{MgEDTA} + \underset{\text{blue}}{In}$$

EDTA Titrations

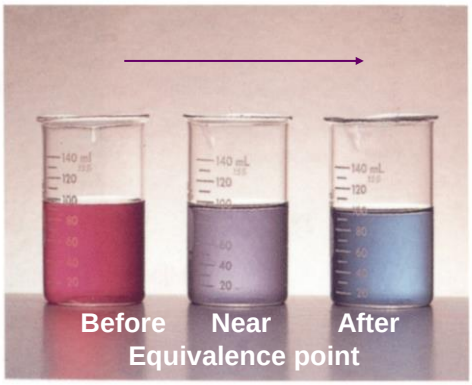
Notes:

Metal Ion Indicators

Titration of Mg^{2+} by EDTA

Eriochrome Black T Indicator

Addition of EDTA

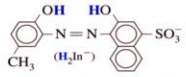
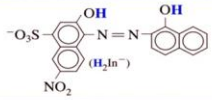
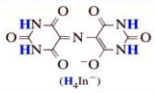
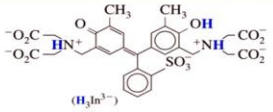
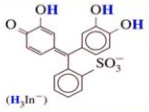


Common Metal Ion Indicators

Notes:

Most are pH indicators and can only be used over a given pH range

Common metal ion indicators

Name	Structure	pK_a	Color of free indicator	Color of metal ion complex
Calmagite		$pK_2 = 8.1$ $pK_3 = 12.4$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Eriochrome black T		$pK_2 = 6.3$ $pK_3 = 11.6$	H_2In^- red HIn^{2-} blue In^{3-} orange	Wine red
Murexide		$pK_2 = 9.2$ $pK_3 = 10.9$	H_4In^- red-violet H_3In^{2-} violet H_2In^{3-} blue	Yellow (with Co^{2+}, Ni^{2+}, Cu^{2+}); red with Ca^{2+}
Xylenol orange		$pK_2 = 2.32$ $pK_3 = 2.85$ $pK_4 = 6.70$ $pK_5 = 10.47$ $pK_6 = 12.23$	H_5In^- yellow H_4In^{2-} yellow H_3In^{3-} yellow H_2In^{4-} violet HIn^{5-} violet In^{6-} violet	Red
Pyrocatechol violet		$pK_1 = 0.2$ $pK_2 = 7.8$ $pK_3 = 9.8$ $pK_4 = 11.7$	H_4In red H_3In^- yellow H_2In^{2-} violet HIn^{3-} red-purple	Blue

Notes:

EDTA Titration Techniques

Almost all elements can be determined by EDTA titration.

Needs to be present at sufficient concentrations.

Some Common Techniques used in these titrations include:

Direct Titrations
Back Titrations
Displacement Titrations
Indirect Titrations
Masking Agents

EDTA Titration Techniques

Notes:

Direct Titrations

- Analyte is buffered to appropriate pH and is titrated directly with EDTA.
- An auxiliary complexing agent may be required to prevent precipitation of metal hydroxide.

Back Titrations

A known excess of EDTA is added to analyte.

Free EDTA left over after all metal ion is bound with EDTA.

The remaining excess of EDTA is then titrated with a standard solution of a second metal ion.

Approach necessary if analyte:

- Precipitates in the presence of EDTA
- Reacts slowly with EDTA
- Blocks the indicator

- Second metal ion must not displace analyte from EDTA

$$K_{f(analyte)}\alpha_{Y^{4-}} > K_{f(second\ metal\ ion)}\alpha_{Y^{4-}}$$

Notes:

Displacement Titration

- Used for some analytes that don't have satisfactory metal ion indicators
- Analyte (M^{n+}) is treated with excess $Mg(EDTA)^{2-}$, causes release of Mg^{2+}.

Requires: $K_{f(M^{n+})}\alpha_{Y^{4-}} > K_{f(Mg^{2+})}\alpha_{Y^{4-}}$

$$Mg^{n+} + MgY^{2-} \longrightarrow MY^{n-4} + Mg^{2+}$$

Amount of Mg^{2+} released is then determined by titration with a standard EDTA solution

Concentration of released Mg^{2+} equals $[M^{n+}]$

Masking and demasking agent

Notes:

Masking agents: are reagents which prevent interfering ion from reaction without physical separation.

These reagents form complexes with interfering ions which are more stable than complexes formed with ind. & **EDTA**.

Examples of masking agent:

KCN: It is used as masking agent for **Ag^{+} , Cu^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+}, Zn^{2+}**

$$M^{+} + 2\,CN^{-} \longrightarrow [M(CN)_2]^{-}$$
$$M^{+} + 4\,CN^{-} \longrightarrow [M(CN)_4]^{2-}$$

Fluoride NH_4F: It is used as masking agent for **Fe^{3+}** and **Al^{3+}** to give hexafluoro complex **$[FeF_6]^{3-}$** and **$[AlF_6]^{3-}$**

Iodide KI: It is used as masking agent for **Hg^{2+}** to give tetraiodo complex **HgI_4**

Notes:

Demasking agents: are reagents which regain the ability of masked ion to enter the reaction with ind. and **EDTA**.

Example:

The masking by CN^- can be removed by:

mixture of formaldehyde – acetic acid

on addition of demasking agent to $[Zn(CN)_4]^{2-}$, **Zn** is liberated and titrated.

Notes:

Detection of End Point

Metal indicator

Acid-base Indicator

Specific Indicator

Turbidity end point (appearance of turbidity)

Instrumental method

Notes:

Murexide: Ammonium salt of Purpuric acid or ammonium purpurate

It can be represented by H_4 **Ind**

$$H_4Ind^- \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} H_3Ind^{2-} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} H_2Ind^{3-}$$

Reddish violet		Violet	Blue
pH :	< 9	9-11	> 11

Metal	Colour of complex	Colour of indicator
Ca^{2+}	Pink	Violet
Cu^{2+}	Orange	Violet
Co^{2+}	Yellow	Violet
Ni^{2+}	Yellow	Violet

Eriochrome Black T (EBT)

Notes:

It can be represented by H_2Ind^- The color of Ind change with the change of pH. EBT contains two replaceable phenolic hydrogen.

$$H_2\,Ind^- \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} H\,Ind^{2-} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} Ind^{3-}$$

	Wine red	Blue	Yellow
pH:	< 7	7-11	> 11

ETB cannot be used for the determination of **Cu^{2+}, Fe^{3+}, Al^{3+}, Co^{2+} and Ni $^{2+}$**

Direct determination of water hardness

Notes:

Water hardness is due to the presence of **Ca^{2+} and Mg^{2+}** salts.

EDTA forms complex with **Ca^{2+} & Mg^{2+},** Ca-EDTA complex is more stable than Mg-EDTA complex. At pH 12 EDTA forms complex with Ca^{2+} only.

Total Ca^{2+} and Mg^{2+} determined by titration with EDTA at pH 10 using ammonia buffer and EBT as ind.

Upon titration with EDTA, Ca^{2+} will be chelated first, then Mg^{2+}.

For Ca^{2+} only: direct titration with EDTA at pH 12 using 8% NaOH and Murexide.

Mg^{2+} is pptd. as $Mg(OH)_2$ leaving Ca^{2+} which is titrated with EDTA.

For Mg^{2+}: **Total – Ca^{2+} = Mg^{2+}**

Notes:

OXIDATION- REDUCTION TITRATION

A titration which deals with a reaction involving oxidation and reduction of certain chemical species.

The act of adding standard solution in small quantities to the test solution till the reaction is complete is termed titration.

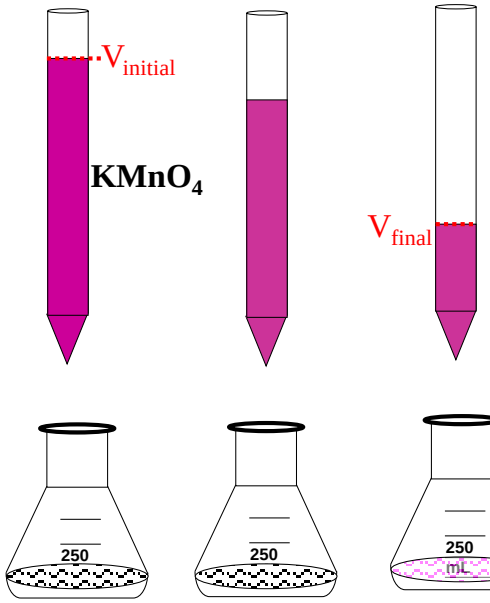
Notes:

How does this relationship concern our experiment?

Titration of **unknown sample of Iron** with **$KMnO_4$**:

The unknown sample of iron contains Iron in Fe^{2+} oxidation state. So we are basically doing a redox titration of Fe^{2+} with $KMnO_4$

Notes:



V_{final}- V_{inital}= V_{used} (in mL)

Important requirement:
The concentration of $KMnO_4$ should be known precisely

End point:
Pale Permanent Pink color

Notes:

$$Moles\ of\ MnO_4^- = Molarity\ of\ MnO_4^- \times V_{KMnO_4\ Used}\ (in\ L)$$

$$Moles\ of\ Fe^{2+} = 5 \times [moles\ of\ MnO_4^-]$$

$$Grams\ of\ Fe^{2+} = \frac{55.85\ g\ of\ Fe^{2+}}{1\ mole\ of\ Fe^{2+}} \times moles\ of\ Fe^{2+}$$

$$\%\ Fe\ in\ sample = \frac{grams\ of\ Fe^{+2}}{mass\ of\ sample\ in\ grams} \times 100\%$$

Common Redox Reagents

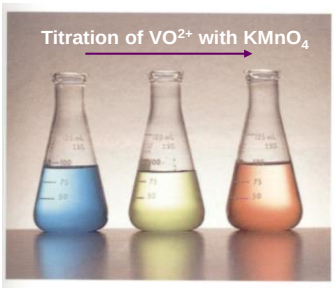
Notes:

Common Titrants for Oxidation Reactions

- **Potassium Permanganate ($KMnO_4$)**

Strong oxidant

Own indicator



Before Near After
Equivalence point

pH ≤ 1

$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{+2} + 4H_2O$ E^o = 1.507 V

Violet colorless

pH neutral or alkaline

$MnO_4^- + 4H^+ + 3e^- \rightleftharpoons MnO_2(s) + 2H_2O$ E^o = 1.692 V

Violet brown

pH stroIngly alkaline

$MnO_4^- + e^- \rightleftharpoons MnO_4^{-2}$ E^o = 0.56 V

Violet green

Notes:

Problem with $KMnO_4$

Unfortunately, the permanganate solution, once prepared, begins to decompose by the following reaction:

$$4\ MnO_4^-{}_{(aq)} + 2\ H_2O_{(l)} \rightarrow 4\ MnO_{2(s)} + 3\ O_{2(g)} + 4\ OH^-_{(aq)}$$

So we need another solution whose concentration is precisely known to be able to find the precise concentration of $KMnO_4$ solution.

Notes:

Titration of Oxalic acid by $KMnO_4$

Primary standard

$$16\ H^+_{(aq)} + 2\ MnO_4^-{}_{(aq)} + 5\ C_2O_4^{-2}{}_{(aq)} \rightarrow 2\ Mn^{+2}{}_{(aq)} + 10\ CO_{2(g)} + 8\ H_2O_{(l)}$$

5 $C_2O_4^{2-}$ ions are oxidized by 2 MnO_4^- ions to 10 CO_2 molecules. Conversely 2 MnO_4^- is reduced by 5 $C_2O_4^{2-}$ ions to $2Mn^{2+}$ ions.

Notes:

5 moles of $C_2O_4^{2-}$ ions are oxidized by 2 moles MnO_4^- ions to 10 moles of CO_2 molecules. Conversely 2 moles of MnO_4^- is reduced by 5 moles of $C_2O_4^{2-}$ ions to 2 moles of Mn^{2+} ions.

$$5\ Moles\ of\ C_2O_4^{2-} = 2\ moles\ of\ MnO_4^-$$

$$1\ Moles\ of\ C_2O_4^{2-} = \frac{2}{5} \times moles\ of\ MnO_4^-$$

Finding the End point with an Indicator

Notes:

Three types of indicators are used to signal a redox titration's end point.

The oxidized and reduced forms of some titrants, such as MnO_4^-, have different colors. A solution of MnO_4^- is intensely purple. In an acidic solution, however, permanganate's reduced form, Mn^{2+}, is nearly colorless.

When using MnO_4^- as a titrant, the titrand's solution remains colorless until the equivalence point.

The first drop of excess MnO_4^- produces a permanent tinge of purple, signaling the end point.

Notes:

Some indicators form a coloured compound with a specific oxidized or reduced form of the titrant or the strand.

Starch, for example of a specific indicator, is thiocyanate, SCN^-, which forms the soluble red-coloured complex of $Fe(SCN)_2^+$ in the presence of Fe^{3+}.

The most important class of indicators are substances that do not participate in the redox titration, but whose oxidized and reduced forms differ in colour.

When we add a redox indicator to the titrand, the indicator imparts a colour that depends on the solution's potential.

As the solution's potential changes with the addition of titrant, the indicator eventually changes oxidation state and changes colour, signalling the end point.

Notes:

To understand the relationship between potential and an indicator's color, consider its reduction half-reaction

$$In_{ox} + ne^- \leftrightarrow In_{red}$$

where In_{ox} and In_{red} are, respectively, the indicator's oxidized and reduced forms. The Nernst equation for this half-reaction is

$$E = E_{In_{ox}/In_{red}} - \frac{0.05916}{n} \log \frac{[In_{red}]}{[In_{ox}]}$$

Notes:

Another method for locating a redox titration's end point is a **potentiometric titration** in which we monitor the change in potential while we add the titrant to the titrand.

The end point is found by examining visually the titration curve. The simplest experimental design for a potentiometric titration consists of a Pt indicator electrode whose potential is governed by the titrand's or the titrant's redox half-reaction, and a reference electrode that has a fixed potential.

Other methods for locating the titration's end point include thermometric titrations and spectrophotometric titrations.

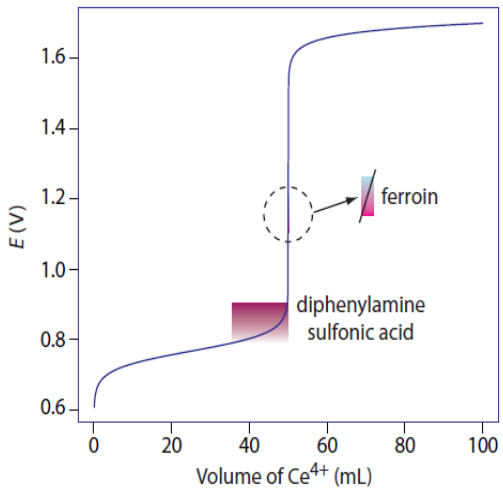
Methods for Finding the End point

Notes:

Titration curve for titration of 50.0 mL of 0.100 M Fe^{2+} with 0.100 M Ce^{4+}.

The end point transitions for the indicators diphenylamine sulfonic acid and ferroin are superimposed on the titration curve.

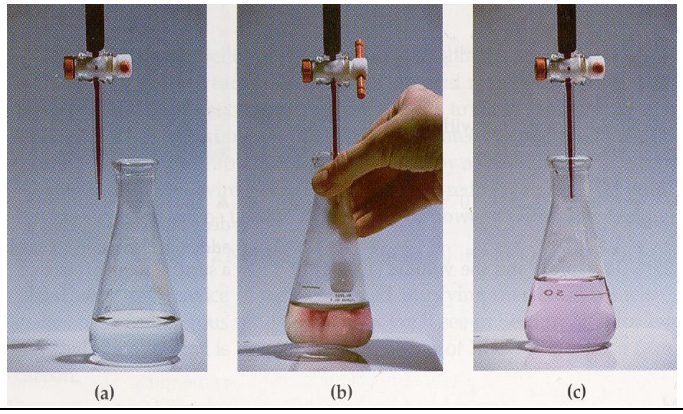
Because the transition for ferroin is too small to see on the scale of the x-axis, it requires only 1-2 drops of titrant. The color change is expanded to the right.



REQUIREMENTS FOR A TITRATION

Notes:

4. There should be a marked change when the reaction is complete. For example, this reaction is self-indicating. The titrant ($KMnO_4$) is deep purple. The analyte ($Na_2C_2O_4$) and products (Mn^{2+}, H_2O, and CO_2) are nearly colorless. The titration is done when the first fraction of a drop of excess MnO_4^- changes the solution from nearly colorless to a faint and stable pink.



REQUIREMENTS FOR A PRIMARY STANDARD

Notes:

1. A primary standard should be 100.00% pure; although a 0.01% to 0.02% impurity is tolerable if it is accurately known.

2. A primary standard should be stable at drying temperatures, and it should be stable indefinitely at room temperature. (A primary standard is always dried before weighing unless it is a hydrate.)

3. It should be readily available.

4. It should have a relatively large formula weight. Therefore, a relatively large mass of it will be weighed for titration. This will reduce error.

Common Titrants for Oxidation Reactions

Notes:

- Cerium (IV) (Ce^{4+})
  - Commonly used in place of $KMnO_4$
  - Works best in acidic solution
  - Can be used in most applications in previous table
  - Used to analyze some organic compounds
  - Color change not distinct to be its own indicator

$$Ce^{4+} + e^- \longrightarrow Ce^{3+}$$

Yellow — colorless

Ce^{4+} binds anions very strongly results in variation of formal potential

Formal potential:
- 1.70V in 1 F $HClO_4$
- 1.61V in 1 F HNO_3
- 1.47V in 1 F HCl
- 1.44V in 1 F H_2SO_4

Measure activity not concentration

Notes:

Common Titrants for Oxidation Reactions

- Potassium dichromate ($K_2Cr_2O_7$)

  Powerful oxidant in strong acid

  Not as strong as $KMnO_4$ or Ce^{4+}

  Primarily used for the determination of Fe^{2+}

  Not an oxidant in basic solution

  Color change not distinct to be its own indicator

$$Cr_2O_7^{-2} + 14H^+ + 6e^- \rightleftharpoons 2Cr^{+3} + 7H_2O$$

orange **green to violet**

$E^o = 1.36$ V

Common Titrants for Oxidation Reactions

Notes:

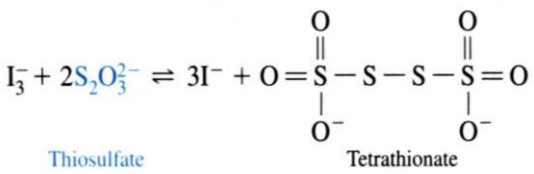
- Iodine (Solution of $I_2 + I^-$)

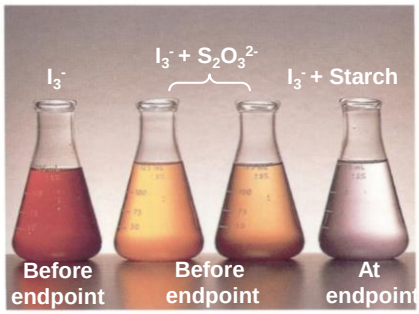
  I_3^- is actual species used in titrations with iodine

  The solubility of iodine in water is small, so the determination of oxidants must be carried out in the presence of a large excess of KI, which forms a soluble unstable complex compound with iodine: **$KI + I_2 \rightarrow K[I_3]$**

$$I_2 + I^- \rightleftharpoons I_3^- \qquad K = 7 \times 10^2$$

Either starch of Sodium Thiosulfate ($Na_2S_2O_3$) are used as indicator





Tasks to Section 8

1. Give definitions of these terms: complexometry, complexometric titration, complex, coordination complex, central metal atom, ligand, coordinate bond, coordination number, Chelate, complexones, EDTA complexes, metal ion indicators, masking agents, oxidation-reduction titration, redox reagent, standard potential.

2. What are the names of complex compounds by the following formulas:

A. $[Cu(NH_3)_4](OH)_2$,

B. $[Co(NH_3)_5NO_2]Cl_2$.

Write the equations of their full dissociation. Can we use the chemical reaction between ammonia hydroxide and metal ions in complexometry?

3. The amount of Fe in a 0.4891-g sample of ore was determined by titrating with $K_2Cr_2O_7$. After dissolving the sample in HCl, the iron was brought into the +2 oxidation state using a Jones reductor. Titration to the diphenylamine sulfonic acid endpoint required 36.92 mL of 0.02153 M $K_2Cr_2O_7$. Report the ore's iron content as %w/w Fe_2O_3.

4. A 25.00-mL sample of a liquid bleach was diluted to 1000 mL in a volumetric flask. A 25-mL portion of the diluted sample was transferred by pipet into an Erlenmeyer flask containing an excess of KI, reducing the OCl^- to Cl^-, and producing I_3^-. The liberated I_3^- was determined by titrating with 0.09892 M $Na_2S_2O_3$, requiring 8.96 mL to reach the starch indicator endpoint. Report the %w/v NaOCl in the sample of bleach.

Section 9: Gravimetric Analyses

Contents:

Introduction

Gravimetry includes all analytical methods in which the analytical signal is a measurement of mass or a change in mass.

All Gravimetric analyses rely on some final determination of weight as a means of quantifying an analyte. These methods are among the oldest of analytical techniques.

Since weight can be measured with greater accuracy than almost any other fundamental property, gravimetric analysis is potentially one of the most accurate classes of analytical methods available. However, samples for gravimetric analyses need to be extensively treated to remove interfering substances. As a result, only a very few gravimetric methods are currently used in environmental analysis. Standards used to calibrate instruments are frequently derived from gravimetric or titrimetric procedures.

In gravimetric analysis, the mass of a product is used to calculate the quantity of the original analyte (the species being analyzed).

In precipitation titrations, the quantity of titrant required for complete precipitation of analyte tells us how much analyte was present.

In combustion analysis, a sample is burned in excess oxygen, and products are measured. Combustion is typically used to measure C, H, N, S, and halogens in organic matter. Organic matter is burned in a closed system to measure other elements. Products and ash (solid residue) are then dissolved in acid or base and measured by inductively coupled plasma with atomic emission or mass spectrometry.

There are four fundamental types of gravimetric analysis.

They differ in the preparation of the sample before weighing of the analyte.

Precipitative gravimetric analysis.

As the name implies, precipitative gravimetric analyses build on the chemical precipitation of an analyte. Its most important application in the environmental field is with the analysis of sulphite.

Thermogravimetry.

With thermogravimetry, samples are heated, and changes in sample mass are recorded. Volatile solids analysis is an actual example of this type of gravimetric analysis.

Electrodeposition.

Electrodeposition involves the electrochemical reduction of metal ions on a cathode and simultaneous deposition of the ions on an anode.

In electrogravimetry, we deposit the analyte as a solid film on an electrode in an electrochemical cell. The deposition of PbO_2 at a Pt anode is one example of electrogravimetry. The reduction of Cu^{2+} to Cu at a Pt cathode is another example of electrogravimetry.

When we use thermal or chemical energy to remove a volatile species, we call the method volatilization gravimetry. In determining the moisture content of bread, for example, we use thermal energy to vaporize the water in the sample. To determine the amount of carbon in an organic compound, we use the chemical energy of combustion to convert it to CO_2.

Finally, in particulate gravimetry, we determine the analyte by separating it from the sample's matrix using filtration or extraction. The determination of total suspended solids is one example of particulate gravimetry.

In Section 9, we will consider specific gravimetric methods. Before that, we will take a moment to develop a broad survey of gravimetry. The descriptions of specific gravimetric methods will focus on their similarities and their differences. It is easier to understand a new analytical method when you can see its relationship to other similar methods.

General Gravimetric Procedure

Notes:

$$aA_{(aq)} + rR_{(aq)} \rightarrow A_aR_{r(s)}$$

analyte — precipitating reagent (in excess) — precipitate

$$\%A = \frac{\text{weight A}}{\text{weight sample}} \times 100\%$$

weight of A determined using stoichiometric ratio between A and A_aR_r

Stoichiometry Calculations

mass A_aR_r → moles A_aR_r → moles A → mass A

FM — stoichiometric ratio — FM

Gravimetric Analysis

Notes:

One form: isolation of a precipitate.

Typical steps:

- Determine mass of unknown solid
- Dissolve unknown in water
- Combine with excess amount of known substance to form a precipitate (excess drives reaction to completion)
- Filter, dry and weigh the precipitate
- Use formula and mass of ppt to find % of ion in unknown solid

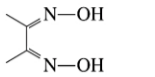
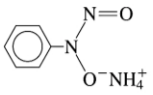
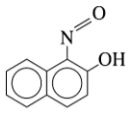
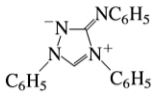
Representative gravimetric analysis

Notes:

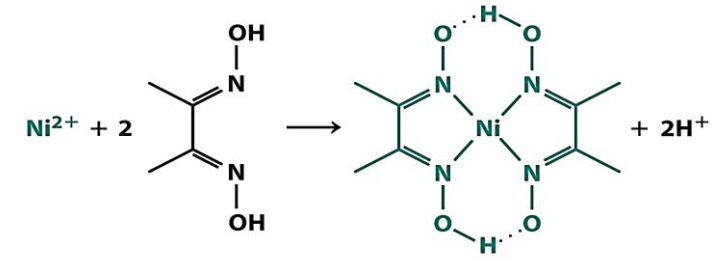
Species analyzed	Precipitated form	Form weighed	Some interfering species
K^+	$KB(C_6H_5)_4$	$KB(C_6H_5)_4$	NH_4^+, Ag^+, Hg^{2+}, Tl^+, Rb^+, Cs^+
Mg^{2+}	$Mg(NH_4)PO_4 \cdot 6H_2O$	$Mg_2P_2O_7$	Many metals except Na^+ and K^+
Ca^{2+}	$CaC_2O_4 \cdot H_2O$	$CaCO_3$ or CaO	Many metals except Mg^{2+}, Na^+, K^+
Ba^{2+}	$BaSO_4$	$BaSO_4$	Na^+, K^+, Li^+, Ca^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Sr^{2+}, Pb^{2+}, NO_3^-
Cr^{3+}	$PbCrO_4$	$PbCrO_4$	Ag^+, NH_4^+
Mn^{2+}	$Mn(NH_4)PO_4 \cdot H_2O$	$Mn_2P_2O_7$	Many metals
Fe^{3+}	$Fe(HCO_2)_3$	Fe_2O_3	Many metals
Co^{2+}	Co(1-nitroso-2-naphtholate)$_3$	$CoSO_4$ (by reaction with H_2SO_4)	Fe^{3+}, Pd^{2+}, Zr^{4+}
Ni^{2+}	Ni(dimethylglyoximate)$_2$	Same	Pd^{2+}, Pt^{2+}, Bi^{3+}, Au^{3+}
Cu^{2+}	CuSCN	CuSCN	NH^+, Pb^{2+}, Hg^{2+}, Ag^+
Zn^{2+}	$Zn(NH_4)PO_4 \cdot H_2O$	$Zn_2P_2O_7$	Many metals
Al^{3+}	Al(8-hydroxyquinolate)$_3$	Same	Many metals
Sn^{4+}	Sn(cupferron)$_4$	SnO_2	Cu^{2+}, Pb^{2+}, As(III)
Pb^{2+}	$PbSO_4$	$PbSO_4$	Ca^{2+}, Sr^{2+}, Ba^{2+}, Hg^{2+}, Ag^+, HCl, HNO_3
NH^+_4	$NH_4B(C_6H_5)_4$	$NH_4B(C_6H_5)_4$	K^+, Rb^+, Cs^+
Cl^-	AgCl	AgCl	Br^-, I^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, CN^-
Br^-	AgBr	AgBr	Cl^-, I^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, CN^-
I^-	AgI	AgI	Cl^-, Br^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, CN^-
SCN^-	CuSCN	CuSCN	NH_4^+, Pb^{2+}, Hg^{2+}, Ag^+
CN^-	AgCN	AgCN	Cl^-, Br^-, I^-, SCN^-, S^{2-}, $S_2O_3^{2-}$.
F^-	$(C_6H_5)_3SnF$	$(C_6H_5)_3SnF$	Many metals (except alkali metals), SiO_4^{4-}, CO_3^{2-}
ClO_4^-	$KClO_4$	$KClO_4$	
SO_4^{2-}	$BaSO_4$	$BaSO_4$	Na^+, K^+, Li^+, Ca^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Sr^{2+}, Pb^{2+}, NO_3^-
PO_4^{3-}	$Mg(NH_4)PO_4 \cdot 6H_2O$	$Mg_2P_2O_7$	Many metals except Na^+, K^+
NO_3^-	Nitron nitrate	Nitron nitrate	ClO_4^-, I^-, SCN^-, CrO_4^{2-}, ClO_3^-, NO_2^-, Br^-, $C_2O_4^{2-}$

Common organic precipitating agents

Notes:

Name	Structure	Some ions precipitated
Dimethylglyoxime		Ni^{2+}, Pd^{2+}, Pt^{2+}
Cupferron		Fe^{3+}, VO_2^+, Ti^{4+}, Zr^{4+}, Ce^{4+}, Ga^{3+}, Sn^{4+}
8-Hydroxyquinoline (oxine)		Mg^{2+}, Zn^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Al^{3+}, Fe^{3+}, Bi^{3+}, Ga^{3+}, Th^{4+}, Zr^{4+}, UO_2^{2+}, TiO^{2+}
1-Nitroso-2-naphthol		Co^{2+}, Fe^{3+}, Pd^{2+}, Zr^{4+}
Nitron		NO_3^-, ClO_4^-, BF_4^-, WO_4^{2-}
Sodium tetraphenylborate Tetraphenylarsonium chloride	$Na^+B(C_6H_5)_4^-$ $(C_6H_5)_4As^+Cl^-$	K^+, Rb^+, Cs^+, NH_4^+, Ag^+, organic ammonium ion $Cr_2O_7^{2-}$, MnO_4^-, ReO_4^-, MoO_4^{2-}, WO_4^{2-}, ClO_4^-, I_3^-

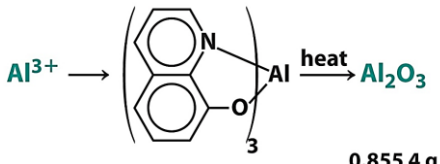
Notes:



FM 58.69

DMG
FM 116.12

Bis(dimethylglyoximate)nickel(II)
FM 288.91

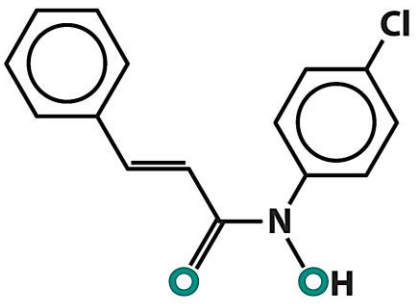


FM 26.982

0.855 4 g
FM 101.961

Notes:

Impurities such as Ag^+, Mn^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+}, Fe^{2+}, and Ga^{3+} are masked using -



***N-p*-Chlorophenylcinnamo-hydroxamic acid (RH)**
(The two oxygen atoms that bind to metal ions are bold.)

Selected Analyses and "Masking"

Notes:

Species Analyzed	Precipitated Form	Form Weighed	Some Interfering Species
Cl^-	AgCl	AgCl	Br^-, I^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, CN^-
Br^-	AgBr	AgBr	Cl^-, I^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, CN^-
I^-	AgI	AgI	Cl^-, Br^-, SCN^-, S^{2-}, $S_2O_3^{2-}$, CN^-
SO_4^{2-}	$BaSO_4$	$BaSO_4$	Na^+, K^+, Li^+, Ca^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}, Sr^{2+}, Pb^{2+}, NO_3^-

Precipitates

Notes:

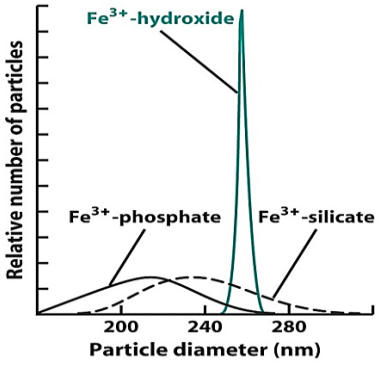
•large particle size ⇒ ease of filtering

•colloids 1-500 nm, charged (migrate in an electric field), don't settle out (suspended by Brownian motion), pass through filter paper

•need to promote particle growth over nucleation

Precipitation mechanisms are still poorly understood, but they do depend on -

1. solubility
2. temperature
3. reactant concentrations
4. rate of mixing



Precipitation in the presence of electrolyte
(e.g. 0.10 M HNO_3)

Notes:

• we want the particles to coagulate together to make bigger particles

• since the colloids are charged however, they repel each other

• the charge on the colloid depends on which lattice ions are in excess in solution, e.g. for AgCl the lattice ions are Ag^+ and Cl^-

• if excess Ag^+ in solution, then + colloids

• if excess Cl^- in solution, then - colloids

• if unknown = Cl^- and it's being precipitated out with Ag^+, then initially the excess lattice ion is Cl^- and the colloids are negatively charged.

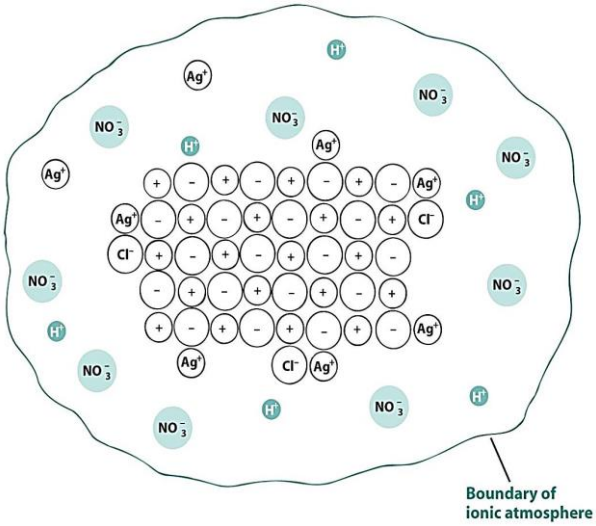
• after all of the Cl^- is precipitated out, adding more Ag^+ will change the colloid charge to +

An AgCl colloid growing in a solution of excess Cl^- will be negatively charged -

Notes:

The added electrolyte $HNO_3 = H^+ + NO_3^-$ adds to the region around the colloid which is called the "ionic atmosphere".

The added electrolyte shrinksthe ionic atmosphere and makes it easier for colloids to "stick" together



A 0.825 g sample of an ionic compound containing chloride ions and an unknown metal is dissolved in water and treated with excess silver nitrate. If 1.725 g of

AgCl precipitate forms, what is the percent by mass of Cl in the original sample?

Notes:

Steps in solution:

- Find the % of Cl in AgCl
- Multiply the % of Cl by the mass of the precipitate to obtain the Cl in the sample
- Divide the mass of Cl in sample by total mass of sample (multiply by 100 for %)

Notes:

$$\%\,\mathrm{Cl} = \frac{35.45\ \mathrm{g\,Cl}}{143.35\ \mathrm{g\ AgCl}} \times 100 = 24.7\%$$

$$0.247 \times 1.725\ \mathrm{g\ AgCl\ ppt} = 0.427\ \mathrm{g\ Cl\ in\ sample}$$

$$\%\,\mathrm{Cl\ in\ unknown} = \frac{0.427\ \mathrm{g\ Cl}}{0.825\ \mathrm{g\ sample}} \times 100 = 51.7\%\,\mathrm{Cl}$$

Thermogravimetric Analysis

Notes:

Thermogravimetry and combustion analysis involve the heating of a sample to 500° C or more with the oxidation and/or volatilization of some of the sample constituents.

Either the change of sample weight is determined (thermogravimetry), or the combustion gases are trapped and weighed (combustion analysis).

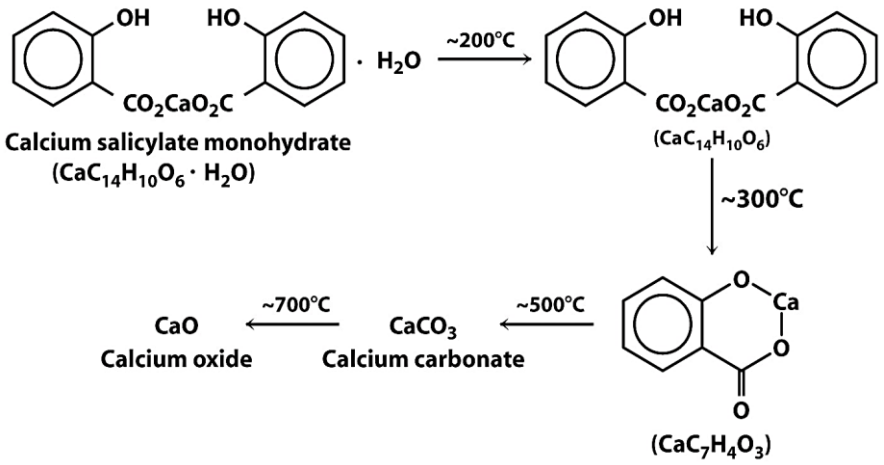
With thermogravimetric methods, it is especially important to return the sample to room temperature before weighing.

The former method is used for volatile solids analysis in engineering. The latter is used in many fields of science for the determination of total carbon and hydrogen in solids.

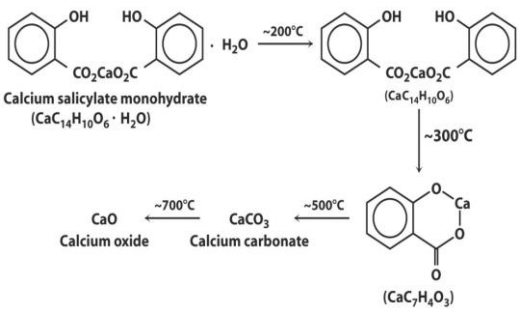
Thermogravimetric Analysis

Notes:

The mass of the sample is measured as a function of temperature

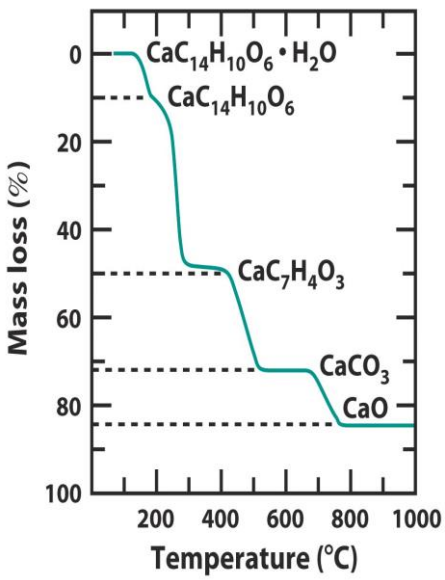


Notes:



For this gravimetric analysis, the precipitate must be heated to at least 800 °C in order to drive off all the water, volatilize the HNO_3, and reduce the sample to CaO.

= **"heating to constant weight"**



Notes:

Precipitation titration

Titrations with precipitating agents are useful for determining certain analyte. Example: Cl^- can be determined when titrated with $AgNO_3$

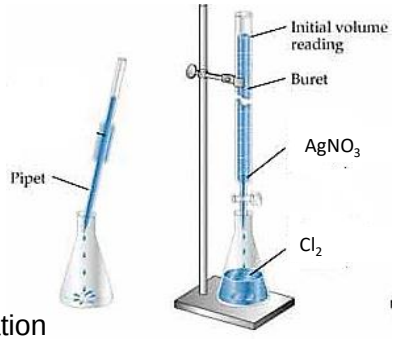
Conditions for precipitation titration :

1. Precipitate must be practically insoluble
2. Precipitation reaction must be rapid
3. Precipitation reaction must be quantitative
4. No interference by adsorption effect (co-precipitation)
5. Able to detect equivalent point during titration

Detection of end point in precipitation titration

Notes:

1. Formation of coloured precipitate
2. Formation of soluble coloured compound
3. Use of adsorption indicator
4. Turbidity method



Formation of coloured precipitate

Chlorides are present in all types of water resources at a varying concentration depending on the geo-chemical conditions in the form of $CaCl_2$, $MgCl_2$ and NaCl.

Chlorides are introduced into the water resources from the discharge of effluents from chemical industries, sewage disposal and seawater intrusion in coastal region.

The concentration of chloride ions more than 250 ppm is not desirable for drinking purpose. The total chloride ions can be determined by argentometric method (Mohr's Method)

Detection of end point in precipitation titration

Notes:

In this method, first the analyte react with the titrant after the analyte is reacted completely the next drop if titrant react with indicator and formed small quantity of colored precipitate which indicate end point of titration (Mohr's method)

Example:

Assay of NaCl with silver nitrate with dilute potassium chromate solution as indicator.

$K_{sp}(AgCl) = 1.2 \times 10^{-10} = [Ag+]\,[Cl^-]$

$K_{sp}(Ag_2CrO_4) = 1.7 \times 10^{-12} = [Ag^+]^2\,[CrO_4^{2-}]$

We expect that the salt with smaller K_{sp} should precipitate first, this is true if both salt dissociate to yield same number of ions. But in this case the chloride ions are in excess than that of chromate ion and concentration of chromate ion very dilute i.e. 0.0014M, hence the chloride precipitate first and then chromate will precipitate as colored compound

Detection of end point in precipitation titration

Notes:

Reactions in the Mohr's Method are given below

In this method Cl^- ion solution is directly titrated against $AgNO_3$ using potassium chromate (K_2CrO_4) as the indicator.

$$\underset{\text{in water}}{AgNO_3} + Cl^- \longrightarrow \underset{\text{white precipitate}}{AgCl\downarrow} + NO_3^-$$

At the end point, when all the chloride ions are removed, the yellow colour of chromate changes into reddish brown due to the following reaction.

$$2AgNO_3 + \underset{\text{yellow}}{K_2CrO_4} \longrightarrow \underset{\text{reddish brown}}{Ag_2CrO_4\downarrow} + 2KNO_3$$

Detection of end point in precipitation titration

Notes:

Conditions for Mohr's method

1. Very dilute solution of pot chromate should be used.
2. The titration should be carried out neutral or slight alkaline condition i.e. pH 6.5 to 9. In acidic condition, hydrogen chromate will be formed and in highly alkaline condition silver hydroxide ($K_{sp} = 2.3 \cdot 10^{-8}$).
3. Solubility product of silver chromate increase with rise in temperature.

Ammonium salt, iodide salts and thiocyanate salt cannot be done by Mohr's method because:

1. In the presence of ammonium salt, the ammonia do have effect of solubility of silver salt due to increase in pH ;
2. AgI and AgSCN adsorb chromate strongly hence false, indistinct end point results.

Notes:

Detection of end point in precipitation titration

Assay of sodium chloride by Mohr's Method:

Preparation and standardization of 0.1 N silver nitrate solution

Preparation of potassium chromate indicator solution

Application: determination of NaCl, KCl

Formation of soluble Precipitate. Determination of chloride by Volhard Method

Notes:

This is an indirect method for chloride determination where an excess amount of standard Ag^+ is added to the chloride solution containing Fe^{3+} as an indicator. The excess Ag^+ is then titrated with standard SCN^- solution until a reddish-brown colour is obtained which results from the reaction:

$$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3 + \text{excess } Ag^+$$

$$\text{Excess } Ag^+ + SCN^- \rightarrow AgSCN \downarrow$$

$$Fe^{3+} + SCN^- = Fe(SCN)^{2+}$$

yellow reddish-brown

The boiling of solution for 10 min is essential to coagulate the precipitate of silver chloride. Nitrobenzene is added in this method which prevents the interactions between silver chloride and ammonium thiocyanate by forming coat over the silver chloride.

Notes:

Differentiate between

Mohr's method	&	Volhard method
Direct titration of halide with silver nitrate		Indirect titration or back titration
Indicator – Pot Chromate		Indicator Ferric ammonium sulphate
End point- red precipitate of silver chromate		End point- red soluble complex of ferric thiocyanate
Condition for titration : Neutral to alkaline (pH 6.5 – 9.0)		Condition for titration : Acidic solution
Titration of Iodide and cyanate is not possible		Can be used for determination of chloride, bromide and iodide
As solubility of silver chromate increases with rising temp, titration are carried out at RT		As the color of ferric thiocynate complex fades above 25°C, the titration are carried below 20°C

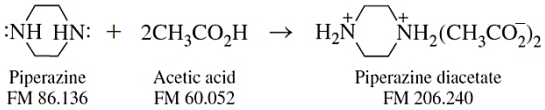
Tasks to Section 9

1. Give definitions of these terms: gravimetric analysis, physical gravimetry, thermogravimetry, precipitative gravimetric analysis, electrodeposition, precipitation titrations, method volatilization gravimetry, particulate gravimetry, electrogravimetry

2. A 10.00-mL solution containing Cl^- was treated with excess $AgNO_3$ to precipitate 0.4368 g of AgCl. What was the molarity of Cl^- in the unknown?

3. Marie Curie measured the atomic mass of the element radium, which she discovered. She knew that radium is in the same family as barium, so the formula of radium chloride is $RaCl_2$. When 0.09192 g of pure $RaCl_2$ was dissolved and treated with excess $AgNO_3$, 0.08890 g of AgCl precipitated. How many moles of Cl^- were in the $RaCl_2$? From this measurement, find the atomic mass of Ra.

4. The piperazine content of an impure commercial material can be determined by precipitating and weighing the diacetate:



In one experiment, 0.312 6 g of sample was dissolved in 25 mL of acetone, and 1 mL of acetic acid was added. After 5 min, the precipitate was filtered, washed with acetone, dried at 110°C, and found to weigh 0.7121 g. Find wt% of piperazine in the sample.

Appendices

A. Dissociation constants and pK_a values for acids at 25°C

Name	Formula	K_{a1}	pK_{a1}	K_{a2}	pK_{a2}	K_{a3}	pK_{a3}	K_{a4}	pK_{a4}
Acetic acid	CH_3CO_2H	$1.75\cdot10^{-5}$	4.756						
Arsenic acid	H_3AsO_4	$5.5\cdot10^{-3}$	2.26	$1.7\cdot10^{-7}$	6.76	$5.1\cdot10^{-12}$	11.29		
Benzoic acid	$C_6H_5CO_2H$	$6.25\cdot10^{-5}$	4.204						
Boric acid	H_3BO_3	$5.4\cdot10^{-10}$*	9.27*	$>1\cdot10^{-14}$*	>14*				
Bromoacetic acid	CH_2BrCO_2H	$1.3\cdot10^{-3}$	2.90						
Carbonic acid	H_2CO_3	$4.5\cdot10^{-7}$	6.35	$4.7\cdot10^{-11}$	10.33				
Chloroacetic acid	CH_2ClCO_2H	$1.3\cdot10^{-3}$	2.87						
Chlorous acid	$HClO_2$	$1.1\cdot10^{-2}$	1.94						
Chromic acid	H_2CrO_4	$1.8\cdot10^{-1}$	0.74	$3.2\cdot10^{-7}$	6.49				
Citric acid	$C_6H_8O_7$	$7.4\cdot10^{-4}$	3.13	$1.7\cdot10^{-5}$	4.76	$4.0\cdot10^{-7}$	6.40		
Cyanic acid	HCNO	$3.5\cdot10^{-4}$	3.46						
Dichloroacetic acid	$CHCl_2CO_2H$	$4.5\cdot10^{-2}$	1.35						
Fluoroacetic acid	CH_2FCO_2H	$2.6\cdot10^{-3}$	2.59						
Formic acid	CH_2O_2	$1.8\cdot10^{-4}$	3.75						
Hydrazoic acid	HN_3	$2.5\cdot10^{-5}$	4.6						
Hydrocyanic acid	HCN	$6.2\cdot10^{-10}$	9.21						
Hydrofluoric acid	HF	$6.3\cdot10^{-4}$	3.20						
Hydrogen selenide	H_2Se	$1.3\cdot10^{-4}$	3.89	$1.0\cdot10^{-11}$	11.0				
Hydrogen sulfide	H_2S	$8.9\cdot10^{-8}$	7.05	$1\cdot10^{-19}$	19				
Hydrogen telluride	H_2Te	$2.5\cdot10^{-3}$‡	2.6‡	$1\cdot10^{-11}$	11				
Hypobromous acid	HBrO	$2.8\cdot10^{-9}$	8.55						
Hypochlorous acid	HClO	$4.0\cdot10^{-8}$	7.40						
Hypoiodous acid	HIO	$3.2\cdot10^{-11}$	10.5						
Iodic acid	HIO_3	$1.7\cdot10^{-1}$	0.78						
Iodoacetic acid	CH_2ICO_2H	$6.6\cdot10^{-4}$	3.18						
Nitrous acid	HNO_2	$5.6\cdot10^{-4}$	3.25						
Oxalic acid	$C_2H_2O_4$	$5.6\cdot10^{-2}$	1.25	$1.5\cdot10^{-4}$	3.81				
Periodic acid	HIO_4	$2.3\cdot10^{-2}$	1.64						
Phenol	C_6H_5OH	$1.0\cdot10^{-10}$	9.99						
Phosphoric acid	H_3PO_4	$6.9\cdot10^{-3}$	2.16	$6.2\cdot10^{-8}$	7.21	$4.8\cdot10^{-13}$	12.32		
Phosphorous acid	H_3PO_3	$5.0\cdot10^{-2}$*	1.3*	$2.0\cdot10^{-7}$*	6.70*				
Pyrophosphoric acid	$H_4P_2O_7$	$1.2\cdot10^{-1}$	0.91	$7.9\cdot10^{-3}$	2.10	$2.0\cdot10^{-7}$	6.70	$4.8\cdot10^{-10}$	9.32
Resorcinol	$C_6H_4(OH)_2$	$4.8\cdot10^{-10}$	9.32	$7.9\cdot10^{-12}$	11.1				
Selenic acid	H_2SeO_4	Strong	Strong	$2.0\cdot10^{-2}$	1.7				
Selenious acid	H_2SeO_3	$2.4\cdot10^{-3}$	2.62	$4.8\cdot10^{-9}$	8.32				
Sulfuric acid	H_2SO_4	Strong	Strong	$1.0\cdot10^{-2}$	1.99				
Sulfurous acid	H_2SO_3	$1.4\cdot10^{-2}$	1.85	$6.3\cdot10^{-8}$	7.2				
meso-Tartaric acid	$C_4H_6O_6$	$6.8\cdot10^{-4}$	3.17	$1.2\cdot10^{-5}$	4.91				
Telluric acid	H_2TeO_4	$2.1\cdot10^{-8}$‡	7.68‡	$1.0\cdot10^{-11}$‡	11.0‡				
Tellurous acid	H_2TeO_3	$5.4\cdot10^{-7}$	6.27	$3.7\cdot10^{-9}$	8.43				
Trichloroacetic acid	CCl_3CO_2H	$2.2\cdot10^{-1}$	0.66						
Trifluoroacetic acid	CF_3CO_2H	$3.0\cdot10^{-1}$	0.52						

* Measured at 20°C, not 25°C.
‡ Measured at 18°C, not 25°C.

B. Dissociation constants and pK_b values for bases at 25°C

Name	Formula	K_b	pK_b
Ammonia	NH_3	1.8×10^{-5}	4.75
Aniline	$C_6H_5NH_2$	7.4×10^{-10}	9.13
n-Butylamine	$C_4H_9NH_2$	4.0×10^{-4}	3.40
sec-Butylamine	$(CH_3)_2CHCH_2NH_2$	3.6×10^{-4}	3.44
tert-Butylamine	$(CH_3)_3CNH_2$	4.8×10^{-4}	3.32
Dimethylamine	$(CH_3)_2NH$	5.4×10^{-4}	3.27
Ethylamine	$C_2H_5NH_2$	4.5×10^{-4}	3.35
Hydrazine	N_2H_4	1.3×10^{-6}	5.9
Hydroxylamine	NH_2OH	8.7×10^{-9}	8.06
Methylamine	CH_3NH_2	4.6×10^{-4}	3.34
Propylamine	$C_3H_7NH_2$	3.5×10^{-4}	3.46
Pyridine	C_5H_5N	1.7×10^{-9}	8.77
Trimethylamine	$(CH_3)_3N$	6.3×10^{-5}	4.20

C. Solubility-product constants (K_{sp}) for compounds at 25°C

Compound Name	Compound Formula	K_{sp}
Aluminium phosphate	$AlPO_4$	9.84×10^{-21}
Barium bromate	$Ba(BrO_3)_2$	2.43×10^{-4}
Barium carbonate	$BaCO_3$	2.58×10^{-9}
Barium chromate	$BaCrO_4$	1.17×10^{-10}
Barium fluoride	BaF_2	1.84×10^{-7}
Barium iodate	$Ba(IO_3)_2$	4.01×10^{-9}
Barium nitrate	$Ba(NO_3)_2$	4.64×10^{-3}
Barium sulfate	$BaSO_4$	1.08×10^{-10}
Barium sulfite	$BaSO_3$	5.0×10^{-10}
Beryllium hydroxide	$Be(OH)_2$	6.92×10^{-22}
Bismuth arsenate	$BiAsO_4$	4.43×10^{-10}
Bismuth iodide	BiI_3	7.71×10^{-19}
Cadmium carbonate	$CdCO_3$	1.0×10^{-12}
Cadmium fluoride	CdF_2	6.44×10^{-3}
Cadmium hydroxide	$Cd(OH)_2$	7.2×10^{-15}
Cadmium iodate	$Cd(IO_3)_2$	2.5×10^{-8}
Cadmium phosphate	$Cd_3(PO_4)_2$	2.53×10^{-33}
Cadmium sulfide	CdS	8.0×10^{-27}
Calcium carbonate	$CaCO_3$	3.36×10^{-9}
Calcium fluoride	CaF_2	3.45×10^{-11}
Calcium hydroxide	$Ca(OH)_2$	5.02×10^{-6}
Calcium iodate	$Ca(IO_3)_2$	6.47×10^{-6}
Calcium phosphate	$Ca_3(PO_4)_2$	2.07×10^{-33}
Calcium sulfate	$CaSO_4$	4.93×10^{-5}
Caesium perchlorate	$CsClO_4$	3.95×10^{-3}
Caesium periodate	$CsIO_4$	5.16×10^{-6}
Cobalt(II) arsenate	$Co_3(AsO_4)_2$	6.80×10^{-29}
Cobalt(II) hydroxide	$Co(OH)_2$	5.92×10^{-15}
Cobalt(II) phosphate	$Co_3(PO_4)_2$	2.05×10^{-35}
Copper(I) bromide	$CuBr$	6.27×10^{-9}
Copper(I) chloride	$CuCl$	1.72×10^{-7}
Copper(I) cyanide	$CuCN$	3.47×10^{-20}
Copper(I) iodide	CuI	1.27×10^{-12}
Copper(I) thiocyanate	$CuSCN$	1.77×10^{-13}
Copper(II) arsenate	$Cu_3(AsO_4)_2$	7.95×10^{-36}
Copper(II) oxalate	CuC_2O_4	4.43×10^{-10}
Copper(II) phosphate	$Cu_3(PO_4)_2$	1.40×10^{-37}
Copper(II) sulfide	CuS	6.3×10^{-36}
Europium(III) hydroxide	$Eu(OH)_3$	9.38×10^{-27}
Gallium(III) hydroxide	$Ga(OH)_3$	7.28×10^{-36}
Iron(II) carbonate	$FeCO_3$	3.13×10^{-11}
Iron(II) fluoride	FeF_2	2.36×10^{-6}
Iron(II) hydroxide	$Fe(OH)_2$	4.87×10^{-17}
Iron(III) hydroxide	$Fe(OH)_3$	2.79×10^{-39}
Iron(III) sulfide	FeS	6.3×10^{-18}
Lanthanum iodate	$La(IO_3)_3$	7.50×10^{-12}
Lead(II) bromide	$PbBr_2$	6.60×10^{-6}
Lead(II) carbonate	$PbCO_3$	7.40×10^{-14}
Lead(II) chloride	$PbCl_2$	1.70×10^{-5}
Lead(II) fluoride	PbF_2	3.3×10^{-8}
Lead(II) hydroxide	$Pb(OH)_2$	1.43×10^{-20}
Lead(II) iodate	$Pb(IO_3)_2$	3.69×10^{-13}
Lead(II) iodide	PbI_2	9.8×10^{-9}
Lead(II)selenite	$PbSeO_4$	1.37×10^{-7}
Lead(II) sulfate	$PbSO_4$	2.53×10^{-8}
Lead(II) sulfide	PbS	8.0×10^{-28}
Lithium carbonate	Li_2CO_3	8.15×10^{-4}
Lithium fluoride	LiF	1.84×10^{-3}
Lithium phosphate	Li_3PO_4	2.37×10^{-11}
Magnesium carbonate	$MgCO_3$	6.82×10^{-6}
Magnesium fluoride	MgF_2	5.16×10^{-11}
Magnesium hydroxide	$Mg(OH)_2$	5.61×10^{-12}
Magnesium phosphate	$Mg_3(PO_4)_2$	1.04×10^{-24}
Manganese(II) carbonate	$MnCO_3$	2.24×10^{-11}
Manganese(II) iodate	$Mn(IO_3)_2$	4.37×10^{-7}
Mercury(I) bromide	Hg_2Br_2	6.40×10^{-23}
Mercury(I) carbonate	Hg_2CO_3	3.6×10^{-17}
Mercury(I) chloride	Hg_2Cl_2	1.43×10^{-18}

Compound Name	Compound Formula	K_{sp}
Mercury(I) fluoride	Hg_2F_2	3.10×10^{-6}
Mercury(I) iodide	Hg_2I_2	5.2×10^{-29}
Mercury(I) oxalate	$Hg_2C_2O_4$	1.75×10^{-13}
Mercury(I) sulfate	Hg_2SO_4	6.5×10^{-7}
Mercury(I) thiocyanate	$Hg_2(SCN)_2$	3.2×10^{-20}
Mercury(II) bromide	$HgBr_2$	6.2×10^{-20}
Mercury (II) iodide	HgI_2	2.9×10^{-29}
Mercury(II) sulfide (red)	HgS	4×10^{-53}
Mercury(II) sulfide (black)	HgS	1.6×10^{-52}
Neodymium carbonate	$Nd_2(CO_3)_3$	1.08×10^{-33}
Nickel(II) carbonate	$NiCO_3$	1.42×10^{-7}
Nickel(II) hydroxide	$Ni(OH)_2$	5.48×10^{-16}
Nickel(II) iodate	$Ni(IO_3)_2$	4.71×10^{-5}
Nickel(II) phosphate	$Ni_3(PO_4)_2$	4.74×10^{-32}
Palladium(II) thiocyanate	$Pd(SCN)_2$	4.39×10^{-23}
Potassium hexachloroplatinate	K_2PtCl_6	7.48×10^{-6}
Potassium perchlorate	$KClO_4$	1.05×10^{-2}
Potassium periodate	KIO_4	3.71×10^{-4}
Praseodymium hydroxide	$Pr(OH)_3$	3.39×10^{-24}
Rubidium perchlorate	$RbClO_4$	3.00×10^{-3}
Scandium fluoride	ScF_3	5.81×10^{-24}
Scandium hydroxide	$Sc(OH)_3$	2.22×10^{-31}
Silver(I) acetate	$AgCH_3CO_2$	1.94×10^{-3}
Silver(I) arsenate	Ag_3AsO_4	1.03×10^{-22}
Silver(I) bromate	$AgBrO_3$	5.38×10^{-5}
Silver(I) bromide	AgBr	5.35×10^{-13}
Silver(I) carbonate	Ag_2CO_3	8.46×10^{-12}
Silver(I) chloride	AgCl	1.77×10^{-10}
Silver(I) chromate	Ag_2CrO_4	1.12×10^{-12}
Silver(I) cyanide	AgCN	5.97×10^{-17}
Silver(I) iodate	$AgIO_3$	3.17×10^{-8}
Silver(I) iodide	AgI	8.52×10^{-17}
Silver(I) oxalate	$Ag_2C_2O_4$	5.40×10^{-12}
Silver(I) phosphate	Ag_3PO_4	8.89×10^{-17}
Silver(I) sulfate	Ag_2SO_4	1.20×10^{-5}
Silver(I) sulfide	Ag_2S	6.3×10^{-50}
Silver(I) sulfite	Ag_2SO_3	1.50×10^{-14}
Silver(I) thiocyanate	AgSCN	1.03×10^{-12}
Strontium arsenate	$Sr_3(AsO_4)_2$	4.29×10^{-19}
Strontium carbonate	$SrCO_3$	5.60×10^{-10}
Strontium fluoride	SrF_2	4.33×10^{-9}
Strontium iodate	$Sr(IO_3)_2$	1.14×10^{-7}
Strontium sulfate	$SrSO_4$	3.44×10^{-7}
Thallium(I) bromate	$TlBrO_3$	1.10×10^{-4}
Thallium(I) bromide	TlBr	3.71×10^{-6}
Thallium(I) chloride	TlCl	1.86×10^{-4}
Thallium(I) chromate	Tl_2CrO_4	8.67×10^{-13}
Thallium(I) iodate	$TlIO_3$	3.12×10^{-6}
Thallium(I) iodide	TlI	5.54×10^{-8}
Thallium(I) thiocyanate	TlSCN	1.57×10^{-4}
Thallium(III) hydroxide	$Tl(OH)_3$	1.68×10^{-44}
Tin(II) hydroxide	$Sn(OH)_2$	5.45×10^{-27}
Tin(II) sulfide	SnS	1.0×10^{-25}
Yttrium carbonate	$Y_2(CO_3)_3$	1.03×10^{-31}
Yttrium fluoride	YF_3	8.62×10^{-21}
Yttrium hydroxide	$Y(OH)_3$	1.00×10^{-22}
Yttrium iodate	$Y(IO_3)_3$	1.12×10^{-10}
Zinc arsenate	$Zn_3(AsO_4)_2$	2.8×10^{-28}
Zinc carbonate	$ZnCO_3$	1.46×10^{-10}
Zinc fluoride	ZnF_2	3.04×10^{-2}
Zinc hydroxide	$Zn(OH)_2$	3×10^{-17}
Zinc selenide	ZnSe	3.6×10^{-26}
Zinc sulfide (wurtzite)	ZnS	1.6×10^{-24}
Zinc sulfide (sphalerite)	ZnS	2.5×10^{-22}

D. Standard reduction potentials at 25°C

Half-reaction	E° (V)
$Ac^{3+} + 3e^- \rightarrow Ac$	−2.20
$Ag^+ + e^- \rightarrow Ag$	0.7996
$AgBr + e^- \rightarrow Ag + Br^-$	0.07133
$AgCl + e^- \rightarrow Ag + Cl^-$	0.22233
$Ag_2CrO_4 + 2e^- \rightarrow 2Ag + CrO_4^{2-}$	0.4470
$AgI + e^- \rightarrow Ag + I^-$	−0.15224
$Ag_2S + 2e^- \rightarrow 2Ag + S^{2-}$	−0.691
$Ag_2S + 2H^+ + 2e^- \rightarrow 2Ag + H_2S$	−0.0366
$AgSCN + e^- \rightarrow Ag + SCN^-$	0.08951
$Al^{3+} + 3e^- \rightarrow Al$	−1.662
$Al(OH)_4^- + 3e^- \rightarrow Al + 4OH^-$	−2.328
$Am^{3+} + 3e^- \rightarrow Am$	−2.048
$As + 3H^+ + 3e^- \rightarrow AsH_3$	−0.608
$H_3AsO_4 + 2H^+ + 2e^- \rightarrow HAsO_2 + 2H_2O$	0.560
$Au^+ + e^- \rightarrow Au$	1.692
$Au^{3+} + 3e^- \rightarrow Au$	1.498
$H_3BO_3 + 3H^+ + 3e^- \rightarrow B + 3H_2O$	−0.8698
$Ba^{2+} + 2e^- \rightarrow Ba$	−2.912
$Be^{2+} + 2e^- \rightarrow Be$	−1.847
$Bi^{3+} + 3e^- \rightarrow Bi$	0.308
$BiO^+ + 2H^+ + 3e^- \rightarrow Bi + H_2O$	0.320
$Br_2(aq) + 2e^- \rightarrow 2Br^-$	1.0873
$Br_2(l) + 2e^- \rightarrow 2Br^-$	1.066
$BrO_3^- + 6H^+ + 5e^- \rightarrow 1/2Br_2 + 3H_2O$	1.482
$BrO_3^- + 6H^+ + 6e^- \rightarrow Br^- + 3H_2O$	1.423
$CO_2 + 2H^+ + 2e^- \rightarrow HCO_2H$	−0.199
$Ca^{2+} + 2e^- \rightarrow Ca$	−2.868
$Ca(OH)_2 + 2e^- \rightarrow Ca + 2OH^-$	−3.02
$Cd^{2+} + 2e^- \rightarrow Cd$	−0.4030
$CdSO_4 + 2e^- \rightarrow Cd + SO_4^{2-}$	−0.246
$Cd(OH)_4^{2-} + 2e^- \rightarrow Cd + 4OH^-$	−0.658
$Ce^{3+} + 3e^- \rightarrow Ce$	−2.336
$Ce^{4-} + e^- \rightarrow Ce^{3+}$	1.72
$Cl_2(g) + 2e^- \rightarrow 2Cl^-$	1.35827
$HClO + H^+ + e^- \rightarrow 1/2Cl_2 + H_2O$	1.611
$HClO + H^+ + 2e^- \rightarrow Cl^- + H_2O$	1.482
$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^-$	0.81
$ClO_3^- + 6H^+ + 5e^- \rightarrow 1/2Cl_2 + 3H_2O$	1.47
$ClO_3^- + 6H^+ + 6e^- \rightarrow Cl^- + 3H_2O$	1.451
$ClO_4^- + 8H^+ + 7e^- \rightarrow 1/2Cl_2 + 4H_2O$	1.39
$ClO_4^- + 8H^+ + 8e^- \rightarrow Cl^- + 4H_2O$	1.389
$Co^{2+} + 2e^- \rightarrow Co$	−0.28
$Co^{3+} + e^- \rightarrow Co^{2+}$	1.92
$Cr^{2+} + 2e^- \rightarrow Cr$	−0.913
$Cr^{3+} + e^- \rightarrow Cr^{2+}$	−0.407
$Cr^{3+} + 3e^- \rightarrow Cr$	−0.744
$Cr_2O_7^- + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$	1.232
$CrO_4^{2-} + 4H_2O + 3e^- \rightarrow Cr(OH)_3 + 5OH^-$	−0.13
$Cs^+ + e^- \rightarrow Cs$	−3.026
$Cu^+ + e^- \rightarrow Cu$	0.521
$Cu^{2+} + e^- \rightarrow Cu^+$	0.153
$Cu^{2+} + 2e^- \rightarrow Cu$	0.3419
$CuI_2^- + e^- \rightarrow Cu + 2I^-$	0.00
$Cu_2O + H_2O + 2e^- \rightarrow 2Cu + 2OH^-$	−0.360
$Dy^{3+} + 3e^- \rightarrow Dy$	−2.295
$Er^{3+} + 3e^- \rightarrow Er$	−2.331
$Es^{3+} + 3e^- \rightarrow Es$	−1.91
$Eu^{2+} + 2e^- \rightarrow Eu$	−2.812
$Eu^{3+} + 3e^- \rightarrow Eu$	−1.991
$F_2 + 2e^- \rightarrow 2F^-$	2.866
$Fe^{2+} + 2e^- \rightarrow Fe$	−0.447
$Fe^{3+} + 3e^- \rightarrow Fe$	−0.037
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.771
$[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$	0.358
$Fe(OH)_3 + e^- \rightarrow Fe(OH)_2 + OH^-$	−0.56
$Fm^{3+} + 3e^- \rightarrow Fm$	−1.89

Half-reaction	E° (V)
$Fm^{2+} + 2e^- \rightarrow Fm$	−2.30
$Ga^{3+} + 3e^- \rightarrow Ga$	−0.549
$Gd^{3+} + 3e^- \rightarrow Gd$	−2.279
$Ge^{2+} + 2e^- \rightarrow Ge$	0.24
$Ge^{4+} + 4e^- \rightarrow Ge$	0.124
$2H^+ + 2e^- \rightarrow H_2$	0.00000
$H_2 + 2e^- \rightarrow 2H^-$	−2.23
$2H_2O + 2e^- \rightarrow H_2 + 2OH^-$	−0.8277
$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O$	1.776
$Hf^{4+} + 4e^- \rightarrow Hf$	−1.55
$Hg^{2+} + 2e^- \rightarrow Hg$	0.851
$2Hg^{2+} + 2e^- \rightarrow Hg_2^{2+}$	0.920
$Hg_2Cl_2 + 2e^- \rightarrow 2Hg + 2Cl^-$	0.26808
$Ho^{2+} + 2e^- \rightarrow Ho$	−2.1
$Ho^{3+} + 3e^- \rightarrow Ho$	−2.33
$I_2 + 2e^- \rightarrow 2I^-$	0.5355
$I_3^- + 2e^- \rightarrow 3I^-$	0.536
$2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O$	1.195
$IO_3^- + 6H^+ + 6e^- \rightarrow I^- + 3H_2O$	1.085
$In^+ + e^- \rightarrow In$	−0.14
$In^{3+} + 2e^- \rightarrow In^+$	−0.443
$In^{3+} + 3e^- \rightarrow In$	−0.3382
$Ir^{3+} + 3e^- \rightarrow Ir$	1.156
$K^+ + e^- \rightarrow K$	−2.931
$La^{3+} + 3e^- \rightarrow La$	−2.379
$Li^+ + e^- \rightarrow Li$	−3.0401
$Lr^{3+} + 3e^- \rightarrow Lr$	−1.96
$Lu^{3+} + 3e^- \rightarrow Lu$	−2.28
$Md^{3+} + 3e^- \rightarrow Md$	−1.65
$Md^{2+} + 2e^- \rightarrow Md$	−2.40
$Mg^{2+} + 2e^- \rightarrow Mg$	−2.372
$Mn^{2+} + 2e^- \rightarrow Mn$	−1.185
$MnO_2 + 4H^+ + 2e^- \rightarrow Mn^{2+} + 2H_2O$	1.224
$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$	1.507
$MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$	0.595
$Mo^{3+} + 3e^- \rightarrow Mo$	−0.200
$N_2 + 2H_2O + 6H^+ + 6e^- \rightarrow 2NH_4OH$	0.092
$HNO_2 + H^+ + e^- \rightarrow NO + H_2O$	0.983
$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$	0.957
$Na^+ + e^- \rightarrow Na$	−2.71
$Nb^{3+} + 3e^- \rightarrow Nb$	−1.099
$Nd^{3+} + 3e^- \rightarrow Nd$	−2.323
$Ni^{2+} + 2e^- \rightarrow Ni$	−0.257
$No^{3+} + 3e^- \rightarrow No$	−1.20
$No^{2+} + 2e^- \rightarrow No$	−2.50
$Np^{3+} + 3e^- \rightarrow Np$	−1.856
$O_2 + 2H^+ + 2e^- \rightarrow H_2O_2$	0.695
$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$	1.229
$O_2 + 2H_2O + 2e^- \rightarrow H_2O_2 + 2OH^-$	−0.146
$O_3 + 2H^+ + 2e^- \rightarrow O_2 + H_2O$	2.076
$OsO_4 + 8H^+ + 8e^- \rightarrow Os + 4H_2O$	0.838
$P + 3H_2O + 3e^- \rightarrow PH_3(g) + 3OH^-$	−0.87
$PO_4^{3-} + 2H_2O + 2e^- \rightarrow HPO_3^{2-} + 3OH^-$	−1.05
$Pa^{3+} + 3e^- \rightarrow Pa$	−1.34
$Pa^{4+} + 4e^- \rightarrow Pa$	−1.49
$Pb^{2+} + 2e^- \rightarrow Pb$	−0.1262
$PbO + H_2O + 2e^- \rightarrow Pb + 2OH^-$	−0.580
$PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O$	1.6913
$PbSO_4 + 2e^- \rightarrow Pb + SO_4^{2-}$	−0.3588
$Pd^{2+} + 2e^- \rightarrow Pd$	0.951
$Pm^{3+} + 3e^- \rightarrow Pm$	−2.30
$Po^{4+} + 4e^- \rightarrow Po$	0.76
$Pr^{3+} + 3e^- \rightarrow Pr$	−2.353
$Pt^{2+} + 2e^- \rightarrow Pt$	1.18
$[PtCl_4]^{2-} + 2e^- \rightarrow Pt + 4Cl^-$	0.755
$Pu^{3+} + 3e^- \rightarrow Pu$	−2.031
$Ra^{2+} + 2e^- \rightarrow Ra$	−2.8

Half-reaction	E° (V)
$Rb^+ + e^- \rightarrow Rb$	−2.98
$Re^{3+} + 3e^- \rightarrow Re$	0.300
$Rh^{3+} + 3e^- \rightarrow Rh$	0.758
$Ru^{3+} + e^- \rightarrow Ru^{2+}$	0.2487
$S + 2e^- \rightarrow S^{2-}$	−0.47627
$S + 2H^+ + 2e^- \rightarrow H_2S(aq)$	0.142
$2S + 2e^- \rightarrow S_2^{2-}$	−0.42836
$H_2SO_3 + 4H^+ + 4e^- \rightarrow S + 3H_2O$	0.449
$SO_4^{2-} + H_2O + 2e^- \rightarrow SO_3^{2-} + 2OH^-$	−0.93
$Sb + 3H^+ + 3e^- \rightarrow SbH_3$	−0.510
$Sc^{3+} + 3e^- \rightarrow Sc$	−2.077
$Se + 2e^- \rightarrow Se^{2-}$	−0.924
$Se + 2H^+ + 2e^- \rightarrow H_2Se$	−0.082
$SiF_6^{2-} + 4e^- \rightarrow Si + 6F^-$	−1.24
$Sm^{3+} + 3e^- \rightarrow Sm$	−2.304
$Sn^{2+} + 2e^- \rightarrow Sn$	−0.1375
$Sn^{4+} + 2e^- \rightarrow Sn^{2+}$	0.151
$Sr^{2+} + 2e^- \rightarrow Sr$	−2.899
$Ta^{3+} + 3e^- \rightarrow Ta$	−0.6
$TcO_4^- + 4H^+ + 3e^- \rightarrow TcO_2 + 2H_2O$	0.782
$TcO_4^- + 8H^+ + 7e^- \rightarrow Tc + 4H_2O$	0.472
$Tb^{3+} + 3e^- \rightarrow Tb$	−2.28
$Te + 2e^- \rightarrow Te^{2-}$	−1.143
$Te^{4+} + 4e^- \rightarrow Te$	0.568
$Th^{4+} + 4e^- \rightarrow Th$	−1.899
$Ti^{2+} + 2e^- \rightarrow Ti$	−1.630
$Tl^+ + e^- \rightarrow Tl$	−0.336
$Tl^{3+} + 2e^- \rightarrow Tl^+$	1.252
$Tl^{3+} + 3e^- \rightarrow Tl$	0.741
$U^{3+} + 3e^- \rightarrow U$	−1.798
$VO_2^+ + 2H^+ + e^- \rightarrow VO^{2+} + H_2O$	0.991
$V_2O_5 + 6H^+ + 2e^- \rightarrow 2VO^{2+} + 3H_2O$	0.957
$W_2O_5 + 2H^+ + 2e^- \rightarrow 2WO_2 + H_2O$	−0.031
$XeO_3 + 6H^+ + 6e^- \rightarrow Xe + 3H_2O$	2.10
$Y^{3+} + 3e^- \rightarrow Y$	−2.372
$Yb^{3+} + 3e^- \rightarrow Yb$	−2.19
$Zn^{2+} + 2e^- \rightarrow Zn$	−0.7618
$Zn(OH)_4^{2-} + 2e^- \rightarrow Zn + 4OH^-$	−1.199
$Zn(OH)_2 + 2e^- \rightarrow Zn + 2OH^-$	−1.249
$ZrO_2 + 4H^+ + 4e^- \rightarrow Zr + 2H_2O$	−1.553
$Zr^{4+} + 4e^- \rightarrow Zr$	−1.45

E. Properties of water

Density: 0.99984 g/cm^3 at 0°C
0.99970 g/cm^3 at 10°C
0.99821 g/cm^3 at 20°C
0.98803 g/cm^3 at 50°C
0.95840 g/cm^3 at 100°C
Enthalpy (heat) of vaporisation: 45.054 kJ/mol at 0°C
43.990 kJ/mol at 25°C
42.482 kJ/mol at 60°C
40.657 kJ/mol at 100°C
Surface tension: 74.23 J/m^2 at 10°C
71.99 J/m^2 at 25°C
67.94 J/m^2 at 50°C
58.91 J/m^2 at 100°C
Viscosity: 1.793 mPa·s at 0°C
0.890 mPa·s at 25°C
0.547 mPa·s at 50°C
0.282 mPa·s at 100°C
Ion-product constant, K_w (or K_{H2O}): 1.15×10^{-15} at 0°C
1.01×10^{-14} at 25°C
5.31×10^{-14} at 50°C
5.43×10^{-13} at 100°C
Specific heat (C_s): 4.2176 J/(g·°C) at 0°C
4.1818 J/(g·°C) at 20°C
4.1806 J/(g·°C) at 50°C
4.2159 J/(g·°C) at 100°C

Vapour pressure of water

T(°C)	P(kPa)	P(mm Hg)	T(°C)	P(kPa)	P(mm Hg)
0	0.61129	4.585	60	19.932	149.50
5	0.87260	6.545	65	25.022	187.68
10	1.2281	9.211	70	31.176	233.84
15	1.7056	12.793	75	38.563	289.24
20	2.3388	17.542	80	47.373	355.32
25	3.1690	23.769	85	57.815	433.64
30	4.2455	31.844	90	70.117	525.91
35	5.6267	42.203	95	84.529	634.01
40	7.3814	55.364	100	101.32	759.95
45	9.5898	71.929	105	120.79	905.99
50	12.344	92.59	110	143.24	1074.38
55	15.752	118.15	115	169.02	1267.74

F. Physical constants

Selected Physical Constants	
Atomic mass unit	1 amu = $1.6605389 \times 10^{-24}$ g
	1 g = 6.022142×10^{23} amu
Avogadro's number	N = 6.022142×10^{23}/mol
Boltzmann's constant	k = 1.380651×10^{-23} J/K
Charge on electron	e = $1.6021765 \times 10^{-19}$ C
Faraday's constant	F = 9.6485338×10^{4} C/mol
Gas constant	R = 0.0820575 (L atm)/(mol K)
	= 8.31447 J/(mol K)
Mass of electron	m_e = 5.485799×10^{-4} amu
	= 9.109383×10^{-28} g
Mass of neutron	m_n = 1.0086649 amu
	= $1.6749273 \times 10^{-24}$ g
Mass of proton	m_p = 1.0072765 amu
	= $1.6726217 \times 10^{-24}$ g
Pi	π = 3.1415927
Planck's constant	h = 6.626069×10^{-34} J s
Speed of light (in vacuum)	c = 2.99792458×10^{8} m/s (exact)

G. Formation constants for complex ions in aqueous solutions

	Complex ion	Equilibrium equation	K_{st}*
Ammonia complexes	$[Ag(NH_3)_2]^+$	$Ag^+ + 2NH_3 \leftrightarrow [Ag(NH_3)_2]^+$	1.1×10^7
	$[Cu(NH_3)_4]^{2+}$	$Cu^{2+} + 4NH_3 \leftrightarrow [Cu(NH_3)_4]^{2+}$	2.1×10^{13}
	$[Ni(NH_3)_6]^{2+}$	$Ni^{2+} + 6NH_3 \leftrightarrow [Ni(NH_3)_6]^{2+}$	5.5×10^8
Cyanide complexes	$[Ag(CN)_2]^-$	$Ag^+ + 2CN^- \leftrightarrow [Ag(CN)_2]^-$	1.1×10^{18}
	$[Ni(CN)_4]^{2-}$	$Ni^{2+} + 4CN^- \leftrightarrow [Ni(CN)_4]^{2-}$	2.2×10^{31}
	$[Fe(CN)_6]^{3-}$	$Fe^{3+} + 6CN^- \leftrightarrow [Fe(CN)_6]^{3-}$	1×10^{42}
Hydroxide complexes	$[Zn(OH)_4]^{2-}$	$Zn^{2+} + 4OH^- \leftrightarrow [Zn(OH)_4]^{2-}$	4.6×10^{17}
	$[Cr(OH)_4]^-$	$Cr^{3+} + 4OH^- \leftrightarrow [Cr(OH)_4]^-$	8.0×10^{29}
Halide complexes	$[HgCl_4]^{2-}$	$Hg^{2+} + 4Cl^- \leftrightarrow [HgCl_4]^{2-}$	1.2×10^{15}
	$[CdI_4]^{2-}$	$Cd^{2+} + 4I \leftrightarrow [CdI_4]^{2-}$	2.6×10^5
	$[AlF_6]^{3-}$	$Al^{3+} + 6F^- \leftrightarrow [AlF_6]^{3-}$	6.9×10^{19}
Other complexes	$[Ag(S_2O_3)_2]^{3-}$	$Ag^+ + 2S_2O_3^{2-} \leftrightarrow [Ag(S_2O_3)_2]^{3-}$	2.9×10^{13}
	$[Fe(C_2O_4)_3]^{3-}$	$Fe^{3+} + 3C_2O_4^{2-} \leftrightarrow [Fe(C_2O_4)_3]^{3-}$	2.0×10^{20}

*Reported values are overall formation constants

H. Densities of acids, alkalis and some other substances

Acids

HCl Hydrochloric acid, Mw=36.46g/M; 20°C

% (w/w)	M	g/L	p
0.36	0.0987	3.60	1
1.36	0.3749	13.67	1.005
2.364	0.6549	23.88	1.01
3.374	0.9393	34.25	1.015
4.388	1.2276	44.76	1.02
5.408	1.5204	55.43	1.025
6.433	1.8173	66.26	1.03
7.464	2.1188	77.25	1.035
8.49	2.4217	88.30	1.04
9.51	2.7257	99.38	1.045
10.52	3.0296	110.46	1.05
11.52	3.3334	121.54	1.055
12.51	3.6370	132.61	1.06
13.5	3.9434	143.78	1.065
14.495	4.2539	155.10	1.07
15.485	4.5657	166.46	1.075
16.47	4.8787	177.88	1.08
17.45	5.1929	189.33	1.085
18.43	5.5098	200.89	1.09
19.41	5.8294	212.54	1.095
20.39	6.1517	224.29	1.1
21.36	6.4736	236.03	1.105
22.33	6.7982	247.86	1.11
23.29	7.1224	259.68	1.115
24.25	7.4493	271.60	1.12
25.22	7.7818	283.73	1.125
26.2	8.1201	296.06	1.13
27.18	8.4611	308.49	1.135
28.18	8.8111	321.25	1.14
29.17	9.1606	334.00	1.145
30.14	9.5066	346.61	1.15
31.14	9.8647	359.67	1.155
32.14	10.2256	372.82	1.16
33.16	10.5956	386.31	1.165
34.18	10.9683	399.91	1.17
36.23	11.7256	427.51	1.18
38.32	12.5071	456.01	1.19
40	13.1432	479.20	1.198

$HClO_4$ Perchloric Acid, Mw=100.46g/M; 20°C

% (w/w)	M	g/L	p
1	0.1000	10.05	1.005
3.61	0.3665	36.82	1.02
6.88	0.7122	71.55	1.04
10.06	1.0615	106.64	1.06
13.08	1.4062	141.26	1.08
16	1.7519	176.00	1.1
18.88	2.1049	211.46	1.12
21.64	2.4557	246.70	1.14
24.3	2.8059	281.88	1.16

26.82	3.1503	316.48	1.18
29.26	3.4951	351.12	1.2
31.61	3.8388	385.64	1.22
33.85	4.1782	419.74	1.24
36.03	4.5190	453.98	1.26
38.1	4.8545	487.68	1.28
40.1	5.1891	521.30	1.3
42.02	5.5212	554.66	1.32
43.89	5.8543	588.13	1.34
45.71	6.1881	621.66	1.36
47.49	6.5236	655.36	1.38
49.23	6.8606	689.22	1.4
50.9	7.1947	722.78	1.42
52.51	7.5268	756.14	1.44
54.03	7.8523	788.84	1.46
55.55	8.1838	822.14	1.48
57.06	8.5198	855.90	1.5
58.54	8.8573	889.81	1.52
60.04	9.2038	924.62	1.54
61.52	9.5532	959.71	1.56
63	9.9084	995.40	1.58
64.5	10.2727	1032.00	1.6
66.01	10.6447	1069.36	1.62
66.76	10.8321	1088.19	1.63
67.51	11.0209	1107.16	1.64
68.26	11.2113	1126.29	1.65
69.02	11.4049	1145.73	1.66
69.77	11.5982	1165.16	1.67
70.15	11.6963	1175.01	1.675

HNO_3 Nitric Acid, Mw=63.01g/M; 20°C

% (w/w)	M	g/L	p
0.3296	0.0523	3.30	1
3.982	0.6446	40.62	1.02
7.53	1.2429	78.31	1.04
10.97	1.8455	116.28	1.06
14.31	2.4528	154.55	1.08
17.58	3.0690	193.38	1.1
20.79	3.6954	232.85	1.12
23.94	4.3313	272.92	1.14
27	4.9706	313.20	1.16
30	5.6182	354.00	1.18
32.94	6.2733	395.28	1.2
35.93	6.9568	438.35	1.22
39.02	7.6789	483.85	1.24
42.14	8.4267	530.96	1.26
45.27	9.1963	579.46	1.28
48.42	9.9898	629.46	1.3
51.71	10.8328	682.57	1.32
55.13	11.7242	738.74	1.34
58.78	12.6870	799.41	1.36
62.7	13.7321	865.26	1.38
66.97	14.8799	937.58	1.4
71.63	16.1426	1017.15	1.42
76.71	17.5309	1104.62	1.44
82.39	19.0905	1202.89	1.46

89.07	20.9211	1318.24	1.48
96.73	23.0273	1450.95	1.5
97.23	23.1772	1460.39	1.502
97.74	23.3298	1470.01	1.504
98.25	23.4827	1479.65	1.506
98.76	23.6359	1489.30	1.508
99.26	23.7871	1498.83	1.51
99.77	23.9410	1508.52	1.512
100	24.0121	1513.00	1.513

H_3PO_4 Phosphoric Acid, Mw= 98.00g/M; 20°C

% (w/w)	M	g/L	p
1	0.1024	10.04	1.0038
2	0.2060	20.18	1.0092
4	0.4163	40.80	1.02
6	0.6312	61.85	1.0309
8	0.8506	83.36	1.042
10	1.0747	105.32	1.0532
12	1.3037	127.76	1.0647
14	1.5377	150.70	1.0764
16	1.7770	174.14	1.0884
18	2.0219	198.14	1.1008
20	2.2722	222.68	1.1134
24	2.7906	273.48	1.1395
28	3.3329	326.62	1.1665
30	3.6138	354.15	1.1805
35	4.3429	425.60	1.216
40	5.1184	501.60	1.254
45	5.9372	581.85	1.293
50	6.8112	667.50	1.335
55	7.7393	758.45	1.379
60	8.7306	855.60	1.426

H_2SO_4 Sulfuric Acid, Mw=98.08g/M; 20°C

% (w/w)	M	g/L	p
0.261	0.0266	2.61	1
3.242	0.3372	33.07	1.02
6.237	0.6613	64.86	1.04
9.129	0.9866	96.77	1.06
11.96	1.3170	129.17	1.08
14.73	1.6520	162.03	1.1
17.43	1.9904	195.22	1.12
18.76	2.1614	211.99	1.13
23.95	2.8570	280.22	1.17
25.21	3.0330	297.48	1.18
27.72	3.3915	332.64	1.2
30.18	3.7540	368.20	1.22
32.61	4.1228	404.36	1.24
35.01	4.4976	441.13	1.26
37.36	4.8757	478.21	1.28
39.68	5.2594	515.84	1.3
41.95	5.6458	553.74	1.32
44.17	6.0346	591.88	1.34
46.33	6.4242	630.09	1.36
48.45	6.8170	668.61	1.38
50.5	7.2084	707.00	1.4
52.51	7.6024	745.64	1.42
54.49	8.0002	784.66	1.44
56.41	8.3971	823.59	1.46
58.31	8.7988	862.99	1.48
60.17	9.2022	902.55	1.5
62	9.6085	942.40	1.52
63.81	10.0191	982.67	1.54
65.59	10.4323	1023.20	1.56
67.35	10.8496	1064.13	1.58

69.09	11.2708	1105.44	1.6
70.82	11.6974	1147.28	1.62
72.52	12.1261	1189.33	1.64
74.22	12.5617	1232.05	1.66
75.92	13.0042	1275.46	1.68
77.63	13.4554	1319.71	1.7
79.37	13.9189	1365.16	1.72
81.16	14.3983	1412.18	1.74
83.06	14.9047	1461.86	1.76
85.16	15.4552	1515.85	1.78
87.69	16.0932	1578.42	1.8
91.11	16.9066	1658.20	1.82
91.56	17.0088	1668.22	1.822
92	17.1093	1678.08	1.824
92.51	17.2230	1689.23	1.826
93.03	17.3388	1700.59	1.828
93.64	17.4716	1713.61	1.83
94.32	17.6177	1727.94	1.832
95.12	17.7865	1744.50	1.834
95.72	17.9085	1756.46	1.835

HCOOH Formic Acid, Mw=46.03g/M; 20°C

% (w/w)	M	g/L	p
5	1.0990	50.59	1.0117
10	2.2262	102.47	1.0247
16	3.6129	166.30	1.0394
22	5.0366	231.84	1.0538
30	6.9933	321.90	1.073
38	9.0150	414.96	1.092
42	10.0515	462.67	1.1016
50	12.1747	560.40	1.1208
58	14.3419	660.16	1.1382
62	15.4535	711.33	1.1473
70	17.7258	815.92	1.1656
74	18.8947	869.72	1.1753
80	20.6144	948.88	1.1861
86	22.3772	1030.02	1.1977
90	23.5509	1084.05	1.2045
92	24.1423	1111.27	1.2079
94	24.7467	1139.09	1.2118
96	25.3588	1167.26	1.2159
98	25.9403	1194.03	1.2184
100	26.5327	1221.30	1.2213

CH_3COOH Acetic Acid Glacial, Mw=60.05g/M; 20°C

% (w/w)	M	g/L	p
5	0.8372	50.28	1.0055
10	1.6863	101.26	1.0126
15	2.5466	152.93	1.0195
20	3.4175	205.22	1.0261
25	4.2981	258.10	1.0324
30	5.1872	311.49	1.0383
35	6.0826	365.26	1.0436
40	6.9862	419.52	1.0488
45	7.8939	474.03	1.0534
50	8.8052	528.75	1.0575
55	9.7187	583.61	1.0611
60	10.6331	638.52	1.0642
65	11.5463	693.36	1.0667
70	12.4566	748.02	1.0686
75	13.3601	802.28	1.0697
80	14.2535	855.92	1.0699
82	14.6057	877.07	1.0696
84	14.9549	898.04	1.0691

86	15.3010	918.82	1.0684
88	15.6422	939.31	1.0674
90	15.9767	959.40	1.066
92	16.3057	979.16	1.0643
94	16.6241	998.28	1.062
96	16.9283	1016.54	1.0589
98	17.2157	1033.80	1.0549
100	17.4804	1049.70	1.0497

Alkalis

KOH Potassium Hydroxide, Mw=56.1g/M; 20°C

% (w/w)	M	g/L	p
0.197	0.0351	1.97	1
2.38	0.4327	24.28	1.02
4.58	0.8491	47.63	1.04
6.74	1.2735	71.44	1.06
8.89	1.7114	96.01	1.08
11.03	2.1627	121.33	1.1
13.14	2.6233	147.17	1.12
15.22	3.0928	173.51	1.14
17.29	3.5751	200.56	1.16
19.35	4.0701	228.33	1.18
21.38	4.5733	256.56	1.2
23.38	5.0844	285.24	1.22
25.36	5.6054	314.46	1.24
27.32	6.1360	344.23	1.26
29.25	6.6738	374.40	1.28
31.15	7.2184	404.95	1.3
33.03	7.7718	436.00	1.32
34.9	8.3362	467.66	1.34
36.73	8.9042	499.53	1.36
38.56	9.4853	532.13	1.38
40.37	10.0745	565.18	1.4
42.15	10.6690	598.53	1.42
43.92	11.2736	632.45	1.44
45.66	11.8830	666.64	1.46
47.39	12.5022	701.37	1.48
49.1	13.1283	736.50	1.5
49.95	13.4447	754.25	1.51
50.8	13.7640	772.16	1.52
51.64	14.0836	790.09	1.53
52.05	14.2418	798.97	1.535

NaOH Sodium Hydroxide, Mw=40.0g/M, 20°C

% (w/w)	M	g/L	p
0.159	0.0398	1.59	1
1.94	0.4947	19.79	1.02
3.74	0.9724	38.90	1.04
5.56	1.4734	58.94	1.06
7.38	1.9926	79.70	1.08
9.19	2.5273	101.09	1.1
11.01	3.0828	123.31	1.12
12.83	3.6566	146.26	1.14
14.64	4.2456	169.82	1.16
16.44	4.8498	193.99	1.18
18.25	5.4750	219.00	1.2
20.07	6.1214	244.85	1.22
21.9	6.7890	271.56	1.24
23.73	7.4750	299.00	1.26
25.56	8.1792	327.17	1.28
27.41	8.9083	356.33	1.3
29.26	9.6558	386.23	1.32
31.14	10.4319	417.28	1.34
33.06	11.2404	449.62	1.36

35.01	12.0785	483.14	1.38
36.99	12.9465	517.86	1.4
38.99	13.8415	553.66	1.42
41.03	14.7708	590.83	1.44
43.12	15.7388	629.55	1.46
45.22	16.7314	669.26	1.48
46.27	17.2356	689.42	1.49
47.33	17.7488	709.95	1.5
48.38	18.2635	730.54	1.51
49.44	18.7872	751.49	1.52
50.5	19.3163	772.65	1.53

Other substances

H_2O_2 Hydrogen Peroxide, Mw=34.01g/M; 18°C

% (w/w)	M	g/L	p
1	0.2947	10.02	1.0022
2	0.5915	20.12	1.0058
4	1.1915	40.52	1.0131
6	1.8002	61.22	1.0204
8	2.4174	82.22	1.0277
10	3.0435	103.51	1.0351
12	3.6783	125.10	1.0425
14	4.3218	146.99	1.0499
16	4.9745	169.18	1.0574
18	5.6360	191.68	1.0649
20	6.3070	214.50	1.0725
22	6.9875	237.64	1.0802
24	7.6777	261.12	1.088
26	8.3779	284.93	1.0959
28	9.0891	309.12	1.104
30	9.8106	333.66	1.1122
35	11.6567	396.45	1.1327
40	13.5678	461.44	1.1536
45	15.6117	530.96	1.1799
50	17.5919	598.30	1.1966
55	19.7101	670.34	1.2188
60	21.9041	744.96	1.2416
65	24.1805	822.38	1.2652
70	26.5448	902.79	1.2897
75	28.9966	986.18	1.3149
80	31.5343	1072.48	1.3406
85	34.1575	1161.70	1.3667
90	36.8653	1253.79	1.3931
95	39.6564	1348.72	1.4197

NH_3 Ammonia, Mw=17.03g/M; 20°C

% (w/w)	M	g/L	p
0.0465	0.0273	0.46	0.998
0.977	0.5703	9.71	0.994
1.89	1.0987	18.71	0.99
3.3	1.9068	32.47	0.984
4.27	2.4572	41.85	0.98
5.75	3.2886	56.01	0.974
6.75	3.8447	65.48	0.97
8.29	4.6926	79.92	0.964
9.34	5.2651	89.66	0.96
10.95	6.1341	104.46	0.954
12.03	6.7108	114.29	0.95
13.71	7.5997	129.42	0.944
14.88	8.2133	139.87	0.94
16.65	9.1316	155.51	0.934
17.85	9.7478	166.01	0.93
19.67	10.6724	181.75	0.924
20.88	11.2799	192.10	0.92

22.75	12.2099	207.94	0.914
24.03	12.8405	218.67	0.91
26	13.8015	235.04	0.904
27.33	14.4433	245.97	0.9
29.33	15.3970	262.21	0.894
30.68	16.0336	273.05	0.89
32.84	17.0467	290.31	0.884
34.35	17.7499	302.28	0.88

NH_2OH Hydroxylamine, Mw=33.03g/M; 20°C

% (w/w)	M	g/L	p
1	0.3028	10.00	1.0002
2	0.6069	20.05	1.0023
4	1.2189	40.26	1.0065
6	1.8360	60.64	1.0107
8	2.4581	81.19	1.0149
10	3.0857	101.92	1.0192
12	3.7184	122.82	1.0235
14	4.3564	143.89	1.0278
16	5.0001	165.15	1.0322
18	5.6490	186.59	1.0366
22	6.9630	229.99	1.0454
26	8.2998	274.14	1.0544
28	8.9781	296.55	1.0591
30	9.6612	319.11	1.0637
35	11.3965	376.43	1.0755
40	13.1698	435.00	1.0875
45	14.9823	494.87	1.0997
50	16.8362	556.10	1.1122
55	18.7313	618.70	1.1249

CH_3OH Methanol, Mw=32.04g/M; 20°C

% (w/w)	M	g/L	p
0	0.0000	0.00	0.9982
5	1.5443	49.48	0.9896
10	3.0634	98.15	0.9815
15	4.5599	146.10	0.974
20	6.0337	193.32	0.9666
25	7.4844	239.80	0.9592
30	8.9092	285.45	0.9515
35	10.3045	330.16	0.9433
40	11.6667	373.80	0.9345
45	12.9944	416.34	0.9252
50	14.2884	457.80	0.9156
55	15.5387	497.86	0.9052
60	16.7528	536.76	0.8946
65	17.9217	574.21	0.8834
70	19.0403	610.05	0.8715
75	20.1124	644.40	0.8592
80	21.1461	677.52	0.8469
85	22.1255	708.90	0.834
90	23.0393	738.18	0.8202
95	23.9042	765.89	0.8062
100	24.7097	791.70	0.7917

C_2H_5OH Ethanol, Mw=46.1g/M; 20°C

% (w/w)	M	g/L	p	volume %
4.02	0.8642	39.84	0.991	5.05
8.05	1.7195	79.27	0.9847	10.04
12.14	2.5778	118.84	0.9789	15.06
16.21	3.4234	157.82	0.9736	20.00
20.4	4.2840	197.49	0.9681	25.03
24.64	5.1429	237.09	0.9622	30.03

28.93	5.9969	276.46	0.9556	35.02
33.33	6.8540	315.97	0.948	40.03
37.83	7.7096	355.41	0.9395	45.03
42.47	8.5686	395.01	0.9301	50.04
44.32	8.9044	410.49	0.9262	52.01
46.23	9.2470	426.29	0.9221	54.01
48.15	9.5872	441.97	0.9179	56.00
50.15	9.9375	458.12	0.9135	58.03
52.12	10.2782	473.82	0.9091	60.03
54.1	10.6158	489.39	0.9046	62.01
56.12	10.9562	505.08	0.9	64.00
58.22	11.3055	521.19	0.8952	66.02
60.29	12.8218	591.08	0.9804	68.02
62.4	11.9859	552.55	0.8855	70.01
64.59	12.3351	568.65	0.8804	72.04
66.79	12.6800	584.55	0.8752	74.06
69	13.0217	600.30	0.87	76.05
73.53	13.7043	631.77	0.8592	80.04
75.85	14.0446	647.46	0.8536	82.03
78.24	14.3887	663.32	0.8478	84.04
80.68	14.7324	679.16	0.8418	86.05
83.17	15.0752	694.97	0.8356	88.05
85.69	15.4130	710.54	0.8292	90.02
88.62	15.7940	728.10	0.8216	92.25
91.02	16.0953	742.00	0.8152	94.02
93.86	16.4387	757.83	0.8074	96.02
96.8	16.7773	773.43	0.799	98.00
100	17.1193	789.20	0.7892	100.00

C_3H_8O Isopropyl Alcohol (2-Propanol) Mw=60.10g/M; 15°C

% (w/w)	M	g/L	p
5	0.8240	49.52	0.9904
10	1.6366	98.36	0.9836
15	2.4402	146.66	0.9777
20	3.2329	194.30	0.9715
25	4.0108	241.05	0.9642
30	4.7666	286.47	0.9549
35	5.5010	330.61	0.9446
40	6.2116	373.32	0.9333
45	6.9035	414.90	0.922
50	7.5740	455.20	0.9104
55	8.2253	494.34	0.8988
60	8.8542	532.14	0.8869
65	9.4656	568.88	0.8752
70	10.0562	604.38	0.8634
75	10.6285	638.78	0.8517
80	11.1774	671.76	0.8397
85	11.7077	703.63	0.8278
90	12.2121	733.95	0.8155
95	12.6867	762.47	0.8026
100	13.2962	799.10	0.7991

$C_3H_8O_3$ Glycerol, Mw=92.09g/M; 20°C

% (w/w)	M	g/L	p
5	0.5484	50.51	1.0101
10	1.1099	102.21	1.0221
15	1.6850	155.18	1.0345
20	2.2739	209.40	1.047
25	2.8768	264.93	1.0597
30	3.4945	321.81	1.0727
35	4.1275	380.10	1.086
40	4.7758	439.80	1.0995

45	5.4377	500.76	1.1128
50	6.1152	563.15	1.1263
55	6.8074	626.89	1.1398
60	7.5142	691.98	1.1533
65	8.2371	758.55	1.167
70	8.9756	826.56	1.1808
75	9.7274	895.80	1.1944
80	10.4932	966.32	1.2079
85	11.2736	1038.19	1.2214
90	12.0668	1111.23	1.2347
95	12.8764	1185.79	1.2482
100	13.6920	1260.90	1.2609

$(CH_3)_2CO$ Acetone, Mw=58.08g/M; 25°C

% (w/w)	M	g/L	p
5	0.8523	49.50	0.99
10	1.6925	98.30	0.983
15	2.5207	146.40	0.976
20	3.3368	193.80	0.969
25	4.1365	240.25	0.961
30	4.9277	286.20	0.954
35	5.6947	330.75	0.945
40	6.4532	374.80	0.937
45	7.1823	417.15	0.927
50	7.8857	458.00	0.916
55	8.5606	497.20	0.904
60	9.2252	535.80	0.893
65	9.8597	572.65	0.881
70	10.4735	608.30	0.869
75	11.0537	642.00	0.856
80	11.6116	674.40	0.843
85	12.1470	705.50	0.83
90	12.6446	734.40	0.816
95	13.1181	761.90	0.802
100	13.5331	786.00	0.786

$C_6H_{12}O_6$ Glucose, Mw=180.16g/M; 20°C

% (w/w)	M	g/L	p
2	0.1117	20.12	1.0058
4	0.2251	40.55	1.0138
6	0.3402	61.30	1.0216
8	0.4572	82.37	1.0296
10	0.5760	103.77	1.0377
12	0.6967	125.52	1.046
14	0.8192	147.59	1.0542
16	0.9437	170.02	1.0626
18	1.0702	192.82	1.0712
20	1.1987	215.96	1.0798
22	1.3293	239.49	1.0886
24	1.4619	263.38	1.0974
26	1.5967	287.66	1.1064
28	1.7334	312.28	1.1153
30	1.8728	337.41	1.1247

$C_{12}H_{22}O_{11}$ Sucrose, Mw=342.30g/M; 20°C

% (w/w)	M	g/L	p	Refraction index
2	0.0587	20.10	1.005	1.3359
4	0.1184	40.52	1.013	1.3388
6	0.1790	61.26	1.021	1.3418
8	0.2405	82.32	1.029	1.3448
10	0.3032	103.80	1.038	1.3478

12	0.3667	125.52	1.046	1.3509
14	0.4311	147.56	1.054	1.3541
16	0.4969	170.08	1.063	1.3573
18	0.5637	192.96	1.072	1.3605
20	0.6316	216.20	1.081	1.3638
22	0.7006	239.80	1.09	1.3672
24	0.7706	263.76	1.099	1.3706
26	0.8416	288.08	1.108	1.3740
28	0.9145	313.04	1.118	1.3775
30	0.9877	338.10	1.127	1.3811
32	1.0629	363.84	1.137	1.3847
34	1.1383	389.64	1.146	1.3883
36	1.2158	416.16	1.156	1.3920
38	1.2944	443.08	1.166	1.3958
40	1.3742	470.40	1.176	1.3997
42	1.4564	498.54	1.187	1.4036
44	1.5387	526.68	1.197	1.4076
46	1.6234	555.68	1.208	1.4117
48	1.7094	585.12	1.219	1.4158
50	1.7967	615.00	1.23	1.4200
52	1.8852	645.32	1.241	1.4242
54	1.9751	676.08	1.252	1.4285
56	2.0663	707.28	1.263	1.4329
58	2.1604	739.50	1.275	1.4373
60	2.2542	771.60	1.286	1.4418
62	2.3510	804.76	1.298	1.4464
64	2.4493	838.40	1.31	1.4509
66	2.5490	872.52	1.322	1.4555

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У книзі представлені основні розділи аналітичної хімії, такі як якісний та кількісний хімічний аналіз, відбір проб та підготовка проб, обробка статистичних даних, методи розділення. Розглянуто сучасні фізико-хімічні методи аналізу. Викладено теоретичні основи методів, визначено умови та галузі їх практичного застосування. Контрольні запитання та завдання, подані в кінці кожного розділу, допоможуть користувачам закріпити вивчений матеріал.

Книга призначена для студентів спеціальностей: хімічна технологія та інженерія, біотехнологія та біоінженерія, фармація та промислова фармація. Конспект лекції складається з двох частин. Перша частина включає розділи 1-9 та охоплює загальні питання аналітичної хімії, рівняння та рівноваги, класичні методи хімічного аналізу. Друга частина включає розділи 10-18 і охоплює інструментальні методи хімічного аналізу.

Навчальне видання

Т. М. Деркач

Аналітична хімія для технологів

Навчальний посібник

Рекомендовано Вченою радою
Київського національного університету технологій та дизайну
як навчальний посібник для студентів закладів вищої освіти
в галузях хімічної технології та інженерії, біотехнології
та біоінженерії, фармації та промислової фармації

Відповідальна за поліграфічне виконання А. В. Пугач

Підп. до друку 23.09.2020 р. Формат 60×84 1/8.
Ум. друк. арк. 24,50. Облік. вид. арк. 22,80. Наклад 300 пр. Зам. 1497.

Видавець і виготовлювач Київський національний університет технологій та дизайну.
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Свідоцтво про внесення суб'єкта видавничої справи до державного реєстру видавців, виготівників і розповсюджувачів видавничої продукції ДК № 993 від 24.07.2002.