Analytical Chemistry

Table -1 Fundamental SI Units

Measurement	Unit	Symbol
Mass	kilogram	kg
Volume	liter	L
Distance	mete	m
Temperature	kelvin	K
Time	second	s
Current	ampere	A
Amount of substance	mole	mol

Table- 2 Other SI and Non-SI Units

Measurement	Unit	Symbol	Equivalent SI units
Length	Angstrom	Å	1 Å = 1 ´ 10^{-10} m
Force	Newton	N	1 N = 1 m ×kg/s^2
pressure	Pascal	Pa	1 Pa = 1 N/m^2 = 1 kg/(m ×s^2)
	Atmosphere	atm	1 atm = 101,325 Pa
energy, work, heat	Joule	J	1 J = 1 N ×m = 1 m^2 ×kg/s^2
power	Watt	W	1 W = 1 J/s = 1 m^2 ×kg/s^3
charge	Coulomb	C	1 C = 1 A ×s
potential	Volt	V	1 V = 1 W/A = 1 m^2 ×kg/(s^3.A)
temperature	Degree Celsius	°C	°C = K – 273.15
	Degree Fahrenheit	°F	°F = 1.8(K – 273.15) + 32

Table- 3 Common Prefixes for Exponential Notation

Exponential	Prefix	Symbol
10^{12}	tera	T
10^{9}	giga	G
10^{6}	mega	M
10^{3}	kilo	k
10^{-1}	deci	d
10^{-2}	centi	c
10^{-3}	milli	m
10^{-6}	micro	m
10^{-9}	nano	n
10^{-12}	pico	p
10^{-15}	femto	f
10^{-18}	atto	a

Periodic Table

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Uuq	115 Uup	116 Uuh	117 Uus	118 Uuo

* لانثنيدات	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu		
** أكتينيدات	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr		

Analytical Chemistry

Qualitative Analysis :
analysis that gives an identification of various substance in the sample. i.e. identification of various elements that make up the sample. Ex.
To identify Ag^{+1} ion, Add Cl^{-1} ion ,AgCl white precipitate indicate the presence of Ag

Quantitative Analysis : Deals with the determination of the amount of various substance in the sample

Methods of Analysis :-

1- Volumetric Analysis : التحليل الحجمي

the amount of substance present is measured indirectly by determining the volume of the solution of known strength which is required to react with the sample.

Ex. Titration the processes Acid – Base titration of a solution of an acid with a solution of base used. The amount of acid is competed from the volume of base used.

2- Gravimetric Analysis: التحليل الوزني

the substance isolated as precipitant and the amount of substance is calculated from the weight of precipitant

Ex A weight of Ag+ (amount) is calculated from the weight of AgCl

3- Instrumental methods of Analysis :التحليل الالي

instrument used to measure certain properties which are related to the amount of substance in the sample Ex 1 - spectrophotometry methods

2 - Gas chromatography

Analytical Chemistry

Reaction of the metals ions or cations

Analytical classification of metals ions:

The common metallic ions divided for the purpose of qualitative analysis into a number of groups which are distinguished by the fact that ***the metals of any group are precipitated by particular group reagent***

group	Group reagent	Ions	Formula of precipitate	Distinguished feature
I Silver group	Dil. HCl	Ag^{+1}, Pb^{+2},Hg^{+2}	AgCl,PbCl,$HgCl_2$	Chlorides insoluble in cold HCl(dil.)
II A copper group	H_2S in presence of Dil. HCl	Hg^{+2},Pb^{+2},Bi^{+3},Cu^{+2} Sn^{+3},As^{+3},Sb^{+3},Sn^{+4}	HgS,PbS,Bi_2S_3,CuS,As_2S_3 Sb_2S_3,SnS_3	Sulfides insoluble in HCl (dil.)
III A Iron group	Aqueous NH_3 in presence NH_4Cl	Al+3,Cr+3,Fe+3	$Al(oH)_3$, $Cr(oH)_3$, $Fe(oH)_3$	Hydroxide Precipitated by aqueous NH_3
III B Zinc group	H_2S in presence of Aq. NH_3&NH_4Cl	Ni^{+2},Co^{+2},Mn^{+2},Zn^{+2}	NiS,CoS,MnS,ZnS	Sulfides Precipitated by H_2S in presence of Aq. NH_3&NH_4Cl
IV Calcium group	$(NH_4)_2CO_3$ in presence of Aq. NH_3&NH_4Cl	Ba^{+2},Sr^{+2},Ca^{+2}	BaCo3 , SrCO3 , CaCO3	Carbonate Precipitated by $(NH_4)_2CO_3$ in presence of Aq. NH_3&NH_4Cl
V Alkali group	No Particular reagent	Mg^{+2},Na^{+1},K^{+1},NH_4^+	Mg^{+2},Na^{+1},K^{+1},NH_4^+	Ions not precipitated in previous groups

The Silver group (group I)

(lead ,Mercury(ous) and Silver)

Compounds of these elements are characterized by their precipitation as chlorides by diluted HCl

$PbCl_2$: Slightly soluble in water, is not completely precipitated as chloride in this group, it is found in group II as PbS

Lead Pb:-

- bluish gray metal
- readily dissolved in dilute HNO_3

$$3Pb + 8\,HNO_3 \longrightarrow 3Pb(NO_3)_2 + 2NO + 4H_2O$$

-With concentrated HNO_3 , protective film of lead nitrate which is insoluble in this acid, prevent complete solute in.

-Dilute HCl and H_2SO_4 : have a little (effect) or action owing to the formation of a protective film of $PbCl_2$ and $PbSO_4$

Reaction of lead ion (Pb^{+2}) :-

- With dilute HCl :

$$Pb(NO_3)_2 + 2HCl \longrightarrow PbCl_2 + 2HNO_3$$

White ppt.

$$PbCl_2 \xrightarrow{\text{(water Soluble in hot)}} \text{Cold (separate out again in needle)}$$

$$PbCl_2 + HCl \longrightarrow H(PbCl_3)$$

Conc. Complex compound

- With Dilute H_2SO_4 :

$$Pb(NO_3)_2 + H_2SO_4 \longrightarrow PbSO_4 + 2HNO_3$$

White ppt.

$$Pb\,SO_4 + 2NH_4\,CH_3\,COOH \longrightarrow Pb(C_2\,H_3\,O_2)_2 + (NH4)_2\,SO_4$$

ammonium acetate lead acetate

- With potassium chromate solution:

$$Pb(NO_3)_2 + K_2CrO_4 \longrightarrow PbCrO_4 + 2KNO_3$$

Yellow ppt.

Detection and Separation of group(1):-

(Silver group) to a given Solution add a diluted HCl (in excess)

filtrate

Residue (ppt.)
AgCl,HgCl2,PbCl2,
Wash with little very dill. Acid

filtrate may
contains other groups
Discharge

Boil with 5-10 ml of water

filtrate

filtrate

residue

filtrate may contain $PbCl_2$

Residue may contain Hg_2Cl_2 , AgCl
ppt. is wash with hot water

filtrate no ppt. with K_2CrO_4
(i.e.) complete removal of $PbCl_2$.
pour 3_4 ml of dil. NH_3

over the ppt.

filtrate

1-Add little ammonium
acetate solution + K_2CrO_4

yellow ppt.
2- cool under tap water
white crystalline ppt. of $PbCl_2$
(Pb is present)

Residue black

$Hg_2Cl_2 + 2NH_3 \longrightarrow Hg(NH_2)Cl + Hg$

Amino mercuric chloride

Hg^{+2} is present

Filtrate

$Ag(NH_3)_2Cl$

↓ dil. HNO3

white ppt.

$Ag\,Cl + NH_3 \longrightarrow Ag(NH_3)_2Cl$

Amino silver chloride

$Ag(NH3)2Cl + HNO3 \xrightarrow[\text{dil.}]{} AgCl$ (White ppt.)

Ag^{+1} is present

The Copper and Arsenic group (II)

Mercury(ic) ,lead , Bismuth ,Cupper, Cadmium, Arsenic ,Antimony and Tin.

Compound of these elements are characterized by their ppt. as sulphides by H_2S from 0.3N HCL

Group II

Copper group
Hg ,Pb ,Bi ,Cu ,Cd
Insoluble in (NH4)S And NaOH

II B
As ,sb ,Sn
Soluble in $(NH_4)S$ and NaOH

The copper Cu : -

- copper is light red metal .
- Soft ,malleable + ductile .
- Unaffected by dil. HCl and H_2SO_4 .

$$Cu + 2H_2SO_4 \xrightarrow{\text{warm,conc.}} CuSO_4 + SO_2 + 2H_2O$$

- Readily attracted by HNO_3

$$3Cu + 8\,HNO_3 \xrightarrow{\text{dil.}} 3Cu(NO_3)_2 + 4H_2O + 2NO$$

Reaction of the cupric ion Cu^{+2}

1- With H_2S :-

$$CuSO_4 + H_2S \longrightarrow \underset{\text{black ppt.}}{CuS} + H_2SO_4$$

$$3CuS + 8\,HNO_3 \xrightarrow[\text{Hot dil.}]{} 3Cu(NO_3)_2 + 4H_2O + 2NO + 3S$$

2- With NaOH :-

$$CuSO_4 + NaOH \longrightarrow \underset{\text{Cupric hydroxide blue ppt.}}{Cu(OH)_2} + Na_2SO_4$$

$$\underset{\text{Blue ppt.}}{Cu(OH)_2} \xrightarrow{\text{boiling}} Cu\,O + H_2O \quad (\text{black})$$

3- With potassium Ferrocyanide :-

$$3CuSO_4 + K_4[Fe(CN)_6] \longrightarrow \underset{\text{Reddish - brown ppt.}}{Cu_2[Fe(CN)6]} + 2K_2SO_4$$

The Tin (Sn) :-

_ Tin : silver white metal .

_ Malleable and ductile at ordinary temperature .

_ Metal dissolves slowly in dill HCl and dill. H_2SO_4 with the liberation of H_2 and formation of stannous salts .

$$Sn + \underset{\text{dill}}{2HCL} \longrightarrow SnCl_2 + H_2$$

$$Sn + H_2SO_4 \longrightarrow SnSO_4 + H_2$$

Readily dissolved by hot concentrated acids

$$Sn + HCl \xrightarrow{\text{Conc.}} SnCl_2 + H_2$$

$$\underset{\text{Readily dissolve}}{Sn} + \underset{\text{conic}}{4H_2SO_4} \longrightarrow Sn(SO_4)_2 + 2SO_2 + 4H_2O$$

$$4Sn + 10HNO_3\ (dill) \longrightarrow 4Sn(NO_3)_2 + NH_4NO_3 + H_2O$$

Dissolve slowly

No gas in last reaction

Reactions of stannous compound

With H_2S :

$$SnCl_2 + H_2S \longrightarrow SnS + 2HCL$$

Brown ppt.

stannous sulphides

With NaOH

$$SnCl_2 + 2NaOH \longrightarrow Sn(OH)_2 + 2NaCl$$

White ppt.

Stannous hydroxide

With HgCl2 mercuric chloride:

$$SnCl_2 + 2HgCl_2 \longrightarrow SnCl_4 + Hg_2Cl_2$$

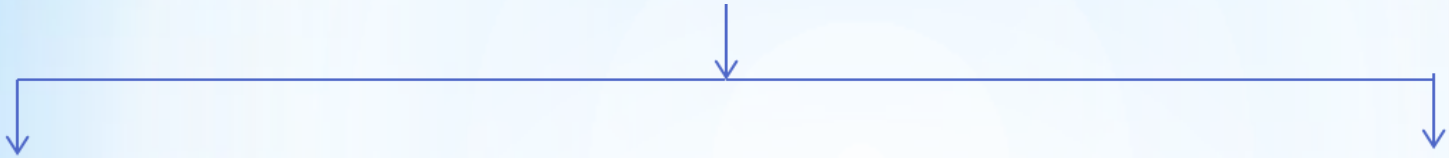
white ppt.

mercurous chloride

The Iron and Zinc group (group III)

Iron ,aluminum ,chromium ,nickel ,cobalt, manganese and zinc .

All ppt. in presence of NH_4Cl



Group(III)A (Iron) :-
Fe ,Al ,Cr ppt. as
Hydroxide by NH_3 Sol.
+ NH_4

Group(III)B(Zinc)
Ni,Co,Mn,Zn
remain in Sol. And may
be pp.t by H2S as sulphides

Iron group : Iron (Fe):-

_ Pure iron : is silver white .

_ Ductile and tenacious metal .

- $Fe + 2HCl \longrightarrow FeCl_2 + H_2$

  Dill and conic

- $Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$

  dissolve with H_2

$2Fe + 6H_2SO_4$ (hot and conc.) $\longrightarrow Fe_2(SO_4)_3 + 6H_2O + 3SO_2$

$4Fe + 10HNO_3$ (cold and dill) $\longrightarrow 4Fe(NO_3)_2 + NH_4NO_3 + 3H_2O$

$4Fe + 10HNO_3$ (warm and dill) $\longrightarrow 4Fe(NO_3)_2 + N_2O + 5H_2O$

Volumetric Analysis (Titrimetric Analysis)

Calculation involving concentration of solution

Measurements usually consist of a unit and a number expressing the quantity of that unit. Many different units may be used to express the same physical measurement. For example, the mass of a sample weighing 1.5 g also may be expressed as 0.0033 lb.

Concentration is a general measurement unit stating the amount of solute present in a known amount of solution

$$\text{Concentration} = \frac{\boldsymbol{amount\ of\ solute}}{\boldsymbol{amount\ of\ solution}}$$

Although the terms “solute” and “solution” are often associated with liquid samples they can be extended to gas-phase and solid-phase samples as well.

Solution : - Homogenous mixture of one or more components in one phase.

The concentration of solution is expressed by:

1- Physical methods

2 - Chemical methods

Physical methods:-

Gram of solute / liter or(100 ml) of solution

1. **Gram of solute / liter or(100 ml) of solvent**
2. **Gram of solute / 1000 gm or (1Kg) or(100 gm) of solution**
3. **Gram of solute / 1000 gm or (1Kg) or(100 gm) of solvent**

1. **Percentage methods:**

a - Weight percent (٪wt) = $\frac{weight\ of\ solute}{weight\ of\ solution}$ X 100

b- Volume percent (٪vol) = $\frac{volume\ of\ solute}{volume\ of\ solution}$ **X 100**

c- Weight / volume percent (٪) = $\frac{weight\ of\ solute}{volume\ of\ solution}$ **X 100**

Chemical Methods:-

Molar Solution :- a solution that contains 1 mole of solute per liter of solution

1- Molarity : number of moles of solute per liter of solution

$$M = \frac{no.of\ moles}{liter\ of\ solution}$$

No. of moles = M x Liter of solution

2- Molal Solution:- A solution that contains one mole of solute per 1 kilograms of solvent.

$$m = \frac{no.of\ mole\ of\ solute}{1\ Kg\ of\ solvent}$$

3-Formal Solution:-

A solution that contain one formula weight of solute per liter of solution .

$$F = \frac{weight}{Fwt} X \frac{1}{liter\ of\ solvent}$$

4-Equivalent methods

A) Equivalent weight of atoms of element :

$$\text{Eq. wt} = = \frac{atomic\ weight}{\text{valency}}$$

A) Equivalent weight of compounds:

1. **Equivalent weight of Acids**;

   Equivalent weight of acid which contains one replaceable hydrogen

$$\text{Eq .wt of acid} = \frac{molecular\ weight}{\text{no.of hydrogen atom}}$$

2 Equivalent weight of a base;

Equivalent weight of base which contains one replaceable hydroxyl group

$$\text{Eq .wt of a base} = \frac{\boldsymbol{molecular\ weight}}{\text{no.of hydroxyl groups}}$$

3 Equivalent weight of a salt;

Equivalent weight of a salt in grams which contains one weight of cat ion can react or replaced by one gram of hydrogen

4 Equivalent weight of Reducing and Oxidizing agent

$$\text{Eq .wt. of reducing agent} = \frac{\boldsymbol{molecular\ weight}}{\text{no.of electrons losses in the reaction}}$$

$$\text{Eq .wt of oxidizing agent} = \frac{\boldsymbol{molecular\ weight}}{\text{no.of electrons gains in the reaction}}$$

5 Normal solution;

A solution that is contains one equivalent of solute per liter solution.

Normality= (no. of equivalent of solute)/(liter of solution)

Normality=(wt.)/(eq.wt.) X(1)/(liter of solution)

Part per million (PPM):

$$\text{ppm} = \frac{\textit{mili grams of solute}}{\text{liter of solution}}$$

millequivalents and mllimoles:

It is convenient to select the unite of concentration by the amount of solute per milliliter of solution; the molar solution is then defined as one containing 0.001 moles per milliliter of solution. Likewise a normal solution is one that contains 0.001 equivalent, or millequivalents per liter

Dilution of solution:

A solution of known normality is frequently prepared from a more concentrated one of known strength by quantitative dilution.

(Normality * volume) $_{conc}$ =(Normality * volume)$_{dilute}$

$$(N * V)_{conc} = (N * V)_{dil}$$

Primary standard:

In volumetric analysisthe usual practice is to prepare solutions of approximate desired strength and then determine the exact strength by titration against a solid primary standard. The primary standard must be :

1. Of high purity 99.99%
2. Of high equivalent weight
3. Stability on drying
4. Of definite chemical formula
5. Has no affinity for water vapor or CO_2

Type of the chemical in titration process:

1. Neutralization methods

- Neutralization of H^+ with OH^- $\longrightarrow$ H_2O
- Widely used as basis and volumetric determination of acids , bases and salt of weak acids
- The reaction is characterized by a rapid change in pH near the equivalence point.
- The change in pH is detected by the :

a. Acid base indicator
b. By followed electrically pH- meter

Neutralization method:-
Acidimetry , acid is standard
Alkalimetry , base is standard

2 Oxidation – Reduction methods

Reaction in which there is change in oxidation state of two substances in the reaction.

ex.

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

The two reaction occur simultaneously n general :

$KMnO_4$ = strong oxidizing agent

H_3AsO_3 strong reducing agent

$Na_2S_2O_3$ =specific reagent for I_2

3 Precipitation Titrations

There is change in the concentration of the ions of the precipitate at the equivalence point.

*the conditions are usually adjusted that only one precipitation is formed at the equivalence poin**t.**

4 Complex ion titration

Depend on the formation of complex between the sample and titrating reagent

Ex. Determination of hardness of water i.e. determination of Mg and Ca ions in water.

Calculation in titrimetric analysis

a) calculation based on normality of solution

b) calculation based on molarity of solution :

Back titration:

To calculate a substance like (B) A + B product + Excess A

Excess A +C ⟶ Product

Back titration term of nolmalty

meqB =[(N_A*V_A) - (V_C*N_C)] eq. wt_B

Back titration term of molarity

aA + bB = product + excess A $R_1 = \frac{b \quad \text{un known}}{a \quad \text{known}}$

cC + dA(excess)= product $R_2 = \frac{d}{c}$

m g B =[(M_A*V_A)-(V_C*M_C * R_2)] R_1 M. wt_B

Equilibrium constant

Chemical reaction at equilibrium when Forward reaction = backward reaction

For the relation

aA + bB = cC + dD

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

K_e= equilibrium constant

[c],[D]=moles conc. of products.

[A],[B]= moles conc. of reactant

A,b,c.d, coefficient of A,B,C,D

Ionization of acid:-

Ionization constant of weak electrolytes:-

- **Salt of strong acid and strong Base :-**

Since neither ion can combine with an ion of water to form a weak electrolyte the pH is 7.0

PH of solution of weak electrolytes

- ***Weak Acid*** **:(In absence of its salts):-.**
- ***Weak Base*** **(in absence of its salts) :-**
- **Weak acid plus its salt**
- **Weak base plus its salt**
- **Salt of weak acid and strong base**
- **Salt of weak base and strong acid**

Titration curves: -

: graphs of PH versus volume of reagent added in titration are known as titration curves

PH may be obtained by:

1-Calculation

2-PH-meter

- **Titration curve of strong acid and strong base**

- **Titration curve of strong bas at weak acid**

Acid-Base Indicators:-

Acid-Base Indicators are highly colored organic dyes which exhibit change in colure when the PH of the solution changes between certain limits

Indicators : -

Mono colored
e.g ph.ph
Phenolphthalein

Di colored
M.O
Methyl organic

Equilibrium in precipitation reaction

- **Solubility product: -**
- **Evolution of k_{sp} value from experimental measurements**
- **Computation of solubility from ksp**
- **Effect of common ion on solubility**
- **Titration curve for precipitation reaction**

Quantitative gravimetric analysis:- التحليل الكمي الوزني depends on the actual weight of the substance or its derivatives methods:

- Precipitation methods
- Volatilization methods

Gravimetric Factor

$$\textbf{G.F} = \frac{equivelent\ weight\ \ of\ unknown\ substance}{equivelent\ weight\ \ of\ known\ substance}$$

$$\textbf{\% substance A} = \frac{G.F\ *\ wt.of\ substance\ B}{wt.of\ sample} \textbf{*100}$$