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الكيمياء التحليلية (المرحلة الاولى-علوم الحياة)

مادة نظرية للدراسة الصباحية والمسائية

الفصل الدراسي الثاني

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Lec 1

Introduction to Analytical Chemistry

Introduction

Analytical chemistry is the science of obtaining, processing, and communicating information about the composition and structure of matter. In other words, it is the art and science of determining what matter is and how much of it exists.Analytical chemistry is science that concerned with the separation, identification, and determination of the relative amounts of the components making up a sample.

Applications of Analytical Chemistry

Analytical chemistry used in many fields:

· In ***medicine***, analytical chemistry is the basis for clinical laboratory tests which help physicians diagnosis disease and chart progress in recovery.

· In ***industry***, analytical chemistry provides the means of testing raw materials and for assuring the quality of finished products whose chemical composition is critical.

· ***Enviermental quality*** is often evaluated by testing for suspected contaminants using the techniques of analytical chemistry.

Classification of analysis

Qualitative analysis: An analysis in which we determine the identity of the constituent species in a sample.

These tests involve conversion the substance usually by using other materials into a new compound which possesses characteristics and properties such as:

A-Formation of colored precipitates:

$Pb^{++} + CrO_4 \leftrightarrow PbCrO_4$ (Yellow PPt.)

B-Solubility in some solvents:

$Ag^{+}+Cl \leftrightarrow AgCl_{(white\ ppt.)} \rightarrow^{2NH3(aq)} \rightarrow Ag(NH_3)_2^{+} + Cl^{-} \rightarrow \rightarrow^{HNO3} \rightarrow AgCl(ppt)$

C-Formation of complex ion (Coloured):

$Cu^{++} + 4NH_3 \leftrightarrow Cu(NH_3)_4^{++}$(Blue complex ion)

D-Emmision of gasses possessor of special smells :Like ammonia, H_2S, etc……..

E-Flame test:

Cations solutions when heated in Bunsen flame, impart a colour to the flame, impart a colour to the flame such as: the flame is coloured an intense yellow by vapors of sodium salts and violet by vapors of potassium salts,

Sr^{++} + flame →Carmine red

Ba^{++} + flame →apple green

Ca^{++} + flame→ brick red

Quantitative analysis: An analysis in which we determine how much of a constituent species is present in a sample.

Sample analysis

Analytes: The constituents of interest in a sample.

Matrix: All other constituents in a sample except for the analytes.

Classifying Analytical Techniques

Classical techniques

Mass, volume, and charge are the most common signals for classical techniques, and the corresponding techniques are:

1- Gravimetric techniques.

2- Volumetric techniques.

3- Coulometeric techniques.

Instrumental techniques

1- **Spectroscopic methods** - measuring the interaction between the analyte and electromagnetic radiation (or the production of radiation by an analyte).

2- **Electroanalytic methods** - measure an electrical property (i.e., potential, current,resistance, amperes, etc.) chemically related to the amount of analyte.

Basic Tools and Operations of Analytical Chemistry

Equipments for Measuring Mass (Analytical Balance)

An object's mass is measured using a **balance.**

Equipment for Measuring Volume

Volumetric flask is designed to contain a specified volume of solution at a stated temperature, usually 20 °C.

Pipette is used to deliver a specified volume of solution. Several different styles of pipets are available.

Burette is volumetric glassware used to deliver variable, but known volumes of solution. A burette is a long, narrow tube with graduated markings, and a stopcock for dispensing the solution.

Preparing Solutions

Preparing a solution of known concentration is perhaps the most common activity in any analytical lab. Two methods for preparing solutions are described in this section. A ***stock solution*** is prepared by weighing out an appropriate portion of a pure solid or by measuring out an appropriate volume of a pure liquid and diluting to a known volume.

Preparing Solutions by Dilution

Solutions with small concentrations are often prepared by diluting a more concentrated stock solution. A known volume of the stock solution is transferred to a new container and brought to a new volume.

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Methods for the expression of concentration

1-Mole: Symbol (mol)

Is defined as the quantity of given substance that contains as many molecules for formula units as the number of atoms in exactly

Number of moles for compounds = $\frac{\text{weight}}{\text{Molecular weight}}$

Note: Molecular weight of compounds is the sum of the atomic weight of all the atoms in the molecular formula of the compounds

For example: number of moles of (NH2)2CO = $\frac{\text{weight}}{(14+(2x1))x2+12+16}$

Number of moles of ion = $\frac{\text{wt}}{\text{Ionic weight}}$, for SO4 = $\frac{\text{weight}}{32+(4x16)}$

Number of moles of element = $\frac{\text{wt}}{\text{Atomic weight}}$, Ag = $\frac{\text{wt}}{108}$

2-Molarity: symbol (M)

When we dissolve a substance in a liquid, we call the substance (solute) and the liquid (solvent), so the molarity of solution defines the number of gram-molecular weight (or) moles of solute dissolved in 1 liter of solution, or the number of millimolecular weight in 1 millimeter of solution

$$M = \frac{number\ of\ moles\ of\ solute}{volumeof\ solution\ in\ liter}$$

$$Number\ of\ moles = \frac{wt}{M.wt}$$

For solid sustances

Thus : $M = \frac{wt}{Mwt} x \frac{1000}{Vol\ ml}$

Notes: (wt) means weight in gram unit (gm)

(vol) means volume of solution in milliter unit (ml)

For liquid substances

Also $M = \frac{Density\ or\ specific\ gravity\ x\ percentage\ x1000}{M.wt}$

Example: 1

What is the molarity of a solution containing (16 gm) CH3OH in 200 ml of solution? M.wt =32.

Sol.

$M=\frac{wt}{M\ wt} \times \frac{1000}{Vol}$

$=\frac{16}{32} \times \frac{1000}{200}$

=2.5 mol/L

Example:2

Calculate the molarity of H2SO4 solution of specific gravity 1.198 , containing 27 % H2SO4 by by weight ?

At.wt. of H=1 , S=32 , O=16 .

Sol.

M.wt of H2So4 = (2x1)+32 +(4x16)=98 gm/mol

$M= \frac{Sp.gr \times \% \times 1000}{M.wt}$

$=\frac{1.198 \times 0.27 \times 1000}{98}$

=3.3 mol/L

3- <u>Normality</u>: symbol (N)

The normality of a solution expresses the number of milliequivalents of solute contained in 1 ml of the solution, or the number of gram

equivalents contained in 1 liter.

$$N = \frac{number\ of\ gram-equivalent\ weight\ of\ solute}{Volume\ of\ solution\ in\ liters}$$

Number of gram-equivalent weight = $\frac{wt}{eq.wt}$

Note: (eq.wt) means equivalent weight. (Its unit is $\frac{gm}{gm.m.eq}$)

So, for solid substances

$$N = \frac{wt.(gm)}{eq.wt} \times \frac{1000}{vol.(ml)}$$

And, for liquid substances

$$N = \frac{specific\ gravity\ or\ density \times \% \times 1000}{eq.wt.}$$

Example :1

How many gram-equivalent of solute are contained in 0.5L of 0.2 N solution?

Sol.

$$N = \frac{number\ of\ gram-equivalent\ weight\ of\ solute}{Volume\ of\ solution\ in\ liters}$$

$0.2 = \frac{x}{0.5}$ = 0.1 gm. Equivalent of solute

Example: 2

How many grams of solute are required to prepare 1 liter of 1N solution of NaCl , M.wt = 58.45 ?

Sol.

$$N = \frac{wt.(gm)}{eq.wt} \times \frac{1000}{vol.(ml)}$$

=58.45 gm.

Note: $N = n \times M$

Which, N=Normality

n= Valence number or equivalence number *

M=Molarity

*Valence number of an element is the number of atoms of hydrogen (or

its equivalent) which one atom of the element combines with or displaces.

So, in NaCl: M.wt =eq.wt

But in H2SO4: eq.wt= M.wt/2 because there are 2 hydrogens (protons) which displaces

Example3

What will be the normality of 3 molar solution of calcium hydroxide Ca $(OH)_2$?

Solution:

N=MXn

3X2=6 N

Calculation of n

HCl=1 , H_2SO4=2 , H_3PO4=3, NaOH =1, $Ca(OH)_2$=2 , $Al(OH)_3$ =3, $CaCl_2$=2, Na_2SO4=2 , Na_2CO3=2, CaSO4=2

4-Percentage concentration:

The percentage composition of a solution can be expressed in several ways. Three of the common methods are defined as follows:

Weight percent = $\frac{weight\ of\ solute}{weight\ of\ solution}$ x100

Volume percent = $\frac{volume\ of\ solute}{volume\ of\ solution}$ x100

(Weight /Volume percent) = $\frac{weight\ of\ solute}{volume\ of\ solution}$ x100

5-parts per million concentration :

For much diluted solution, the concentration is more conveniently expressed is part per million (ppm). This term is defined by equation:

ppm = $\frac{weight\ of\ solute\ (g)}{total\ weight\ of\ solution\ (g)}$ x 10^6

ppm = $\frac{weight\ of\ solute\ (mg)}{total\ volume\ in\ L)}$ x or mg/L

$$\text{ppm} = \frac{volume\ of\ solute\ (ml)}{total\ volume of\ solution\ (ml)} \times 10^6$$

The relation between (ppm) and (molarity) is

ppm= molarity x molecular weight x 1000

The relation between (ppm) and (normality) is:

ppm = normality x equivalent weight x 1000

Example :

Aqueous solution of $NiCl_2$ with a concentration of 500 ppm, what is the molarity and normality of this solution? At.wt of : Ni=58.69 , Cl=35.5

Diluting solutions:

Example:

You are given a solution of 14.8 M NH_3 , How many milliliters of this solution do you require to give 100ml of 1M NH_3 when dilute ?

In this kinds of examples and if you need to get a diluted solution, follow the dilution equation:

$$Mi \times Vi = Mf \times Vf$$

$14.8 \times Vi = 1 \times 100$

Vi = 6.76 ml

Home work

Question: 45.57 mL of a solution is diluted to 63.40 mL. The diluted solution is found to have a concentration of 0.433 N. What was the concentration of the original solution?

Question: Calculate the weight of Calcium hydroxide present in 250 ml of two normal solution?

Question: If 40 grams of NaOH with an equivalent weight of 40 is dissolved in one liter of a solution, does the normality of the solution is one , give the calculation ?

Question: Calculate the molarity of 0.650 N HCl.

Question : What will be the normality of 3 molar solution of calcium hydroxide?

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Volumetric analysis

An important method for determining the amount of particular substance which is based on measuring the volume of reactant solution.

Suppose substance ((A)) react in solution with substance ((B)). If you know the volume and concentration of ((B)) that just react with substance ((A)) in a sample, you could determine the amount of ((A)).

*The reagent of exactly known composition (volume and concentration) in a titration is called a ((**Standard solution**)).

Commonly, the concentration of standard solution is arrived at in either of two ways:

1- From preparatory data obtained when a carefully weighed quantity of the pure reagent is diluted to an exactly known volume.

2- Form data obtained by titration of a weighed quantity of a pure compound with the reagent.

The first is named primary standard solution; the second is named secondary standard solution.

A primary standard substance should satisfy the following requirements:

1- It must be of the highest purity.

2- It should be stable, not be attacked by constituents of the atmosphere.

3- The compound should not be hygroscopic, otherwise drying and weighing would be difficult

4- It should be available and not too expensive.

5- It should have a high equivalent weight.

Titration:

It is a process for determining the amount of the substance by adding to it a carefully measured volume of standard solution until the reaction between them is just complete. The point at which this occurs is called the equivalence point or the theoretical end point.

Equivalence point: is the point where the amount of titrating solution added is chemically equivalent to the amount of substance being titrated:

Number of milliequivalent of titrant=Number of milliequivalent of titrated

Volume × normality = volume × normality

The completion of the titration should be detectable by the addition of a reagent, known as an indicator.

Indicator: is a substance that undergoes color change when a reaction approaches completion.

After the reaction between the substance and the standard solution is practically complete, the indicator should give a clear visual change in the liquid being titrated. The point at which this occurs is called the end point of titration.

End point: is the point where the indicator changes color. In the ideal titration the visible end point will coincide with the equivalence point. In practice, however, a very small difference usually occurs, this represents the titration error.

Titration error: is the volume difference between the end point and equivalence point, (it must be very small).

Example:

Titration of HCl with NaOH solution.

Transfer an accurate volume of HCl solution to conical flask and add a few drops of phenolphthalein indicator. Phenolphthalein indicator is

colorless in HCl solution but turns pink at the completion of the reaction of the reaction of NaOH with HCl.

Sodium hydroxide is contained in a buret.

Buret: is a glass tube graduated to measure the volume of liquid delivered from the stopcock.

The solution in the buret is added to HCl in the flask until the indicator just change from colorless to pink. (This is the end point). At this point the reaction is complete and the volume of NaOH that react with HCl is read from the buret. This volume then used to obtain the concentration of HCl in the original solution.

Reactions used in volumetric analysis:

To be suitable for a volumetric analysis, a chemical reaction should meet certain requirements:

1- The reaction must be simple which can be expressed by a chemical equation; this requirement implies the absence of side reactions between the reagent and the unknown or other constituents of the solution.

2- The reaction should be rapid, and the substance to be determined should react completely with the reagent in equivalent proportions.

3- There must be available a method for detecting the equivalence point in the reaction, that is a satisfactory end point is required.

4- An indicator should be available which should sharply define the end point of the reaction.

Volumetric analysis Reaction Types:

Volumetric methods may be divided conveniently into four categories based upon reaction type, these include:

1- Acid-base reactions or (neutralization):

This titration reaction involves the determination of the volume of

solution of an acid (or base) of known concentration termed the "standard solution" (titrant) required to be added to a base (or acid) of unknown concentration. When the total number of milliequivalents of reactant added are unknown (ml × N = milliequivalents) we will then have a numerically exact and equal measure of the quantity of the substance that it has neutralized.

$NaOH + HCl \longrightarrow NaCl + H_2O$

A number of indicators are used in this titration such as:

	Methyl orange	Phenolphthalein	Methyl red
pH range	**3.1-4.4**	**8-9.6**	**4.2-6.2**
Acid color	Red	colorless	Red
Base color	yellow	pink	Yellow

Approximate pH range for color change

2- <u>Precipitation reactons:</u>

Based on the formation of a slightly soluble precipitate.

For example: $Ag^+ + Cl^- \longrightarrow AgCl_{(s)}$

A chemical indicator produces in solution readily observable change – usually of color or of turbidity- that serves to signal a state of chemical equivalence between the participants of a titration.

3- <u>Oxidation –reduction reactions:</u>

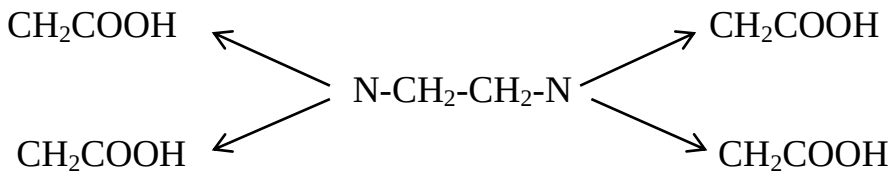
Potassium permanganate in the most widely used in this reaction. It is powerful oxidant. The intense color of permanganate ion is sufficient to signal the end point titrations:

$MnO_4^- + 5\ Fe^{++} + 8\ H^+ \longrightarrow 5\ Fe^{+++} + Mn^{++} + 4H_2O$

<u>4-Complex formation reactions:</u>

Twenty five (25) metals that can be determined by direct titration with organic material as a titrant is that it combines with metal ions in a 1:1 ratio regardless of the charge on the cation in order to produce complex

compound such as EDTA (Ethylene di- amine tetra acetic acid).



(EDTA)

A number of metal- ion indicators have been developed for use in complexometric titrations with EDTA. In general, these indicators are organic dyes that form colored chelates with several metal ions.

Lec 4

Volumetric Calculations:

Equivalent weight:

1- Acid-base titration:

The gram- equivalent weight of an acid, or simply the gram- equivalent, is that weight of the acid which contains 1 gram-equivalent, (1.008 gm) of replaceable hydrogen.

The gram- equivalent weight of a base is that weight of the base which contains 1 gm-equivalent (17.008 gm) of replaceable hydroxyl ion, (OH).

$$Equivalent\ weight\ of\ acid = \frac{Molecular\ weight}{number\ of\ replaceable(hydrogen)}$$

$$Equivalent\ weight\ of\ base = \frac{Molecular\ weight}{number\ of\ replaceable(hydroxyl)}$$

EX.

Eq.wt of HCl $= \frac{M.wt}{1}$ eq.wt of NaOH $= \frac{M.wt}{1}$

Eq.wt of $H_2SO_4 = \frac{M.wt)}{2}$ eq.wt of $Ba(OH)_2 = \frac{M.wt}{2}$

Eq.wt of $CH_3COOH = \frac{M.wt}{1}$ eq.wt of $Al(OH)_3 = \frac{M.wt}{3}$

Eq.wt of $H_3PO_4 = \frac{M.wt}{3}$ eq.wt of $NH_3 = \frac{M.wt}{1}$

2- Precipitation or complex formation titration:

The equivalent weight of a salt in which a change of oxidation state does not occur during the reaction is equal to its molecular weight divided by the total charge of all positive ions (or the equal total charge of all negative ions).

Equivalent weight of salt $= \frac{Molecular\ weight}{total\ charge\ of\ positive\ ions}$

Eq.wt of KCL $= \frac{M.wt}{1}$

Eq.wt of $Na_2CO_3 = \frac{M.wt}{2}$

Eq.wt of $BaCl_2 = \frac{M.wt}{2}$

Eq.wt of $FeCl_3 = \frac{M.wt}{3}$

Eq.wt of $Ca_3(PO_4)_2 = \frac{M.wt}{6}$

3- Oxidation – reduction titration:

The equivalent weight of an oxidizing or reducing agent for a particular reaction is equal to its molecular weight divided by the total number of electrons gained or lost when the reaction occurs (or divided by the total change in oxidation state).

Equivalent weight of oxidizing or reducing agent = $\frac{molecular\ weight}{change\ in\ oxidation\ state}$

Ex.

$$KMnO_4 \xrightarrow{H^+} MnO + \text{--------}$$

$+5e^-$

Eq.wt of $KMnO_4 = \frac{M.wt}{5}$

$$K_2Cr_2O_7 \xrightarrow{H^+} 2Cr^{+++}$$

$+6e^-$

$$Cr_2O_7^{2-} + 3\,Sn^{++} + 14H^+ \longrightarrow 3Sn^{++++} + 2Cr^{+++} + 7H_2O$$

Eq.wt of $Cr_2O_7^{--} = \frac{M.wt}{6}$

Eq.wt of Sn $= \frac{M.wt}{2}$

6e

$$KIO_3 + 6H^+ \longrightarrow I^- + H_2O$$

eq.wt for $KIO_3 = \frac{M.wt}{6}$

$$H_2C_2O_4 \longrightarrow 2CO_2$$

Eq.wt for $H_2C_2O_4 = \frac{M.wt}{2}$

$HNO_3 + 3H^+ \longrightarrow NO + H_2O$

Eq.wt for $HNO_3 = \frac{M.wt}{3}$

This reaction is named oxidation- reduction reaction.

Calculation of normality of results from titration data:

The fundamental reaction of acidimetry and alkalimetry is as follows:

$H^+ + OH^- \longrightarrow H_2O$

Since a gram- milliequivalent weight of an acid will just neutralize a gram- milliequivalent weight of base and since the number of milliequivalent in each case is found by multiplying the number of milliliters of solution by its normality, we have the following simple relationship between tow reacting solutions:

$V_A \times N_A = V_B \times N_B$

$V_A \times N_A = V_B \times \frac{wt\ (B)}{eq.wt\ (B)} \times \frac{1000}{V\ (B)}$

$Wt_{(B)\ (gm)} = \frac{VA \times NA \times eq.wt(B)}{1000}$

Or $wt_{(B)}\ (mg) = V_A \times N_A \times eq.wt_{(B)}$

$\%_{(B)} = \frac{wt\ (B)}{wt.of\ sample} \times 100$

Example 1:

A solution of $Ba(OH)_2$ was standardized by titration against (0.128 N) HCl. Exactly 31.76 ml of the base were required to neutralize 46.25 ml of the acid. What is the normality of the $Ba(OH)_2$ solution?

Sol.

At equivalent point

$Ba(OH)_2 = HCl$

$N1 \times V1 = N2 \times V2$

$N1 \times 31.76 = 0.128 \times 46.25$

$N1 = 0.1864$ gm.eq/l

Example2:

a. What the volume of (5N) H_2SO_4 is required to neutralize a solution containing 2.5 gm NaOH? M.wt (NaOH) = 40.

b. How many grams of pure H_2SO_4 are required? M.wt(H_2SO_4) = 98.

Sol.

a. $Wt._{(NaOH)} = \frac{VH2SO4 \times NH2SO4 \times eq.wt\ NaOH}{1000}$

$2.5 = \frac{5 \times V \times 40}{1000}$ $M.wt_{(NaOH)} = eq.wt_{(NaOH)}$

V = 12.5 ml

b. $N = \frac{Wt.(gm)}{eq.wt} \times \frac{1000}{Vol.(ml)}$

$5 = \frac{Wt.(gm)}{49} \times \frac{1000}{12.5}$

Wt = 3.06 gm

Not: H_2SO_4 include 2 hydrogens , thus: eq.wt = $\frac{M.wt}{2}$ = 98/2= 49.

Example 3:

A 0.25 gm sample of a solid acid was dissolved in water and exactly neutralized by 40 ml of 0.125 N base.

What is the equivalent weight of the acid?

Sol.

$Wt_{(acid)} = \frac{Vbase \times Nbase \times eq.wt\ acid}{1000}$

:

Example 4:

A sample of soda ash (impure Na_2CO_3) is titrated with 0.5 N H_2SO_4. If the sample weight 1.1 gm and required 35 ml of the acid for complete neutralization, what is the percentage of Na_2CO_3 in the ash? $M.wt_{Na2Co3}$= 106

Sol.

$Eq.wt_{(Na2CO3)} = \frac{M.wt}{2} = 106/2 = 53$

$Wt_{(Na2Co3)} = \frac{V\ H2SO4 \times N\ H2SO4 \times eq.wtNa2CO3}{1000}$

$= \frac{0.5 \times 35 \times 53}{1000} = 0.928$ gm

$\% = \frac{0.928}{1.1} \times 100 = 84.36\ \%$

Calculation of molarity of results from titration data:

Let us take this example.

$aA + bB \longrightarrow$ product A= titrant مسحح , B=titrate مسححه

a= No. of mols of substance A

b= No. of mols of substance B

$R \times V_A \times M_A = V_B \times M_B$ because mmol of B =R×mmol ofA

$R \times V_A \times M_A = V_B \times \frac{wt}{M.wt} \times \frac{1000}{V\ B}$ $R = \frac{b}{a}$

$Wt_B = \frac{R \times VA \times MA \times M.wtB}{1000}$

EX. A sample of impure Na_2CO_3 is titrated with 0.1 M HCl. If the sample weight 1 gm and requires 20 ml of the acid for complete neutralization .what is the % of Na_2CO_3, M.wt =106 $gmol^{-1}$

$2HCl + Na_2CO_3 \longrightarrow 2NaCl + H_2O + CO_2$

$Wt._{Na2\ CO3} = R \times V_A \times M_A \times M.wt_{\ Na2\ Co3} / 1000$ R= 1/2

$= \frac{\frac{1}{2} \times 20 \times 0.1 \times 106}{1000} = 0.106$

$\% = 0.106/1 \times 100 = 10.0\%$

Lec 5

Ionic equilibria

Aqueous solutions contain hydronium ions as well as hydroxide ions:

As we have seen, water is itself ionized to a very slight extent:

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

H_3O^+ in the equation above represents the total hydrogen ion concentration in the solution from all sources, and OH^- represents the total hydroxide ion concentration.

Applying the equilibrium law to this equilibrium at constant temperature:

$\frac{[H3O+][OH-]}{[H2O]2}$ = constant (K)

In dilute aqueous solutions the concentration of $[H_2O]$ is greater than the concentration of any other species.

Its concentration is substantially constant (around 55.5 mol/ L), so

$[H3O^+][OH^-] = K[H_2O]^2$

$[H3O+][OH-] = K_w$

Where (K_w) is called the ion product constant for water.

At 25 Cº the numerical value of this constant (1×10^{-14} mol^2/L^2). In pure water on in the presence of a solute that does not react to give H^+ or OH^- , the concentration of these two species are identical, and therefore there concentration must equal the square root of the ion- product constant: that is 1×10^{-7} mol/L at 25 Cº.

The hydrogen- ion exponent ((pH))

For many purposes, especially when dealing with small concentrations, it is cumbersome التثاقل to express concentrations of hydrogen and hydroxyl ions in terms of gram equivalents per liter. A very convenient method was proposed by Sorensen. He introduced the hydrogen- ion exponent (pH) defined by the relationship:

$$pH = -\log_{10} [H^+]$$

The quantity pH is thus the logarithm of the hydrogen- ion concentration with negative sign. This method has the advantage that all states of acidity and alkalinity between those of solutions molar with respect to hydrogen and hydroxyl ions can be expressed by a series of positive numbers between 1 and 14.

Thus a neutral solution with $[H^+]= 10^{-7}$ has a pH of 7.

$K_w = [H_3O^+][OH^-]$

$-\log K_w = -\log [H_3O^+] + (-\log [OH^-])$

$PK_w = pH + pOH = 14$

I----------I----------I

1 ⟵ ⟶ acid ↑ **7** ⟵ ⟶ alkaline 14

Neutral

Ex. Calculate the pH and pOH of a solution in which the H_3O^+ is $2\times10^{3-}$ M?

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

$= -\log 2 \times 10^{3-}$

$= 2.7$

$pOH = 14-2.7 = 11.3$

Ex. Calculate the pH of 0.01 M solution of acetic acid ((the degree of dissociation is 12.5 %))

Dissociation $\% = \frac{amount\ dissociated}{Initial\ concentration} X100$

$[H_3O^+]= 12.5/100 \times 0.01= 1.25 \times10^{3-}$

$PH = -\log [H_3O^+]$

$= -\log 1.25 \times 10^{3-} = 2.903$

Solutions of strong acids and strong bases bronsted- Lowry definition:

- A substance functions as an acid when it donated proton to a base.

- A substance functions as a base when it accepts proton from an acid.

Acids are proton donors, Bases are proton acceptors

These definitions imply acids and bases always react together.

The acid which has exactly one proton more than a particular base is called the **conjugate acid** of that base. Likewise, the base which has exactly one proton less than a particular acid is called the **conjugate base** of that acid Such as acid – base reactions:

a) In an aqueous solution of HCl functions as an acid, and water functions as a base:

$HCl + H_2O \longleftrightarrow H_3O^+ + Cl^-$

Acid Base conjugate Acid conjugate Base

The conjugate acid – base pairs are HCl/Cl^- and H_3O^+/H_2O

b) In an ammonia solution of NH_3 functions as a base and water functions as an acid:

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

Base Acid conjugate Acid conjugate Base

The conjugate acid – base pairs are NH_4^+ / NH_3 and H_2O / OH-

From reactions (a) and (b) we notice that water can function both as an acid and as a base. Such a substances are described as amphoteric.

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

Acid Base conjugate Acid conjugate Base

Strength of acids and bases

Different acids hydrolyze in water to differing extents. The greater the extent of hydrolysis, the stronger is the acid or base.

Ex.: HCl, $HClO_4$, H_2SO_4, HNO_3 are stronger acids.

HCN, CH_3COOH, $H_2PO_4^-$ are weak acids.

(NaOH , KOH) ~~Strong~~ bases

(NH_3 , CN^-) ~~Weak~~ bases

The acidity constant may be used to compare acid strength's, so also one may define basicity constant for a base.

For example: $CH_3COOH = 10^{5-}$ (weak)

$HCl = 10^{7}$ (strong)

Calculation of pH or pOH of aqueous solution of strong acids or bases is straight forward, since the H_3O^+ or OH^- concentration can be calculated directly from the formal concentration of the solute. In such calculation the fraction of H_3O^+ and OH^- resulting from the dissociation of water is ordinarily vanishingly small and is not taken into account.

Ex. Calculate the pH and PoH of 0.05 M solution of HCl?

Since the acid is completely dissociated, the $[H_3O^+]$ is numerically equal to the molar concentration of HCl in the solution.

$[H_3O^+] = 0.05$

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

$= -\log 0.05$

$= 1.3$

$pOH = 14-1.3$

$= 12.7$

Ex: Calculate the pH and pOH of a $3.2\times 10^{4-}$ M $Ba(OH)_2$ solution?

$Ba(OH)_2$ is stronger base containing 2 moles of OH^- for each formula weight of base.

Thus: $Ba(OH)_2 \longrightarrow Ba^{2+} + 2OH^-$

$[OH^-] = 2 \times 3.2\times 10^{4-}$

$= 6.4 \times 10^{4-}$ mol/l

$pOH = -\log [OH^-]$

$= -\log (6.4\times 10^{4-}) = 3.19$

$pH = 14-3.19$

$= 10.81$

Calculation of pH solution of a weak acids and bases

Weak acids and bases react incompletely with the solvent. As a consequence, the H_3O^+ or OH- concentration in such solutions will be less than the formal solute concentration.

Calculation of pH or pOH requires a numerical value for the equilibrium constant for the reaction of the substance with water.

When the weak acid HA is dissolved in water, the reaction:

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

Or $HA \longleftrightarrow H^+ + A^-$

is incomplete and the resulting equilibrium is described by the equation:

$K_a = \frac{[H+][A-]}{[HA]}$

Where K_a is the ionization constant or dissociation constant of the acid.

$[H^+] \rightleftharpoons [A^-]$

$K_a = \frac{[H+]2}{[HA]}$

$[H^+]^2 = K_a\ [\ HA]$

$[H^+] = \sqrt{Ka\ [HA]}$

Or $[H^+] = \sqrt{Ka \times Ca}$ Which C_a = concentration of acid

$pH = -\log H^+$

for bases : $B + H_2O \longleftrightarrow BH^+ + OH^-$

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

$[BH^+] = [OH^-]$

$K_b = \frac{[OH-]2}{[B]}$

$[OH^-]^2 = K_b[B]$

$[OH^-] = \sqrt{Kb\ [B]}$

Or $[OH^-] = \sqrt{Kb\ \times Cb}$ which C_b = concentration of base

$pOH = -\log [OH^-]$

Ex:

Calculate the hydronium ion concentration and pH of a $4\times 10^{2-}$M solution of formic acid, $K_a = 1.74\times 10^{4-}$?

$[H^+]= \sqrt{Ka \times Ca}$

$=\sqrt{\ } 1.74 \times 10^{4-}\times 4\times 10^{2-}$

$= 2.64\times 10^{3-}$ mol/L

pH = - log H^+

$= - \log 2.64 \times 10^{3-} = ??$

Ex:

Calculate the pH of 0.075 m solution of NH_3 , $K_b= 1.86 \times 10^{5-}$

$[OH^-] =\sqrt{Kb \times Cb}$

$= \sqrt{\ } 1.86\times 10^{5-}\times 0.075$

$= 1.18\times 10^{3-}$ mol/L

pOH= - log $[OH^-]$

$= - \log 1.18 \times 10^{3-}$

$= 2.93$

PH = 14 – 2.93 = 11.07

Relation between Ka and Kb :

Consider the hydrolysis reactions for the acid HA, and its conjugate base A^- :

$K_a \longrightarrow HA + H_2O \longleftrightarrow H_3O^+ + A^-$

$K_b \longrightarrow A^- + H_2O \longleftrightarrow HA + OH^-$

The acidity and basicity constant are defined as:

$K_{a(HA)}= \frac{[H3O+][A-]}{[HA]}$

$K_{b(A)}= \frac{[HA][OH-]}{[A-]}$

Now the product:

$K_a \times K_b = \frac{[H3O+][A-]}{[HA]} \times \frac{[HA][OH-]}{[A-]}$

$K_a \times K_b = [H_3O^+][OH^-]$

Thus $K_a \times K_b = K_w$

Ex: Find the $K_b(NH_3)$ at 25 C°, given $K_a(NH_4^+) = 6.3 \times 10^{10-}$

Since $K_b = K_w / K_a$

$K_b = 10^{14-} / (6.3 \times 10^{10-})$

$= 1.6 \times 10^{5-}$

Ex: Find the p $K_b(NS^-)$ at 25 C°, given $pK_a(H_2S) = 7.2$

Since $K_a \times K_b = K_w$

$pK_a + pK_b = pK_w = 14$

$pK_b = 14 - 7.2 = 6.8$

Lec 6

Hydrolysis

Is the interaction between the ions of salt and the ions of water with the production of a weak acid or a weak base or of both a weak acid and a weak base.

Calculation of the pH of solutions of salts

Salts may be divided into four main groups:

1- Those derived from the strong acids and strong bases, e.g., (KCl)
2- Those derived from the weak acids and strong bases, e.g., (CH_3COONa).
3- Those derived from the strong acids and weak bases, e.g.,(NH_4Cl)
4- Those derived from the weak acids and weak bases, e.g.,(CH_3COONH_4).

When any of these is dissolved in water, the resulting solution may be neutral, acid, or alkaline according to nature of the salt.

Calculations:

1- Salts of strong acid and base:

These salts in aqueous solutions, the anions do not have any tendency to combine with the $[H^+]$ also the cations with the hydroxyl ions of water, since the related acids and bases are strong electrolytes. The equilibrium between H^+ and OH^- ions in water:

$H_2O \longleftrightarrow H^+ + OH^-$

$[H^+]= [OH^-] \longrightarrow pH= 7$

The solutions remain neutral.

2- Salts of weak acid- strong base:

The essential chemistry of the solubi/lization of the completely ionic solid sodium acetate CH_3COONa, in water and which endows its solution with

a basic character (pH greater than 7) is formulated as:

$CH_3COONa \longrightarrow CH_3COO^- + Na^+$

$CH_3COO^- + H_2O \longleftrightarrow CH_3COOH + OH^-$

$K_h = K_b = \frac{[OH-][CH3COOH]}{[CH3COO-]}$

$K_b \times K_a = K_w$

$K_h \times K_a = K_w$

The end of the derivation yields:

$H^+ = \sqrt{\frac{kw\ ka}{[Salt]}}$

$PH = \frac{1}{2}[\ pK_w + pK_a + \log C]$

Which C= salt concentration.

3- Salts of weak base- strong acid:

Like ammonium chloride, its aqueous solution is acidic because of hydrolysis:

$NH_4Cl \longleftrightarrow NH_4^+ + Cl^-$

$NH_4^+ + H_2O \longleftrightarrow NH_3 + H_3O^+ \text{ or } H^+$

$K_h = \frac{[NH3][H+]}{[NH4+]}$

When the derivation is completed, we found this equation:

$H^+ = \sqrt{\frac{Kw[\ salt]}{Kb}}$

$pH = \frac{1}{2}[pK_w - pK_b - \log C]$

4-Salt of weak base- weak acid:

As an example (ammonium acetate).

Whether the final solution at equilibrium will be acidic, basic or neutral will obviously depend upon the relative strengths of the acid and base formed- that is, upon the respective values of K_a and K_b. When these are nearly identical- as in the present instant.($K_b(NH_3) = K_a\ (CH_3COOH) = 1.8 \times 10^{5-}$ at 25 C°).

We obtain a neutral solution pH = 7. When $K_a > K_b$ the solution will be acidic; When $K_b > K_a$ the solution will be basic.

The equation of salt derived from weak acid and base is:

$pH = \frac{1}{2}[pK_w + pK_a - pK_b]$

Ex:

Calculate:

1- pH of 0.01 M solution of sodium acetate, $K_a = 1.82 \times 10^{5-}$

2- pH of 0.02 M solution of NH_4Cl, $K_b = 1.85 \times 10^{5-}$

3- pH of solution of ammonium format, $K_b(NH_3) = 1.8 \times 10^{5-}$, $K_a(HCOOH) = 1.77 \times 10^{4-}$

Sol.

1- $pH = \frac{1}{2}[pK_w + pK_a + \log C]$ $pK_a = - \log K_a$

$= \frac{1}{2}[14 + (- \log 1.82 \times 10^{5-}) + \log 0.01]$

$= 8.37$

2- $pH = \frac{1}{2}[pK_w - pK_b - \log C]$ $pK_b = - \log K_b$ $=- \log 1.8 \times 10^{5-}$

$pH = \frac{1}{2}[14 - 4.74 - \log 0.02]$

$= 4.98$

3- $pH = \frac{1}{2}[pK_w + pK_a - pK_b]$

$= \frac{1}{2}[14 + 3.76 - 4.74]$

$= 6.51$

ملاحظه عامة: اذا كان التركيز بوحدات غم/ لتر, في هذه الحالة نقسم على الوزن الجزيئي ليكون بوحدات مول/ لترفمثلا اذا كان تركيز الملح = 0.6 غم / لتر فيجب ان نقسم على الوزن الجزيئي فيكون التركيز بوحدات مول / لتر.

$\frac{0.6\ gm/L}{M.wt(\frac{gm}{mol})}$ = mol/L/ or molarity

Buffer solutions:

Buffer solutions usually consist of solutions containing a mixture of weak

acid or base and its salt. Buffers are of great importance in chemistry because they have the property of resistance changes in pH both upon dilution and upon addition of strong acid and base. In order to understand buffer action, let us study first the equilibrium between a weak acid and its salt. The dissociation of a weak acid is given by:

$HA \longleftrightarrow H^+ + A^-$

$K_a = \frac{[H+][A-]}{[HA]}$

$[H^+] = \frac{Ka[HA]}{[A-]}$

$[H^+] = K_a(\frac{HA}{A-})$

Or $[H^+] = K_a(\frac{acid}{salt})$

$-\log H^+ = -\log K_a - \log(\frac{acid}{salt})$

$pH = pK_a + \log \frac{[salt]}{[acid]}$

Similarly for a mixture of a weak base of dissociation constant K_b and its salt:

$pOH = pK_b + \log \frac{[salt]}{[base]}$

How can buffer solution resist the changes in pH upon addition of strong acids or bases?

Let us take an acid buffer ($CH_3COOH + CH_3COONa$)

CH_3COOH $+HCl(H^+) \Leftarrow CH_3COOH$ weak acid(pH const.)

or $\longrightarrow$

CH_3COONa $+ NaOH(OH^-) \Leftarrow H_2O$ neutral (pH= 7).

If we add a small concentration of H^+ to such a solution, it will combine with the acetate ions from the salt to form un dissociated acetic acid.

Similarly, if a small concentration of hydroxyl ions be added, the latter

will combine with the hydrogen ions arising from the dissociation of the acetic acid and form unionized water; the equilibrium will be disturbed, and more acetic acid will dissociated to replace the hydrogen ions removed in this way.

Example 1:

Calculate the pH value of a liter of an aqueous solution concentration 6 gm of CH_3COOH (M.wt = 60.05) and 8.2 gm of CH_3COONa (M.wt = 82.05), $K_a = 1.8 \times 10^{5-}$.

Sol:

$pK_a = - \log K_a$

$= - \log 1.8 \times 10^{5-}$

$= 4.74$

$pH = pK_a + \log \frac{[salt]}{[acid]}$

$= 4.74 + \log \frac{[\frac{8.2}{82.05}]}{[6/60.05]}$

$= 4.74 + \log 0.1/0.1$

$= 4.74$

Example 2 :

To 50 ml of 0.1 N acetic acid. 10 ml of 0.2 N NaOH solutions have been added. Calculate the pH of the resulting solution, $K_a = 1.8 \times 10^{5-}$

Sol:

Before reaction:

(V×N)

(50 ml) × 0.1 g-meq./ ml)= 5 g- meq of CH_3COOH

(10 ml) ×0.2 g-meq./ ml)= 2g-meq. Of NaOH

After reaction

$CH_3COOH + NaOH \rightarrow CH3COONa + H_2O$

5g-meq 2g-mg 0 0

3g-meq 0 2g-meq

As a result of reaction between the acid and the base , 2g-meq. Of sodium acetate will be formed and an access of 3g-meq. of acetic acid will remain in the solution.

The resulting solution is a buffer since it contains a weak acid and its salt. (CH3COOH, CH3COONa).

The normality of CH3COOH after reaction, is no longer 0.1 since part of it has been converted to sodium acetate and also the volume has been increased to 60 ml.

$C_{(acid)}$ =3g-meq/60ml=0.05 g-meq/ml or 0.05N=0.05M

$C_{(salt)}$=2g-meq/60ml=0.033 g-meq/ml 0r 0.033N=0.033M

$pH=pK_a + \log \frac{Salt}{acid}$

$pH=4.74 + \log \frac{0.033}{0.05}$ $pK_a = -\log 1.8x10^{5-}$

$=4.74$

$=4.57$

Buffer Capacity: Is defined as the number of mmols of any acid or base that causes one milliliter of the buffer to undergo a one unit change in pH. The capacity of a buffer depends not only on the total concentration of the two buffer components but also on their concentration ratio.

Capacity of buffer solution when added strong acid is the number of millimoles of strong acid added to one milliliter of buffer solution to decrease the value of pH one unit.

Capacity of buffer solution when added strong base(beta value) is the number of millimoles of strong base added to one milliliter of buffer solution to increase the value of pH one unit.

Ex: Calculate: **a)** pH, **b**) capacity to acid added to solution contains 12 mmol of acetic acid (pK_a = 4.74) and 8 mmol of sodium acetate in 100 ml.

Sol: **a)** pH= pK_a + log C_s/C_a ⟶ pH= 4.74+ log $\frac{8/100}{\frac{12}{100}}$ ⟶ pH= 4.56

b)pH= 4.56- 1= 3.56

pH= pK_a+ log C_s/C_a ⟶ 3.56= 4.74+logC_s/C_a ⟶ - log C_s/C_a= 1.18

C_a/C_s= 15.1 ⟶ C_a =15.1 C_s

No. of mmol of total= No. mmol of acid + No. of mmol of salt

8+12 =(15.1) No. of mmol of salt + No. mmol of salt

20 = (15.1 +1) No.of mmol of salt

No. of mmol of salt= 20/16.1= 1.24= No. mmol of salt remained

No. mmol of acid added= No. mmol of salt- No.mmol of salt remained

No.mmol of acid added= 8- 1.24= 6.8

Capacity= $\frac{No.mmol\ of\ acid\ added}{Total\ volume\ of\ buffer\ solution}$ = 6.8/100= 0.067mmol/ml

Lec 7

Titration of solution of strong acid with strong base

Let us consider the titration of 50 ml of (0.1 N) solution of HCl with (0.1 N) NaOH solution:

1- To calculate the initial pH, is:

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

$= - \log 0.1$

$= 1$ ⟵ acidic

2- To calculate pH after addition of 10 ml of base:

We may write:

Number of m.eq. of HCl remaining = (50 ×0.1)-(10×0.1)=4

Thus, Normality of HCl= $\frac{4}{Vacis+Vbase} = \frac{4}{50+10}$

$pH = - \log (4/60)$

$= 1.18$ ⟵ acidic

3- To calculate pH after addition of 50 ml of base:

When 50 ml of base have been added, the titration is at equivalence point;

$NaOH + HCl \longrightarrow NaCl + H_2O$

Since the dissociation of water involves formation of equal amounts of H_3O^+ and OH^- and pH = 7 (neutral).

4- To calculate pH after addition of 50.01 ml of base:

The addition of 50.01 ml of NaOH produces a slight excess of base in the solution, we can obtain the pH from its concentration:

$N_{NaOH} = [OH^-] = \frac{950.01\times0.1)-(50\times0.1)}{50+50.01}$

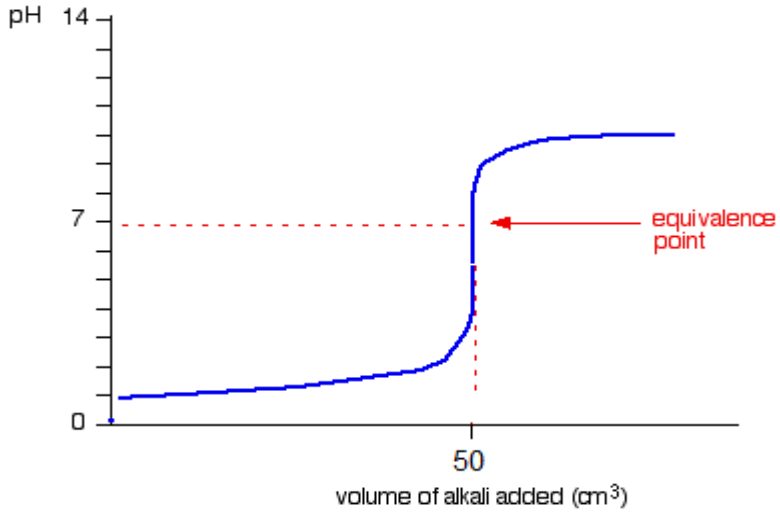
$= 1\times10^{5-}$

$pOH = - \log OH^-$

$= - \log 1 \times 10^{5-} = 5$

pH = 14- 5 = 9 ⟵ basic.

Note: concentration is high, Δ pH is high, indicator is used : M.O or Ph.Ph.



Titration of solutions of weak acid or bases:

- **Titration of solutions of weak acid with strong base:**

Let us consider the titration of 50 ml of (0.1 N) CH_3COOH (K_a= 1.75 × 10^{5-} with 0.1 N NaOH solution:

1- To calculate the initial pH:

$H^+ = \sqrt{Ka \times Ca}$

$= \sqrt{0.1 \times 1.75 \times 10^{5-}}$

pH= - log H^+

= 2.88

2- To calculate OH after addition of 10 ml of NaOH:

$CH_3COOH + NaOH \longleftrightarrow CH_3COONa + H_2O$

50×0.1= 5 10×0.1=1 0.0

5-1=4 0.0 10×0.1=1

A buffer solution consisting CH_3COOH and its salt.

$[acid] = \frac{(50\times0.1)-(10\times40.1)}{50+10} = 4/60$

$[salt] = \frac{10\times0.1}{50+10} = 1/60$

$pH = pK_a + \log \frac{[salt]}{[acid]}$

$pH = (- \log 1.75 \times 10^{5-}) + \log \frac{1/60}{4/60}$

= 4.15

3- At equivalence point (after adding 50 ml of NaOH):

$CH_3COOH + NaOH \longleftrightarrow CH_3COONa$

(50×0.1) (50×0.1) 0.0

0.0 0.0 (50×0.1)

Acetic acid has been converted to sodium acetate

$pH = 1/2 [pK_w + pK_a + \log C]$

$N_{CH3COOH} = \frac{50 \times 0.1}{50+50} = 0.05$

$pH = 1/2 [14 + (- \log 1.75 \times 10^{5-}) + \log 0.05]$

= 8.73

4- To calculate pH after addition of 50.01 ml of base.

In this solution:[OH^-]arise from both the excess of NaOH and the reaction of the acetate ion with water.

$NaOH \longrightarrow Na^+ + OH^-$

$CH_3COONa \longrightarrow CH_3COO^- + Na^+$

$CH_3COO^- + H_2O \longleftrightarrow CH_3COOH + OH^-$ (very small neglected).

So $N_{NaOH} = \frac{(50.01 \times 0.1) - (50 \times 0.1)}{50+50.01} = 1 \times 10^{4-}$

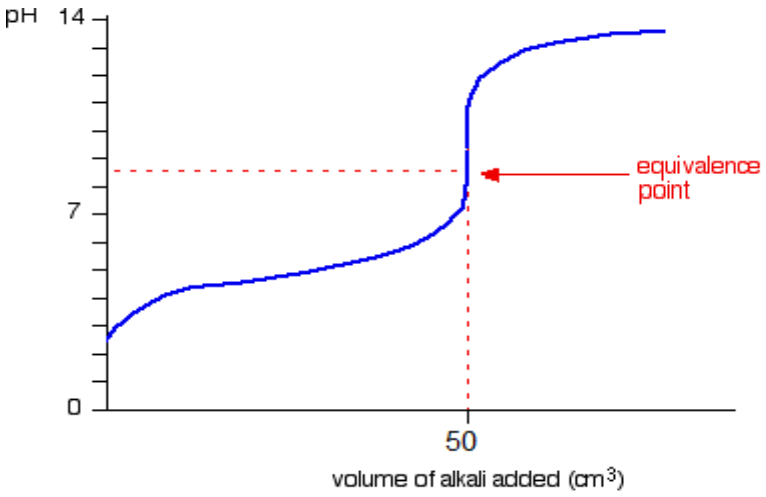
$pOH = - \log OH^-$

$pOH = - \log 1 \times 10^{4-}$

= 4

pH = 14- 4

= 10 ⟵ basic



Acid – Base Indicators

The acid- base indicator is a weak organic base whose undissociated form differs in color from its conjugate form. For example, the behavior of an acid- type indicator (HIn) is described by the equilibrium.

$HIn + H_2O \rightleftharpoons In^- + H_2O^+$

Acid color base color

The equilibrium for a base- type indicator (In) is

$In^- + H_2O \rightleftharpoons HIn + OH^-$

Base color acid color

The equilibrium constant expression for the dissociation of an acid-type indicator takes the form

$K_a = \frac{[H3O+][In-]}{[HIn]} \longrightarrow [H_3O^+] = K_a \frac{[HIn]}{[In-]}$

The human eye is not very sensitive to color differences in a solution containing a mixture of In- and HIn, particularly when the ratio [HIn] /[In] is greater than about 10 or smaller than 0.1, because the color becomes essentially constant to the eye and is independent of the ratio. Consequently, the color imparted to the solution by a typical indicator appears to the average observer to change rapidly only within the limited concentration ratio of approximately 10 to 0.1.

$[H_3O^+] = 10\ K_a$ for acid color, **$[H_3O^+] = 0.1\ K_a$** for base color

Indicator pH range = $pK_a \pm 1$

Example:

Calculate the pH range of methyl red indicator if acid dissociation constant of 1×10^{-5}.

Sol.

$pK_a = -\log K_a = -\log (1\times 10^{-5}) = 5$

pH range = $pK_a \pm 1$

pH = 5-1 = 4 pH = 5+1 = 6

pH range from 4 to 6

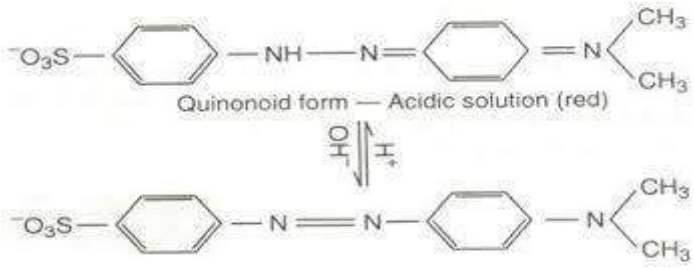
Acid – Base indicators:

The list of acid- base indicators includes a number of organic compounds.

Some Important acid- Base Indicators			
Common Name of Indicator	**pH range**	**Acidic Color**	**Basic Color**
Methyl Yellow (M.Y)	2.9- 4.0	red	Yellow
Methyl Orange (M.O)	3.0- 4.4	Red	Yellow
Methyl Red (M.R)	4.4- 6.2	Red	Yellow
Bromothymol Blue (B.T.B)	6.0 – 7.6	Yellow	Blue
Phenolphthalein(ph.ph)	8.0 – 10.0	Colorless	pink

Methyl Orange

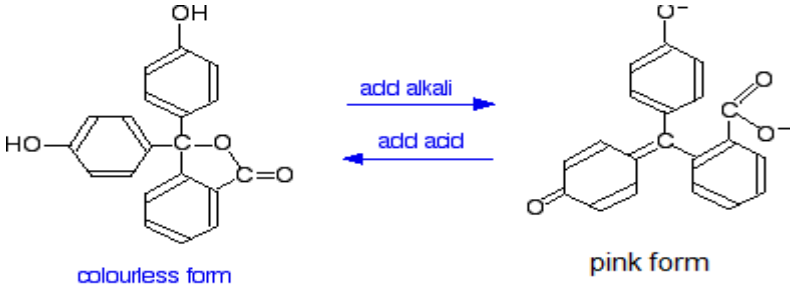
It is benzenesulforic acid, 4-[[4-(dimethylamino)phenyl]azo]-, whereas its chemical structure is(I).



yellow

Phenolphthalein

It is 1(3H)-isobenzofuranone, 3,3-bis(4-hydroxyphenyl)-, whereas its chemical structure is (I)



Titration with strong acid for one base or mixture from two bases.

Sample	**Indicator**		**Volume of HCL,ml**
	Ph.ph (Change solution from pink to colorless)	M.O (Change solution from yellow to red)	
NaOH	V_1= NaOH	-------	V_1
Na_2Co_3	V_1=1/2 Na_2CO_3	V_2=1/2 Na_2CO_3	V_1=V_2
$NaHCO_3$	-------	V_2=$NaHCO_3$	V_2
NaOH+Na_2CO_3	V_1=NaOH+1/2Na_2CO_3	V_2=1/2Na_2CO_3	V_1>V_2
Na_2CO_3+$NaHCO_3$	V_1=1/2 Na_2CO_3	V_2=1/2 Na_2CO_3+ $NaHCO_3$	V_1< V_2

$NaOH + HCl \xrightarrow{ph.ph} NaCl + H_2O$

$Na_2CO_3 + HCl \xrightarrow{ph.ph} NaCl + NaHCO_3$

$NaHCO_3 + HCl \xrightarrow{M.O} NaCl + H_2CO_3$

Note:

Do not used mixture of NaOH and $NaHCO_3$ to titrate because of the

following reaction for mixture:

$NaOH + NaHCO_3 \longrightarrow Na_2CO_3 + H_2O$

Sodium hydroxide Sodium bicarbonate Sodium carbonate

(Sodium hydrogen carbonate)

Example:

The mixture of two bases is titrated with 0.1 HCl if the mixture requires 15 ml. of acid for reach to end point of phenolphthalein indicator and 40 ml. of HCl for reach to end point of methyl orange indicator, identify the bases and calculate the number of milliequivalent of each base.

Sol.

V_1= 15 ml, V_2 = 40 ml, $\Longrightarrow$ $V_1 < V_2$

The mixture is Na_2CO_3 and $NaHCO_3$

V_1= 1/2 Na_2CO_3, V_2= 1/2 Na_2Co_3 + $NaHCO_3$

$V_{HCl} = Na_2CO_3 = V_1 \times 2 = 15 \times 2 = 30$ ml

$V_{HCl} = NaHCO_3 = V_2 - V_1 = 40 - 15 = 25$ ml

No. meq of HCl = no. meq of $Na_2CO_3 = N_{HCl} \times V_{HCl} = 0.1 \times 30 = 3$

No.meq of HCl = no. meq of $NaHCO_3 = N_{HCl} \times V_{HCl} = 0.1 \times 25 = 2.5$

Example: A basic sample is titrated with 0.1 N HCl if the sample weight 0.6 g and requires 40 ml of the acid for reach to end point of phenolphthalein indicator and 13 ml of the acid for reach to end point of methyl orange indicator.(a) identify the sample contents. (b) What is the percentage of each content in the sample?

Sol.

V_1 = 40 ml, V_2 = 13 ml $\Longrightarrow$ $V_1 > V_2$

The mixture is NaOH and Na_2CO_3

V_1= NaOH + 1/2 Na_2CO_3, V_2 = 1/2 Na_2CO_3

$V_{HCl} = Na_2CO_3 = V_2 \times_2 = 13 \times 2 = 26$ ml

$V_{HCl} = NaOH = V_1 - V_2 = 40 - 13 = 27$ ml

No.meq of HCl = no. meq of Na2 CO3

$N_{HCl} \times V_{HCl} = Wt_{Na2CO3} / eq.wt_{Na2CO3} \times 1000$; (eq.wt Na_2CO_3=M.wt /n= 106/2= 53 g eq^{-1})

$0.1 \times 26 = wt_{Na2CO3} / 53 \times 1000 \longrightarrow wt_{Na2\,CO3} = 0.138$ g

$\%(w/w)_{Na2CO3} = wt_{Na2CO3} / wt_s \times 100$; wt_s = weight of sample= 0.6 g

$\%(w/w)_{Na2CO3} = 0.138/0.6 \times 1000$ $\%(w/w)_{NaCO3} = 23$

No. meq of Hcl = no.mq=eq of NaOH

$N_{HCl} \times V_{HCl} = wt_{NaOH} / eq.wt_{NaOH} \times 1000$; $eq.wt_{NaOH} = M.wt/n = 40/1 = 40$ g eq^{-1}

$0.1 \times 27 = wt_{NaOH} / 40 \times 1000 \longrightarrow wt_{NaOH} = 0.108$ g

$\%(w/w)_{NaOH} = wt_{NaOH} / wt_s \times 100$

$\%(w/w)_{NaOH} = 0.108/0.6 \times 100 \longrightarrow \%\ (w/w)_{NaOH} = 18$

Lec 8

Precipitation Titrations

Precipitation titration is based on reaction between the analyte and titrant to form an insoluble precipitate.

Precipitation titration is a titration in which the reaction between the analyte and titrant involves a precipitation.

Conditions for Precipitation Titrations

1- The formed precipitate is insoluble in water.

2- The precipitation process is rapidly occurred.

3- The distinguishing of end point is readily by using visual indicator.

Classification of Precipitation Titrations

Precipitation titrations are classified into two types:

1- Argentometric Titrations are used $AgNO_3$ (silver nitrate) as titrant.

2- Mercurimetric Titrations are used $Hg(NO_3)_2$ (mercuric nitrate) as titrant.

Titration Curves

The titration curve for a precipitation titration follows the change in either the analyte's or titrant's concentration as a function of the volume of titrant. For example, in an analysis for I^- using Ag^+ as a titrant.

$$Ag^+_{(aq)} + I^-_{(aq)} \rightleftharpoons AgI_{(s)}$$

The titration curve may be a plot of pAg or pI as a function of the titrant's volume.

Example:

Calculate the pAg and pCl of the solution during the titration 50 mL of 0.05 M NaCl with 0.1 M $AgNO_3$ after the addition the following volumes of reagent: 0, 5, 10, 15, 20, 25, 30, 35, 40, 45, 50 mL. If K_{sp} of AgCl = 1.8×10^{-10}

Solution:

$$AgNO_3 + NaCl \longrightarrow \underset{\text{white}}{AgCl_{(s)}} + NaNO_3$$

Initial Point

Before any $AgNO_3$ is added, $[Ag^+] = 0$ and pAg is indeterminate.

$[NaCl] = 0.05\ M = [Cl^-]$ and $pCl = -\log [Cl^-] = -\log 0.05$ ⟹ **pCl =**

1.30 ***After Addition of 10 mL of $AgNO_3$***

$$[NaCl] = \frac{\text{no. mmol NaCl remaining after addition of } AgNO_3}{\text{Total volume of solution}}$$

$$[NaCl] = \frac{\text{original no. mmol NaCl} - \text{no. mmol } AgNO_3 \text{ added}}{\text{Total volume of solution}}$$

$$[NaCl] = \frac{(0.05 \times 50) - (0.1 \times 10)}{50 + 10}$$

$$[NaCl] = \frac{(2.5 - 1)}{60} = \frac{1.5}{60} = 0.025\ M = [Cl^-]$$

$pCl = -\log [Cl^-] = -\log 0.025 \Rightarrow$ **pCl = 1.60**

$$K_{sp} = [Ag^+] \times [Cl^-] \Rightarrow [Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{0.025} = 7.2 \times 10^{-9}\ M$$

$pAg = -\log [Ag^+] = -\log (7.2 \times 10^{-9}) \Rightarrow$ **pAg = 8.14**

After Addition of 15 mL of $AgNO_3$

$$[NaCl] = \frac{\text{original no. mmol NaCl} - \text{no. mmol } AgNO_3 \text{ added}}{\text{Total volume of solution}}$$

$$[NaCl] = \frac{(0.05 \times 50) - (0.1 \times 15)}{50 + 15}$$

$$[NaCl] = \frac{(2.5 - 1.5)}{65} = \frac{1}{65} = 0.0154\ M = [Cl^-]$$

$pCl = -\log [Cl^-] = -\log 0.0154 \Rightarrow$ **pCl = 1.81**

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.8 \times 10^{-10}}{0.0154} = 1.17 \times 10^{-8}\ M$$

$pAg = -\log [Ag^+] = -\log (1.17 \times 10^{-8}) \Rightarrow$ **pAg = 7.93**

Additional points defining the curve in the region before the equivalence point are obtained in the same way. The results of such calculations are shown in the second and third column of Table 1.

Table 1: Changes in pCl and pAg During the Titration of NaCl with $AgNO_3$

Volume of $AgNO_3$, mL	50 mL of 0.05 M NaCl with 0.1 M $AgNO_3$	
	pCl	pAg
0	1.30	---
5	1.44	8.31
10	1.60	8.14
15	1.81	7.93
20	2.15	7.60
25	4.89	4.89
30	7.54	2.20
35	7.82	1.93
40	7.97	1.78
45	8.07	1.68
50	8.14	1.60

Equivalence Point

At the equivalence point neither NaCl nor $AgNO_3$ is in excess and $[Ag^+] = [Cl^-]$, $K_{sp} = [Ag^+] \times [Cl^-]$

$K_{sp} = [Cl^-]^2 \Rightarrow [Cl^-] = \sqrt{K_{sp}} = \sqrt{1.8 \times 10^{-10}} = 1.3 \times 10^{-5}$ M

$pCl = -\log [Cl^-] = -\log (1.3 \times 10^{-5}) \Rightarrow$ **pCl = 4.89 = pAg**

After Addition of 35 mL of $AgNO_3$

The solution now contains an excess of $AgNO_3$.

$[AgNO_3] = \frac{\text{no. mmol } AgNO_3 \text{ added} - \text{original no. mmol NaCl}}{\text{Total volume of solution}}$

$[AgNO_3] = \frac{(0.1 \times 35) - (0.05 \times 50)}{35 + 50} = \frac{3.5 - 2.5}{85} = \frac{1}{85} = 0.0118\ M = [Ag^+]$

$pAg = -\log [Ag^+] = -\log 0.0118 \Rightarrow$ **pAg = 1.93**

$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{1.8 \times 10^{-10}}{0.0118} = 1.53 \times 10^{-8}\ M$

$pCl = -\log [Cl^-] = -\log (1.53 \times 10^{-8}) \Rightarrow$ **pCl = 7.82**

After Addition of 50 mL of $AgNO_3$

$[AgNO_3] = \frac{\text{no. mmol } AgNO_3 \text{ added} - \text{original no. mmol NaCl}}{\text{Total volume of solution}}$

$[AgNO_3] = \frac{(0.1 \times 50) - (0.05 \times 50)}{50 + 50} = \frac{5 - 2.5}{100} = \frac{2.5}{100} = 0.025\ M = [Ag^+]$

$pAg = -\log [Ag^+] = -\log 0.025 \Rightarrow$ **pAg = 1.60**

$[Cl^-] = \frac{K_{sp}}{[Ag^+]} = \frac{1.8 \times 10^{-10}}{0.025} = 7.2 \times 10^{-9}\ M$

$pCl = -\log [Cl^-] = -\log (7.2 \times 10^{-9}) \Rightarrow$ **pCl = 8.14**

Additional data defining the curve beyond the equivalence point are computed in the same way. The results of such computations are shown in Table 1. The calculations of Table 1 are shown in Figure 1.

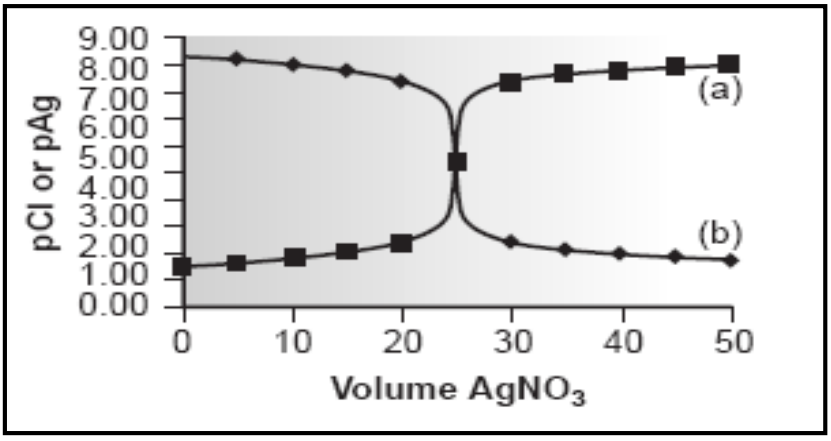


Figure 1

Precipitation Titration Curve for 50 mL of 0.05 M NaCl with 0.1 M $AgNO_3$.

(a) pCl versus volume of titrant; (b) pAg versus volume of titrant.

Lec 9

Determination Methods of End Point in Argentometric Titrations

1- Mohr Method (formation of a colored precipitate, direct method)

The Mohr method, involving the formation of a precipitate of reddish-brown silver chromate with the appearance of an excess of silver ions signals the end point.

Titration reaction: $Ag^+ + X^- \rightleftharpoons AgX_{(s)}$; $X^- = Cl^-, Br^-$

white

Indicator reaction: $2Ag^+ + CrO_4^{-2} \rightleftharpoons Ag_2CrO_{4\,(S)}$

reddish-brown

Effect of Amount of Indicator (K_2CrO_4) on Mohr Method

Because potassium chromate imparts a yellow color to the solution, obscuring the end point, the amount of chromate ion added is small enough that the end point is always later than the equivalence point. To compensate for this positive determinate error an analyte free reagent blank is analyzed to determine the volume of titrant needed to effect a change in the indicator's color. The volume for the reagent blank is subsequently subtracted from the experimental end point to give the true end point.

Effect of pH on Mohr Method

The Mohr method must be carried out at a **pH of 7 to 10** because chromate ion is a weak base, the solution usually is maintained at a slightly alkaline pH. **If the pH is too acidic**, chromate ion is present as $HCrO_4^-$, and the Ag_2CrO_4 end point will be in significant error, because the chromate ion concentration is too low to produce the reddish-brown precipitate at the end point.

$$2CrO_4^{-2} + 2H^+ \rightleftharpoons 2HCrO_4^- \longrightarrow Cr_2O_7^{-2} + H_2O$$

The pH also must be kept below a level of 10 to avoid precipitating silver hydroxide.

$$2Ag^+ + 2OH^- \longrightarrow 2AgOH \longrightarrow Ag_2O_{(s)} + H_2O$$

black

Normally, a suitable pH is achieved by saturating the analyte solution with sodium hydrogen carbonate ($NaHCO_3$).

Effect of Temperature on Mohr Method

In Mohr method, the titration is carried out **at room temperature** because solubility of silver chromate increase with rising temperature.

Example:

A mixture containing only KCl and NaBr is analyzed by the Mohr method. A 0.3172 g sample is dissolved in 50 mL of water

and titrated to the Ag_2CrO_4 end point, requiring 36.85 mL of 0.112 M $AgNO_3$. A blank titration requires 0.71 mL of titrant to reach the same end point. Report the %w/w KCl and NaBr in the sample. If M.wt of KCl = 74.551 g mol^{-1} and M.wt of NaBr = 102.89 g mol^{-1}.

Solution:

The volume of titrant reacting with the analytes is

$\mathbf{V_{AgNO3} = V_{AgNO3} - V_{Blank}} = 36.85 - 0.71 \Rightarrow \mathbf{V_{AgNO3} = 36.14\ mL}$

Since the sample contains just KCl and NaBr, we know that

$\mathbf{wt_{NaBr} = wt_s - wt_{KCl}} = 0.3172 - wt_{KCl}$

no. mol of $AgNO_3$ = no. mol of KCl + no. mol of NaBr

$$M_{AgNO3} \times V_{AgNO3} = (M_{KCl} \times V_{KCl}) + (M_{NaBr} \times V_{NaBr})$$

$$M_{AgNO3} \times V_{AgNO3} = \left(\frac{wt_{KCl}}{M.wt_{KCl}} \times \frac{1}{V_{KCl}}\right) + \left(\frac{wt_{NaBr}}{M.wt_{NaBr}} \times \frac{1}{V_{NaBr}}\right)$$

$$0.112 \times \frac{36.14}{1000} = \frac{wt_{KCl}}{74.551} + \frac{(0.3172 - wt_{KCl})}{102.89}$$

$$4.048 \times 10^{-3} = \frac{1}{74.551} \times wt_{KCl} + \frac{0.3172}{102.89} - \frac{1}{102.89} \times wt_{KCl}$$

$4.048 \times 10^{-3} = 1.341 \times 10^{-2} \times wt_{KCl} + 3.083 \times 10^{-3} - 9.719 \times 10^{-3} \times wt_{KCl}$

$3.691 \times 10^{-3} \times wt_{KCl} = 9.650 \times 10^{-4}$

$\mathbf{wt_{KCl} = 0.2614\ g}$

$wt_{NaBr} = wt_s - wt_{KCl} = 0.3172 - 0.2614 \Rightarrow \mathbf{wt_{NaBr} = 0.0558\ g}$

$$\% (w/w)_{KCl} = \frac{wt_{KCl}}{wt_s} \times 100$$

$$\% (w/w)_{KCl} = \frac{0.2614}{0.3172} \times 100 \Rightarrow \% (w/w)_{KCl} = 82.41$$

$$\% (w/w)_{NaBr} = \frac{wt_{NaBr}}{wt_s} \times 100$$

$$\% (w/w)_{NaBr} = \frac{0.0558}{0.3172} \times 100 \Rightarrow \% (w/w)_{NaBr} = 17.59$$

2- Volhard Method (formation of a soluble colored complex, indirect method)

The most important application of the Volhard method is for the indirect determination of halide ions. A measured excess of standard silver nitrate solution is added to the sample, and the excess silver ion is determined by back-titration with a standard thiocyanate solution using iron (III) as the indicator. For example, in an analysis for chloride ion:

$$Ag^+ + Cl^- \rightleftharpoons AgCl_{(s)}$$

excess white

Back-titration: $SCN^- + Ag^+ \rightleftharpoons AgSCN_{(s)}$

white

Indicator reaction: $Fe^{+3} + SCN^- \rightleftharpoons Fe(SCN)^{+2}$

red

Silver chloride is more soluble than silver thiocyanate. Therefore, the following reaction occurs to a significant extent near the end of the back-titration of the excess silver ion.

$$AgCl_{(s)} + SCN^{-} \rightleftharpoons AgSCN_{(s)} + Cl^{-}$$

Silver chloride — silver thiocyanate

This reaction causes the end point to fade and results in an over consumption of thiocyanate ion, which in turn leads to low values for the chloride analysis. This error can be removed by filtering the silver chloride before determination of the excess silver ion by back-titration. Filtration is not required in the determination of other halide ions (Br^- and I^-) because they all form silver salts that are less soluble than silver thiocyanate.

The Volhard method must be carried out in **acidic solution** to prevent precipitation of iron (III) as the hydrate oxide.

$$2Fe^{+3} + 6OH^{-} \rightleftharpoons 2Fe(OH)_{3(s)} \rightleftharpoons Fe_2O_{3(s)} + 3H_2O$$

reddish-brown — ferric oxide

In aqueous solution occurs hydrolysis of ferric ion leading to yellow or brown complexes: $Fe^{+3} + H_2O \rightleftharpoons Fe(OH)^{+2} + H^{+}$

yellow complex

Example:

The %w/w I^- in a 0.6712 g sample was determined by a Volhard titration. After adding 50 mL of 0.05619 M $AgNO_3$ and allowing the precipitate to form, the remaining silver was back titrated with 0.05322 M KSCN, requiring 35.14 mL to reach the end point. Report the %w/w I^- in the sample. If A.wt$_{I^-}$ = 126.9 g mol^{-1}

Solution:

no. mol of I^- = no. mol of $AgNO_3$ added – no. mol of KSCN added

$(M \times V)_{I^-} = (M \times V)_{AgNO3} - (M \times V)_{KSCN}$

$\left(\frac{wt_{I^-}}{A.wt_{I^-}} \times \frac{1}{V_{I^-}}\right) = (M \times V)_{AgNO3} - (M \times V)_{KSCN}$

$\frac{wt_{I^-}}{126.9} = (0.05619 \times 50 \times 10^{-3}) - (0.05322 \times 35.14 \times 10^{-3})$

$\frac{wt_{I^-}}{126.9} = (0.05619 \times 50 \times 10^{-3}) - (0.05322 \times 35.14 \times 10^{-3})$

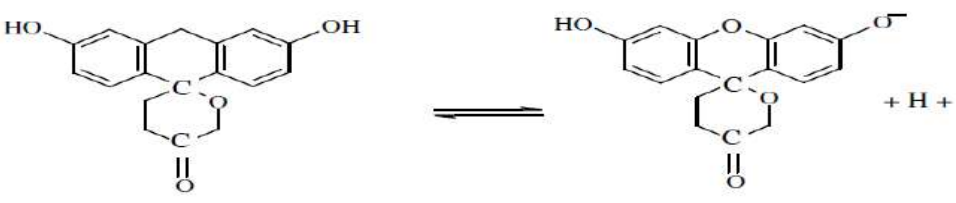
$\frac{wt_{I^-}}{126.9} = 9.393 \times 10^{-4} \Rightarrow$ **$wt_{I^-} = 0.1192$ g**

$\%\ (w/w)_{I^-} = \frac{wt_{I^-}}{wt_s} \times 100$

$\%\ (w/w)_{I^-} = \frac{0.1192}{0.6712} \times 100 \Rightarrow$ **$\%\ (w/w)_{I^-} = 17.76$**

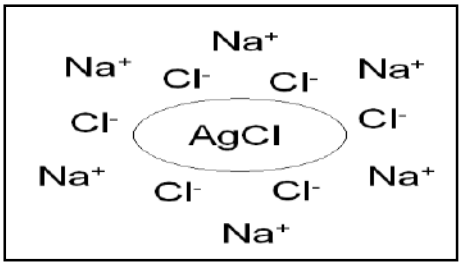
3- Fajans Method (adsorption indicators)

Adsorption indicators consist of organic dyes such as fluorescein (FL) which are used in argentometric titrations to determine chloride or bromide ion. The Fajans method uses an adsorption indicator whose color when adsorbed to the precipitate is different from that when it is in solution.

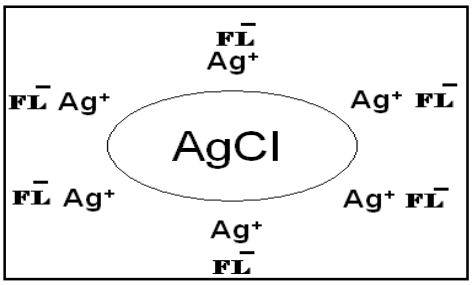


Fluorescein Fluoresceinate anion(Yellow green)

Before the end point, the precipitate of AgCl has a negative surface charge due to the adsorption of excess chloride ion. The anionic indicator is repelled by the precipitate and remains in solution where it has a greenish yellow color.



After the end point, the precipitate has a positive surface charge due to the adsorption of excess silver ion. The anionic indicator now adsorbs to the precipitate's surface where its color is pink. This change in color signals the end point.



Ag^+ + Fl^- (greenish yellow) ⇌ AgFl (pink)

The color of the adsorbed indicator is different from that of the un-adsorbed indicator, signaling the completion of the titration. The degree of adsorption of the indicator can be decreased by increasing the acidity. Since fluorescein and its derivatives are weak acids, the pH of the solution

should be **slightly alkaline** to keep the indicator in the anion form but, at the same time, is not alkaline enough to convert Ag^+ into AgOH.

Titrations involving adsorption indicators are rapid, accurate and reliable. Their application, however, is limited to the relatively few precipitation reactions in which a colloidal precipitate is formed rapidly.

Lec 10

Gravimetric Methods of Analysis

Gravimetric methods are quantitative methods based on determining the weight of a pure compound to which the analyte is chemically related.

Gravimetric method is one in which the analysis is completed by a weighing operation.

Types of Gravimetric Methods

There are two major types of gravimetric methods:

1- **Precipitation methods**

2- **Volatilization methods**

In **precipitation methods**, the analyte is converted to a sparingly soluble precipitate. This precipitate is then filtered, washed free of impurities, and converted to a product of known composition by suitable heat treatment, and the product is weighed.

In **volatilization methods**, the analyte or its decomposition products are volatilized at a suitable temperature. The volatile product is then collected and weighed, or alternatively, the weight of the product is determined indirectly from the loss in weight of the sample. The two most common gravimetric methods based on volatilization are those for water and carbon dioxide.

Properties of Precipitates and Precipitating Reagents

A gravimetric precipitating agent (the precipitant) should react **specifically** or, if not that, at least **selectively** with the analyte. **Specific**

reagents, which are rare, react only with a single chemical species. **Selective reagents**, which are more common, react with a limited number of species. In additional to specificity or selectivity, the ideal precipitating reagent would react with the analyte to give a product that is:

1- Readily filtered and washed free of contaminants.

2- Of sufficiently low solubility so that no significant loss of the solid occurs during filtration and washing.

3- Unreactive with constituents of the atmosphere.

4- Of known composition after it is dried or, if necessary, ignited.

Calculation of Results from Gravimetric Data

The results of a gravimetric analysis are generally computed from two experimental measurements:

1- The weight of sample.

2- The weight of a product of known composition.

The weight of analyte obtains by multiplying the weight of the final product by a constant. This constant is called the **gravimetric factor (GF)**.

A general definition for the gravimetric factor is

$$GF = \frac{a \times \text{M.wt of substance analyzed(A)}}{b \times \text{M.wt of substance weighed (B)}}$$

where **a** and **b** are small whole numbers that have values such that the number of molecular weights in the numerator and the denominator are chemically equivalent.

$$wt_A = wt_B \times GF$$

wt_A = weight of analyte, wt_B = weight of the final product

$$\%\,(w/w)_A = \frac{wt_A}{wt_S} \times 100$$

$$\%\,(w/w)_A = \frac{wt_B \times GF}{wt_S} \times 100$$

Table 2 shows calculations some of gravimetric factors.

Table 2: Calculations Some of Gravimetric Factors

Substance Analyzed	Substance Weighed	Gravimetric Factor
$BiCl_3$	Bi_2O_3	$\frac{2 \times \text{M.wt of } BiCl_3}{1 \times \text{M.wt of } Bi_2O_3}$
KNO_3	K_2PtCl_6	$\frac{2 \times \text{M.wt of } KNO_3}{1 \times \text{M.wt of } K_2PtCl_6}$
K_3PO_4	K_2PtCl_6	$\frac{2 \times \text{M.wt of } K_3PO_4}{3 \times \text{M.wt of } K_2PtCl_6}$
P_2O_5	$Mg_2P_2O_7$	$\frac{1 \times \text{M.wt of } P_2O_5}{1 \times \text{M.wt of } Mg_2P_2O_7}$
Fe	$CaCO_3$	$\frac{\text{eq.wt of Fe}}{\text{eq.wt of } CaCO_3} = \frac{\text{A.wt of Fe} / 3}{\text{M.wt of } CaCO_3 / 2}$

The following examples illustrate how such computations are carried out.

Example:

An iron ore was analyzed by dissolving a 1.1324 g sample in concentrated HCl. The resulting solution was diluted with water, and the iron(III) was precipitated as the hydrous oxide (Fe_2O_3. x H_2O) by the addition of NH_3. After filtration and washing, the residue was ignited at a high temperature to give 0.5394 g of pure Fe_2O_3 (159.69 g / mol). Calculate the percent Fe (55.847 g / mol) in the sample.

Solution:

wt Fe = wt Fe_2O_3 × GF

$$GF = \frac{2 \text{ mol Fe} \times \text{A.wt Fe}}{1 \text{ mol } Fe_2O_3 \times \text{M.wt } Fe_2O_3}$$

$$GF = \frac{2 \text{ mol Fe} \times 55.847 \text{ g / mol Fe}}{1 \text{ mol } Fe_2O_3 \times 159.69 \text{ g / mol } Fe_2O_3} \Longrightarrow \textbf{GF = 0.6994 } \frac{\textbf{g Fe}}{\textbf{g } Fe_2O_3}$$

$$\text{wt Fe} = 0.5394 \text{ g } Fe_2O_3 \times 0.6994 \frac{\text{g Fe}}{\text{g } Fe_2O_3} \Longrightarrow \textbf{wt Fe = 0.3773 g}$$

$$\% \text{ (w / w) Fe} = \frac{\text{wt Fe}}{\text{wt}_S} \times 100$$

$$\% \text{ (w / w) Fe} = \frac{0.3773}{1.1324} \times 100 \Longrightarrow \textbf{\% (w / w) Fe = 33.32}$$

Example:

A 0.3516 g sample of a commercial phosphate detergent was ignited at a red heat to destroy the organic matter. The residue was then taken up in hot HCl, which converted the P to H_3PO_4. The phosphate was precipitated as $MgNH_4PO_4.6H_2O$ by addition of Mg^{+2} followed by

aqueous NH_3. After being filtered and washed, the precipitate was converted to $Mg_2P_2O_7$ (222.57 g / mol) by ignition at 1000°C. This residue weighed 0.2161 g. Calculate the percent P (30.974 g / mol) in the sample.

Solution:

wt P = wt $Mg_2P_2O_7$ × GF

$$GF = \frac{2 \text{ mol P} \times \text{A.wt P}}{1 \text{ mol } Mg_2P_2O_7 \times \text{M.wt } Mg_2P_2O_7}$$

$$GF = \frac{2 \text{ mol P} \times 30.974 \text{ g / mol P}}{1 \text{ mol } Mg_2P_2O_7 \times 222.57 \text{ g / mol } Mg_2P_2O_7} \Longrightarrow \textbf{GF = 0.2783 g P / g } \textbf{Mg}_2\textbf{P}_2\textbf{O}_7$$

$$\text{wt P} = 0.2161 \text{ g } Mg_2P_2O_7 \times 0.2783 \frac{\text{g P}}{\text{g } Mg_2P_2O_7} \Longrightarrow \textbf{wt P = 0.0601 g}$$

$$\% \text{ (w / w) P} = \frac{\text{wt P}}{\text{wt}_S} \times 100$$

$$\% \text{ (w / w) P} = \frac{0.0601}{0.3516} \times 100 \Longrightarrow \textbf{\% (w / w) P = 17.09}$$

Example:

The calcium in a 200 mL sample of natural water was determined by precipitating the cation as CaC_2O_4. The precipitate was filtered, washed, and ignited in a crucible with an empty weight of 26.6002 g. The weight of the crucible plus CaO (56.077 g / mol) was 26.7134 g. Calculate the concentration of Ca (40.078 g / mol) in the water in units of grams per 100 mL.

Solution:

wt CaO = 26.7134 – 26.6002 ⟹ **wt CaO = 0.1132 g**

wt Ca = wt CaO × GF

$$GF = \frac{1 \text{ mol Ca} \times \text{A.wt Ca}}{1 \text{ mol CaO} \times \text{M.wt CaO}}$$

$$GF = \frac{1 \text{ mol Ca} \times 40.078 \text{ g / mol Ca}}{1 \text{ mol CaO} \times 56.077 \text{ g / mol CaO}} \Longrightarrow \textbf{GF = 0.7147 } \frac{\textbf{g Ca}}{\textbf{g CaO}}$$

$$\text{wt Ca} = 0.1132 \text{ g CaO} \times 0.7147 \frac{\text{g Ca}}{\text{g CaO}} \Longrightarrow \textbf{wt Ca = 0.0809 g}$$

$$\% \text{ (w / v) Ca} = \frac{\text{wt Ca}}{V_S} \times 100$$

$$\% \text{ (w / v) Ca} = \frac{0.0809}{200} \times 100 \Longrightarrow \textbf{\% (w / v) Ca = 0.04045}$$

Concentration of Ca in the water (in units of grams per 100 mL) = **0.04045 g / 100 mL**.

Lec 11

Instrumental Methods

Early in the twentieth century, chemists began to exploit phenomena other than those used for classical methods (volumetric and gravimetric methods) for solving analytical problems. Thus, measurements of physical properties of analytes (such as conductivity, electrode potential, light absorption or emission, mass-to-charge ratio, and fluorescence) began to be used for quantitative analysis of a variety of inorganic, organic and biochemical analytes. Furthermore, highly efficient chromatographic and electrophoretic techniques began to replace distillation, extraction and precipitation for the separation of components of complex mixtures prior to their qualitative or quantitative determination. These newer methods for separating and determining chemical species are known collectively as **instrumental methods of analysis**.

Instruments for Analysis

An instrument for chemical analysis converts information stored in the physical or chemical characteristics of the analyte to information that may be manipulated and interpreted by a human. Thus, an analytical instrument can be viewed as a communication device between the system under study and the investigator. To retrieve the desired information from the analyte, it is necessary to provide a stimulus, which

is usually in the form of electromagnetic, electrical, mechanical or nuclear energy.

Spectroscopic Instruments

Optical spectroscopic methods are based upon four phenomena:

1- Absorption (in atomic and molecular absorption methods).

2- Emission (in atomic emission methods).

3- Luminescence (in atomic and molecular fluorescence, phosphorescence and chemiluminescence methods).

4- Scattering (in Raman scattering, turbidimetry and nephelometry methods).

Typical spectroscopic instruments contain five components, including:

1- A stable source of radiant energy.

2- A transparent container for holding the sample.

3- A device that isolates a restricted region of the spectrum for measurement.

4- A radiation detector, which converts radiant energy to a usable signal (usually electrical).

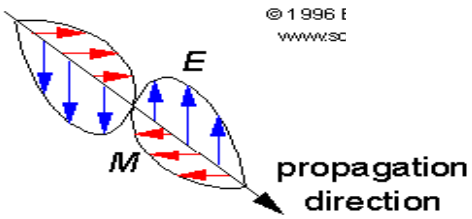
5- A signal processor and readout, which displays the transduced signal on a meter scale, a digital meter or a recorder chart.

Spectroscopy is the use of the absorption, emission or scattering of

electromagnetic radiation by atoms or molecules (or atomic or molecular ions) to qualitatively or quantitatively study the atoms or molecules or to study physical processes.

The interaction of radiation with matter can cause redirection of the radiation and/or transitions between the energy levels of the atoms or molecules. A transition from a lower energy level to a higher energy level with transfer of energy from the radiation field to the atom or molecule is called **absorption**. A transition from a higher energy level to a lower energy level is called **emission** if energy is transferred to the radiation field or nonradiative decay if no radiation is emitted. Redirection of light due to its interaction with matter is called **scattering**, and may or may not occur with transfer of energy, i.e., the scattered radiation has a slightly different or the same wavelength.

Electromagnetic radiation is an energy wave that is composed of an electric field component and a magnetic field component. The electric and magnetic fields are orthogonal to each other and orthogonal to the direction of propagation of the wave.



Electromagnetic radiation possesses a certain amount of energy. The energy of a unit of radiation, called the photon, is related to the frequency or wavelength by

$$E = h\upsilon = \frac{hc}{\lambda}$$

where **E** is the energy of the photon in ergs, **h** is Planck's constant ($h = 6.626 \times 10^{-34}$ J s), **υ** is the frequency (the number of cycles passing a fixed point per unit time) in reciprocal seconds (s^{-1}) or hertz (Hz), **c** is the velocity of light ($c = 3 \times 10^{10}$ cm s^{-1}) and **λ** is the wavelength (the distance of one complete cycle) in centimeters (cm).

Wavenumber (the number of waves in a unit length or distance per cycle) is represented by ϋ, in cm^{-1}:

$$\ddot{\upsilon} = \frac{1}{\lambda} = \frac{\upsilon}{c}$$

Wavelength in the ultraviolet (UV) and visible (Vis) regions are on the order nanometers (nm).

Working ranges of the UV / Vis spectra, including:

1- UV, 200 – 380 nm.

2- Vis, 380 – 780 nm.

Spectrometric methods are the methods based on the absorption, emission or scattering of electromagnetic radiation that is related to the amount of analyte in the sample.

Spectra are plots of absorbance, transmittance or emission intensity as a function of wavelength, frequency or wavenumber.

Spectrometer is an instrument equipped with a monochromator or polychromator, a photodetector and an electronic readout to display a number that is proportional to the intensity of an isolated spectral band.

Spectrophotometer is a spectrometer designed for the measurement of the absorption of ultraviolet, visible or infrared radiation. The instrument

includes a source of radiation, a monochromator and an electrical means of measuring radiation intensity.

Absorption Spectrometric Methods

In **spectrometric methods**, the sample solution absorbs electromagnetic radiation from an appropriate source and the amount absorbed is related to the concentration of the analyte in the solution.

Absorption spectrometry, including:

1- Molecular absorption spectrometry

2- Atomic absorption spectrometry.

Absorption spectrometry is based on the absorption of photons by the analyte.

A solution contains copper ions is blue because it **absorbs** the complementary color **yellow** from white light and **transmits** the remaining **blue light** (Table 3). The more concentrated the copper solution, the more yellow light is absorbed and the deeper the resulting blue color of the solution.

A solution of $Fe(SCN)^{+2}$ is red because the complex **absorbs green-blue light** in the 490 – 500 nm region of the spectrum and **transmits red light**.

To the eye, permanganate solutions appear to be purple because they **transmit red and blue** radiation but **absorb green**. The color appears more intense at higher concentrations because of an increase in absorption of the latter.

Table 3: Colors of Different Wavelength Regions

Wavelength Absorbed (nm)	Absorbed Color	Transmitted Color (Complement)
380 – 435	Violet	Yellow-green
435 – 480	Blue	Yellow
480 – 490	Blue-green	Orange
490 – 500	Green-blue	Red
500 – 560	Green	Purple
560 – 580	Yellow-green	Violet
580 – 595	Yellow	Blue
595 – 650	Orange	Blue-green
650 – 750	Red	Green-blue

Quantitative absorption methods require two power measurements: one before a beam has passed through the medium that contains the analyte (P_0) and the other after (P_T). Two terms, which are widely used in absorption spectrometry and are related to the ratio of P_0 and P_T, are transmittance and absorbance.

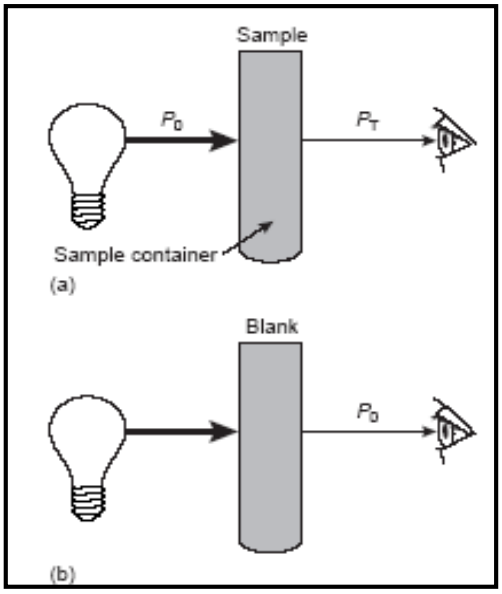


Figure 2

(a) Schematic diagram showing the attenuation of radiation passing through a sample; P_0 is the radiant power from the source and P_T is the radiant power transmitted by the sample. (b) Schematic diagram showing that P_0 is redefined as the radiant power transmitted by the blank, correcting the transmittance in (a) for any loss of radiation due to scattering, reflection or absorption by the cuvette, and absorption by the sample's matrix.

Transmittance

The transmittance (T) of the medium (that has a thickness of b cm and a concentration C of an absorbing species) is then the fraction of incident radiation transmitted by the medium:

$$T = \frac{P_T}{P_0}$$

Where, P_T is intensity of transmitted light, and P_0 is intensity of incident light.

Transmittance is often expressed as a percentage or

$$\%T = \frac{P_T}{P_0} \times 100$$

Absorbance

The absorbance (A) of a medium is defined by the equation:

$$A = -\log T = \log \frac{P_0}{P_T}$$

$$A = 2 - \log \%T$$

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Beer's Law

For monochromatic radiation, absorbance is directly proportional to the pathlength **b** through the medium and the concentration **C** of the absorbing species. These relationships are given by: **A = a b C**

where **a** is a proportionality constant called the **absorptivity**. The magnitude of a will clearly depend upon the units used for **b** and **C**. For solutions of an absorbing species, **b** is often given in terms of centimeters (**cm**) and **C** in grams per liter (**g L^{-1}**). Absorptivity (a) then has units of **L g^{-1} cm^{-1}**.

Absorptivity depending on: **1-** Nature of substance, **2-** Wavelength, **3-** Pathlength of radiation in solution, **4-** Type of solvent.

When the concentration (C) is expressed in moles per liter (mol L^{-1}) and the cell length (b) is in centimeters (cm), the absorptivity (a) is called the **molar absorptivity** and is given the special symbol **ε**. Thus, when **b** is in **cm** and **C** in **mol L^{-1}**,

A = ε b C where **ε** has the units **L mol^{-1} cm^{-1}**.

The molar absorptivity of a species at an absorption maximum is characteristic of that species. Peak molar absorptivities for many organic compounds range from **10 or less to 10^4 or more**. Some transition metal complexes have molar absorptivities of 1×10^4 to 5×10^4. **High molar absorptivities** are desirable for quantitative analysis **because** they lead to **high analytical sensitivity**.

Beer's law is the relationship between a sample's absorbance and the concentration of the absorbing species ($A = \varepsilon b C$).

Example:

A 7.5×10^{-5} M solution of potassium permanganate ($KMnO_4$) has a transmittance of 36.4% when measured in a 1 cm cell at a wavelength of 525 nm. Calculate (a) the absorbance of this solution and (b) the molar absorptivity of $KMnO_4$.

Solution:

(a) $A = 2 - \log \%T = 2 - \log 36.4 = 2 - 1.561 = 0.439$

(b) $$\varepsilon = \frac{A}{b\,C} = \frac{0.439}{1 \times 7.5 \times 10^{-5}} = 5.853 \times 10^{3}\ L\ mol^{-1}\ cm^{-1}$$

Example:

A sample in a 1 cm cell is determined with a spectrometer to transmit 80% light at a certain wavelength. If the absorptivity of this substance at this wavelength is 2 L g^{-1} cm^{-1}, what is the concentration of the substance?

Solution:

$A = a\,b\,C = 2 - \log \%T$

$2 \times 1 \times C = 2 - \log 80$

$2\,C = 2 - 1.903 \Longrightarrow C = \frac{0.097}{} = 0.049\ g\ L^{-1}$

Limitations of Beer's Law

1- The incident radiation (P_0) is monochromatic (only one wavelength).

2- All rays of the incident radiation travel equidistant parallel paths through the absorbing sample (highly collimated beam with no internal reflections).

3- The incident radiant power is not sufficient to significantly alter the ground-state population of the absorbing molecules (avoid nonlinear optics such as high-power laser light sources).

4- The absorbing sample must be homogeneous and not scatter or reflect the incident radiation.

5- The absorbing species must behave as independent moieties (no molecular interactions with other like or unlike molecules, only at high dilution, for example).

Limits to Beer's Law

1- Real Limitations to Beer's Law

Beer's law describes the absorption of **dilute solutions only** and in this sense is a limiting law. At concentration exceeding about 0.01 M, the average distances between ions or molecules of the absorbing species are diminished to the point where each particle affects the charge distribution, and thus extent of absorption, of its neighbors. Because the extent of interaction depends on concentration, the occurrence of this phenomenon causes deviations from the linear relationship between absorbance and concentration.

2- Chemical Deviations

Apparent deviations from Beer's law are frequently encountered as a consequence of association, dissociation or reaction of the absorbing species with the solvent. A classic example of a chemical deviation is observed with unbuffered potassium dichromate solutions, in which the following equilibria exist:

$$Cr_2O_7^{-2} + H_2O \rightleftharpoons 2HCrO_4^- \rightleftharpoons 2H^+ + 2CrO_4^{-2}$$

Dichromate ion

Chromate ion

At most wavelengths, the molar absorptivities of dichromate ion and the two chromate species are quite different. Thus, the total absorbance of any Cr(VI) solution is dependent upon the ratio of concentrations between the dimeric and monomeric forms. This ratio, however, changes markedly with dilution and causes a pronounced deviation from linearity between the absorbance and the total concentration of chromium. Nevertheless, the absorbance due to the dichromate ion remains directly proportional to its molar concentration; the same is true for the chromate ions. This fact is easily demonstrated by making measurements in **strongly acidic** or **strongly basic** solution where one or the other of these species will predominate.

Thus, deviations in the absorbance of this system from Beer's law are more apparent than real **because** they result from shifts in chemical

equilibria. These deviations can, in fact, be readily predicted from the **equilibrium constants** for the reactions and the **molar absorptivities** of the dichromate and chromate ions.

3- Instrumental Deviation

Strict adherence of an absorbing system to Beer's law is observed only when monochromatic radiation is employed. This observation is another manifestation of the limiting character of the relationship. Use of a truly monochromatic beam for absorbance measurements is seldom practical, however, and **polychromatic radiation** may lead to departures from Beer's law.

Experiments show that deviations from Beer's law resulting from the use of a polychromatic beam are not appreciable provided the radiation used does not encompass a spectral region in which the absorber exhibits large changes in absorbance as a function of wavelength. Hence, **to avoid deviations**, it is advisable to select a wavelength band near the wavelength of maximum absorption where the analyte absorptivity changes little with wavelength.

Polychromatic light (multicolored light) is light of many wavelengths, such as that from a tungsten light bulb.

Monochromatic light is light of a single wavelength, such as that from a laser or a single small band of wavelengths. It can be produced by filtering, diffracting or refracting polychromatic light.

Stray radiation, commonly called stray light, is defined as radiation from the instrument that is outside the nominal wavelength band chosen for the determination. This stray radiation is often the result of **scattering** and the surfaces of gratings, lenses or mirrors, filters and windows.

The deviations due to **stray light** are most significant at high absorbance values. Because stray radiation levels can be as high as 0.5% in modern instruments, absorbance levels above 2 are rarely measured unless special precaution are taken or special instruments with extremely low stray light levels are used. Some inexpensive filter instruments can exhibit deviations from Beer's law at absorbances as low as 1 because of high stray light levels or the presence of polychromatic light.

Another almost trivial, but important, deviation is caused by **mismatched cells**. If the cells holding the analyte and blank solutions are not of equal path length and equivalent in optical characteristics, an intercept will occur in the calibration curve, and $\mathbf{A = \varepsilon bc + k}$ will be the actual equation instead of $\mathbf{A = \varepsilon bc}$. This error can be avoided either by using **matched cells** or by using a **linear regression procedure** to calculate both the slope and intercept of the calibration curve. In most cases, the linear regression strategy is best because an intercept can also occur if the blank solution does not totally compensate for interferences. Another way to avoid the mismatched cell problem with **single-beam instruments** is to use **only one cell** and keep it in the same position for both blank and analyte measurements. After obtaining the blank reading, the cell is emptied by aspiration, washed and rinsed and filled with analyte solution.

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Instrument Designs for Molecular UV/Vis Absorption

The simplest instrument currently used for molecular UV/Vis absorption is the **filter photometer** shown in Figure 3, which uses an absorption or interference filter to isolate a band of radiation.

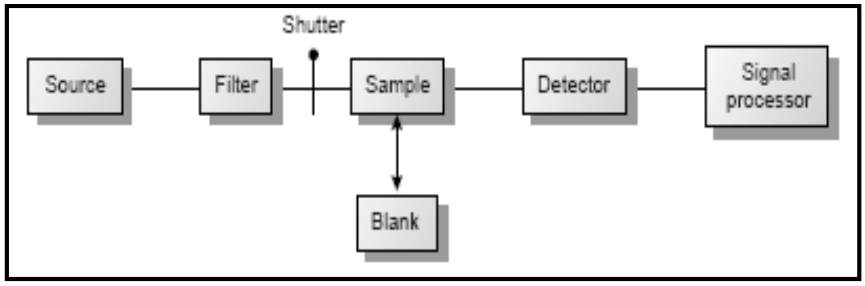


Figure 3

Block diagram for a filter photometer with photo showing a typical hand-held instrument suitable for field work

Filter photometer is a simple instrument for measuring absorbance that uses absorption or interference filters to select the wavelength.

The **filter** is placed between the source and sample to prevent the sample from decomposing when exposed to high-energy radiation. A filter photometer has a single optical path between the source and detector and is called a single-beam instrument.

In comparison with other spectroscopic instruments, **photometers** have the following **advantages**: **1-** relatively inexpensive, **2-** rugged, **3-** easy to maintain, and **4-** portability, making it a useful instrument for conducting spectroscopic analyses in the field.

A **disadvantage** of a photometer is that it cannot be used to obtain an absorption spectrum.

Instruments using **monochromators** for wavelength selection are called **spectrometers**. All spectrometers require:

1- A source of continuous radiation over the wavelengths of interest.

2- A monochromator for selecting a narrow band of wavelengths from the source spectrum.

3- A sample cell.

4- A detector for converting radiant energy into electrical energy.

5- A device to read out the response of the detector.

In absorbance spectroscopy, where the transmittance is a ratio of two radiant powers, the instrument is called a **spectrophotometer**. The simplest **spectrophotometer** is a single-beam instrument equipped with a fixed wavelength monochromator, the block diagram for which is shown in Figure 4.

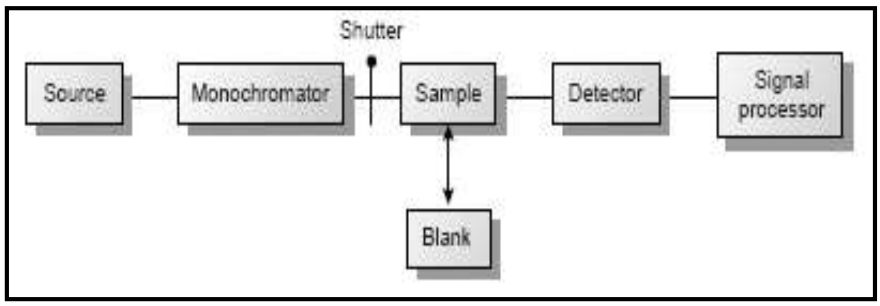
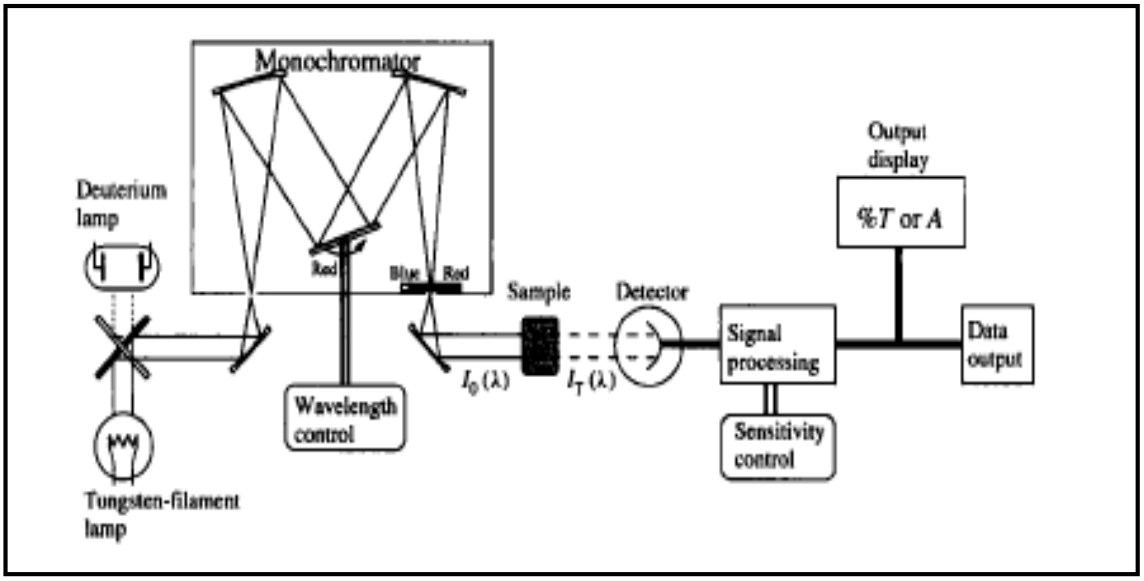


Figure 4

Block diagram for a single-beam fixed wavelength spectrophotometer

with photo of a typical instrument



Schematic representation of a single-beam UV-visible spectrophotometric system.

Spectrophotometer is an instrument for measuring absorbance that uses a monochromator to select the wavelength.

The limitations of fixed-wavelength, single-beam spectrophotometers are minimized by using the double-beam in-time spectrophotometer as shown in Figure 5.

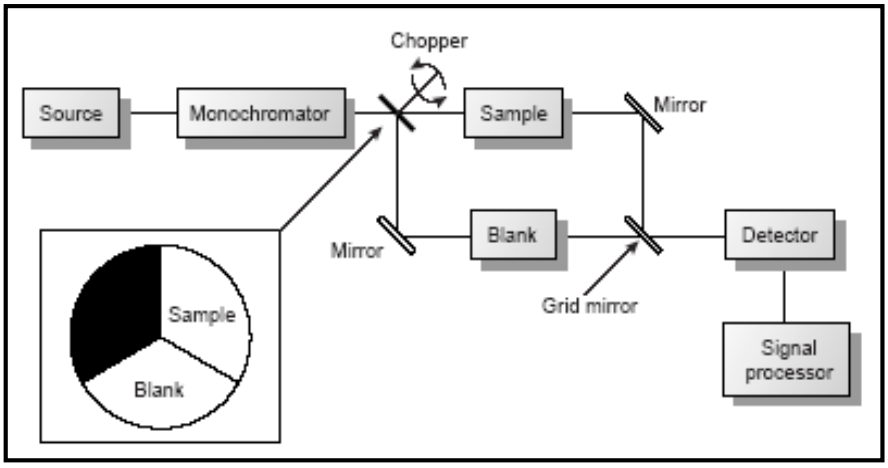
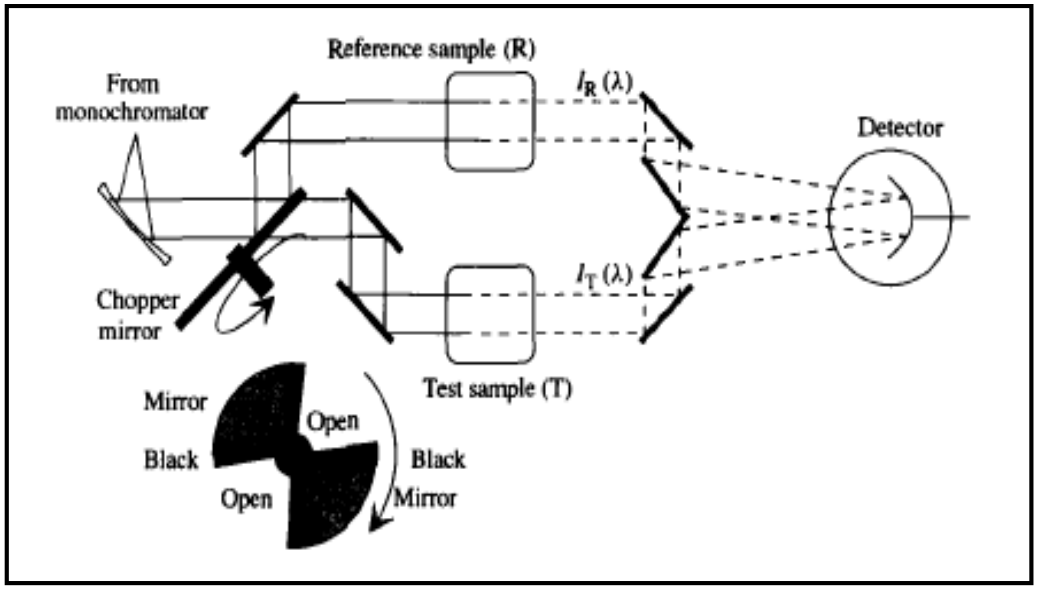


Figure 5

Block diagram for a double-beam in-time scanning spectrophotometer with photo of a typical instrument



Schematic representation of a double-beam UV-visible spectrophotometric system

A scanning monochromator allows for the automated recording of spectra. Double-beam instruments are more versatile than

single-beam instruments, being useful for both quantitative and qualitative analyses; they are, however, more expensive.

The sample compartment for the instruments in Figures 3–5 provides a light-tight environment that prevents the loss of radiation, as well as the addition of stray radiation. Samples are normally in the liquid or solution state and are placed in cells constructed with UV/Vis-transparent materials, such as quartz, glass, and plastic (Figure 6). **Quartz** or **fused-silica cells** are required when working at wavelengths of less than 300 nm where other materials show a significant absorption by absorption of UV radiation.

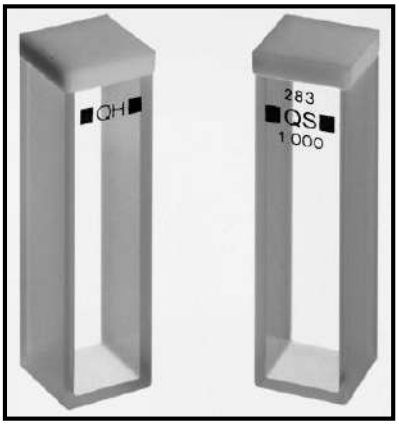


Figure 6

Typical cells used in UV/Vis spectroscopy

The most common cell has a pathlength of 1 cm, although cells with shorter ($\geq$ 1 mm) and longer pathlengths ($\leq$ 10 cm) are available. Cells with a longer pathlength are useful for the analysis of very dilute solutions or for gaseous samples. The highest quality cells are constructed in a rectangular shape, allowing the radiation to strike the cell at a 90° angle, where losses to reflection are minimal. These cells which are usually available in **matched pairs** having identical optical properties are the cells

of choice for double-beam instruments. Cylindrical test tubes are often used as a sample cell for simple, single-beam instruments, although differences in the cell's pathlength and optical properties add an additional source of error to the analysis.

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Analytical Separation Methods

1- Extraction

Extraction is the process by which a solute is transferred from one phase to a new phase.

Types of Extraction:

1- Liquid–Liquid Extraction**, 2-** Solid–Liquid Extraction

1) Liquid–Liquid Extraction

One popular method of separating an analyte species from a complicated liquid sample is the technique known as **liquid–liquid extraction** or **solvent extraction**.

In **liquid–liquid extraction**, the liquid solution containing the analyte (usually a water solution) is brought into contact with a liquid solvent (usually a nonpolar organic solvent, such as n-hexane, cyclohexane, n-heptane, methylene chloride, toluene, diethyl ether, chloroform) that is immiscible with the first solvent. The container is usually a separatory funnel (Fig. 7).

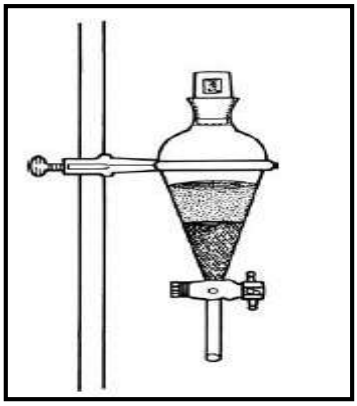

Figure 7

A drawing of a separatory funnel, containing two immiscible liquids, held in an iron ring clamped to a ring stand.

<u>This technique involves two liquid phases</u>:

1- The original solution. **2-** The extracting solvent.

<u>The important criteria for a successful separation of the analyte are</u>:

1- The two liquids are immiscible.

2- The analyte be more soluble in the extracting solvent than the original solvent.

Shaking the separatory funnel brings the two solvents into intimate contact such that the analyte then moves from the original (first) solvent to the new (second) solvent. Being immiscible, the two layers can then be separated from each other by allowing the desired solution is then carried forward to the next step.

2) Solid–Liquid Extraction

An analyte may be present in one material phase (either a solid or liquid sample) and, as part of the sample preparation scheme, be required to be separated from the sample matrix and placed in another phase (a liquid). Such a separation is known as an **extraction**. **Extraction** the analyte is extracted from the initial phase by the liquid and is deposited (dissolved) in the liquid, while other sample components are insoluble and remain in the initial phase. If the sample is a solid, the extraction is referred to as a **solid–liquid extraction**.

Solid–liquid extraction a solid sample is placed in the same container as the liquid and the analyte is separated from the solid **because** it dissolves in the liquid while other sample components do not.

<u>The process can take one of two forms</u>:

1- The sample and liquid are shaken (or otherwise agitated) together in the same container, the resultant mixture filtered, and the filtrate, which then contains the analyte, collected.

2- Fresh liquid is continuously cycled over a period of hours through the solid sample via a continuous evaporation–condensation process (that usually does not require an extra filtration step), and the liquid is collected. This latter method is known as a **<u>Soxhlet extraction</u>.**

The Soxhlet apparatus is shown in Fig. 8.

- The extracting solvent is placed in the flask at the bottom.

- The weighed solid sample is placed in the solvent-permeable thimble in the compartment directly above the flask.
- A condenser is situated directly above the thimble.
- The thimble compartment is a sort of cup that fills with solvent.
- When the solvent in the flask is boiled, evaporated, and condensed on the condenser. The sample is thus exposed to freshly distilled solvent as the cup fills.
- When the cup is full, the glass tube next to the cup is also full, and when it (the tube) begins to overflow, the entire contents of the cup are siphoned back to the lower chamber and the process repeated.

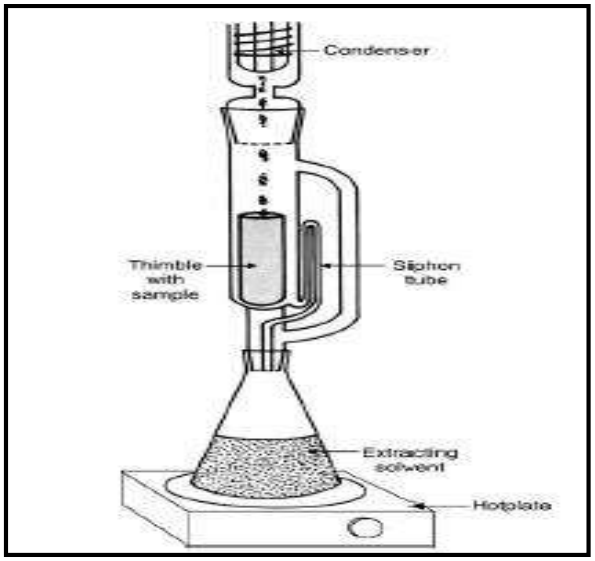

Figure 8

A drawing of a Soxhlet extraction apparatus

<u>The advantages of such an apparatus are</u>:

1- Fresh solvent is continuously in contact with the sample (without having to introduce more solvent, which would dilute the extract).

2- The experiment takes place unattended and can conveniently occur overnight if desired.

2- Filtration

Filtration is a method used to separate a liquid and a solid that does not dissolve in the liquid. For example, a mixture of water (the liquid) and sand (the solid).

During filtration, a mixture of water and sand is passed through a piece of filter paper fitted in a filter funnel. The water drains through the filter paper, but the sand is left behind. The substance that is left behind is called the residue and the substance that drains through is called **the filtrate**. When muddy water is poured through the sand filter, the mud and larger particles are trapped by the sand. The water that drains through is clear.

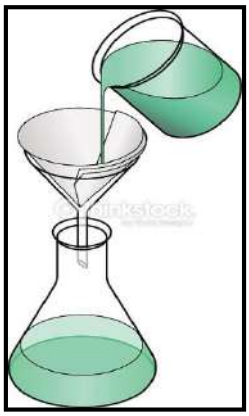

Figure 9

A drawing of filtration apparatus

3- Distillation

Distillation is a method of purification of liquids contaminated with either dissolved solids or miscible liquids. It is a process in which a liquid or vapour mixture of two or more substances is separated into its component fractions of desired purity, by the application and removal of heat.

- The method consists of boiling and evaporating the mixture followed by recondensation of the vapors in a condenser, which is a tube usually cooled by isolated cold tap water.
- The theory is that the vapors (and thus recondensed liquids) will be **purer** than the original liquid.
- The separation is based on the fact that the **contaminants** have **different** boiling points and vapor pressures than the liquid to be purified.
- Thus, when the liquid is boiled and evaporated, the vapors (and recondensed liquids) created have a composition **different** from the original liquid.
- The substances with **lower** boiling points and **higher** vapor pressures are therefore separated from substances that have **high** boiling points and **low** vapor pressures.

For example distillation of ammonia (Fig. 10) that produced from organic nitrogen (for example protein) using **Kjeldahl method**.

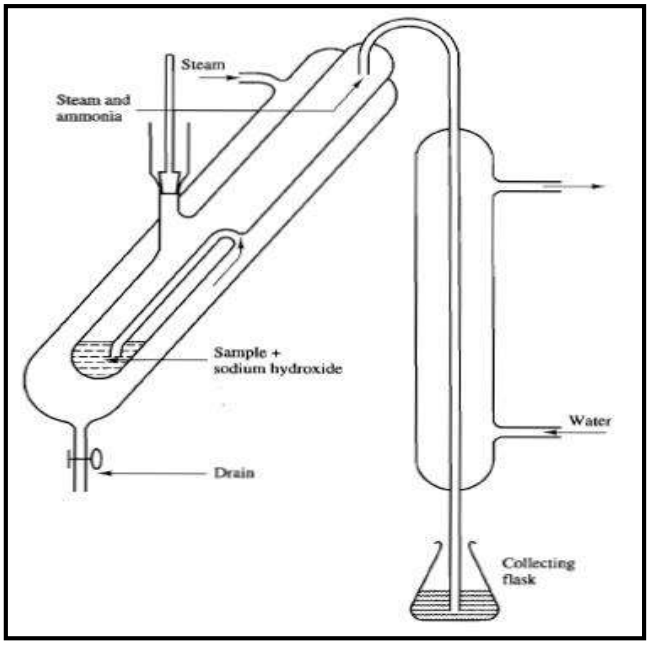

Figure 10

Apparatus for the distillation and collection of ammonia

In digestion stage

- The nitrogen containing compounds are oxidized to ammonia by heating the sample with **concentrated sulfuric acid** together with a catalyst, usually **cupric ions**, although mercuric ions and metallic selenium have been used.
- **Potassium or sodium sulfate** is usually included to **increase** the boiling point of the mixture, although excessive heating must be avoided to prevent decomposition of the **ammonium sulfate**.
- This digestion stage is important and usually takes **several hours** during which the sample initially turns **brown or black** and sulfur dioxide fumes are given off.
- The solution eventually **clears** and heating should be continued for about a **further 2 hours**.

In distillation stage

- The cooled mixture is transferred to a steam distillation flask, and after making the mixture alkaline with excess sodium hydroxide the ammonia is distilled into a receiver flask (Fig. 10).

In titration stage

- The ammonia is trapped in a **boric acid** solution to formed and the ammonium ions are titrated directly with a standard hydrochloric acid solution.
- Although boric acid is the most convenient, it is possible to trap the ammonia in a known volume of **standard hydrochloric acid** and **back-titrate** the residual acid with a sodium hydroxide solution. The **advantage** of the latter method is that the detection of the end-point of the titration (a strong acid and a strong base) is **easier** than that for the ammonium borate and hydrochloric acid titration.

Kjeldahl method is a titration method for the determination of nitrogen in organic compounds in which the nitrogen is converted to ammonia, which is then distilled and determined by a neutralization titration.

4- Chromatography

A myriad of techniques used to separate complex samples come under the general heading of chromatography. The nature of chromatography allows much more versatility, speed, and applicability than any of the other techniques.

Chromatography is the separation of the components of a mixture based on the different degrees to which they interact with two separate material phases. One of the two phases is a moving phase (**the mobile phase**), while the other does not move (**the stationary phase**). **The mobile**

phase can be either a **gas** or a **liquid**, while the **stationary phase** can be either a **liquid** or **solid**.

Mobile phase is a liquid or gas that carries analytes through a liquid or solid stationary phase.

Stationary phase is a solid or immobilized liquid in chromatography upon which analyte species are partitioned during passage of a mobile phase.

The two principal types of chromatography are

1- Gas Chromatography (GC) **2-** Liquid Chromatography (LC)

- GC separates gaseous substances based on adsorption on or partitioning in a stationary phase from a gas phase.
- LC includes high-performance liquid chromatography (HPLC) which separates liquid substances based on adsorption on or partitioning in a stationary phase from a liquid phase.
- GC and HPLC are the **most widely used forms** of chromatography.

Classification of chromatography methods is based on the nature of the two phases:

1- Gas-Liquid Chromatography (GLC)

The mobile phase is a gas and stationary phase is a liquid.

2- Gas-Solid Chromatography (GSC)

The mobile phase is a gas and stationary phase is a solid.

3- Liquid-Liquid Chromatography (LLC)

The mobile phase is a liquid and stationary phase is a liquid.

4- Liquid-Solid Chromatography (LSC)

The mobile phase is a liquid and stationary phase is a solid.

Gas Chromatography

Most gas chromatography procedures utilize a liquid stationary phase, or GLC.

Gas chromatography is a chromatographic technique that can be used to separate volatile organic compounds. A gas chromatography consists of a flowing mobile phase, an injection port, a separation column containing the stationary phase, and a detector. The organic compounds are separated due to differences in their partitioning behavior between the mobile gas phase and the stationary phase in the column.

GC instruments (Fig. 11) consist of:

1- **Mobile phases** are generally inert gases such as helium, argon, or nitrogen.

2- The **injection port** consists of a rubber septum through which a syringe needle is inserted to inject the sample. The injection port is maintained at a higher temperature than the boiling point of the least volatile component in the sample mixture. Since the partitioning behavior is dependant on temperature.

3- The **separation column** is usually contained in **a thermostat-controlled oven**. Separating components with a wide range of boiling points is accomplished by starting at a low oven temperature and increasing the temperature over time to elute the high-boiling point components. Most columns contain a liquid stationary phase on a solid support. Separation of low-molecular weight gases is accomplished with solid adsorbents.

4- Detector is designed to generate an electronic signal when a gas other than the carrier gas elutes from the column.

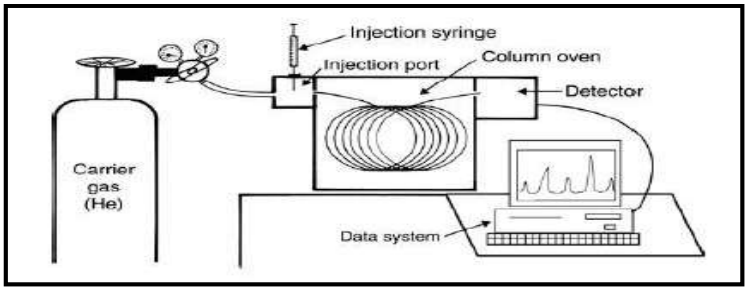

Figure 11

A drawing of a gas chromatography instrument components

High-Performance Liquid Chromatography (HPLC)

HPLC is a form of liquid chromatography to separate compounds that are dissolved in solution. A variation of liquid chromatography that utilizes high-pressure pumps to increase the efficiency of the separation.

HPLC is column chromatography in which the stationary phase is made up of small particles and the mobile phase is forced through the particles by high pressure.

HPLC instruments (Fig. 12) consist of:

1- Reservoir of mobile phase **2-** Pump **3-** Injector

4- Separation column **5-** Detector

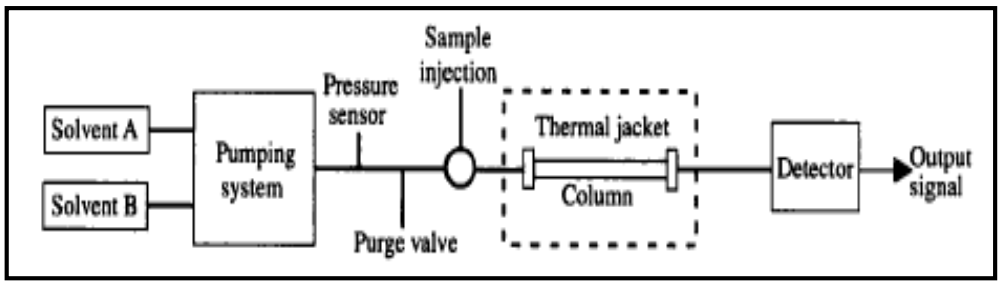

Figure 12

Schematic representation of a basic HPLC system

- Compounds are separated by injecting a plug of the sample mixture into the column.
- The different components in the mixture pass through the column at **different rates** due to differences in their partitioning behavior between the mobile liquid phase and the stationary phase.
- Solvents must be degassed to eliminate formation of bubbles.
- The pumps provide a **steady high pressure** with no pulsating, and can be programmed to vary the composition of the solvent during the course of the separation.
- Detectors rely on a change in refractive index, UV-VIS absorption, or fluorescence after excitation with a suitable wavelength.