विघ्न विचारत भीरु जन, नहीं आरम्भे काम,   विपति देख छोड़े तुरंत मध्यम मन कर श्याम।
पुरुष सिंह संकल्प कर, सहते विपति अनेक,   'बना' न छोड़े ध्येय को, रघुबर राखे टेक।।

रचितः मानव धर्म प्रणेता
सद्गुरु श्री रणछोड़दासजी महाराज

STUDY PACKAGE
This is TYPE 1 Package please wait for Type 2

Subject : CHEMISTRY
Topic : STOICHIOMETRY
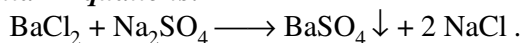
Teko® CLASSES

.....the support
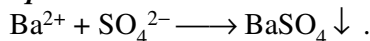
Student's Name :_____

Class :_____

Roll No. :_____

ADDRESS: R-1, Opp. Raiway Track,
New Corner Glass Building, Zone-2, M.P. NAGAR, Bhopal
☎ : (0755) 32 00 000,   98930 58881,   www.tekoclasses.com

OXIDATION & REDUCTION

Molecular Equations:

$$BaCl_2 + Na_2SO_4 \longrightarrow BaSO_4 \downarrow + 2\,NaCl\,.$$

Ionic Equations :

$$Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4 \downarrow\,.$$

Spectator Ions :

Ions which do not undergo change during a reaction , they are not included in the final balanced equation .

Rules For Writing Ionic Equations :

(i) All soluble electrolytes involved in a chemical change are expresses in ionic symbols and covalent substances are written in molecular form .

(ii) The electrolyte which is highly insoluble , is expressed in molecular form .

(iii) The ions which are common and equal in number on both sides (spectator ions) are cancelled .

(iv) Besides the atoms , the ionic charges must also balance on both the sides .

Valency :

Valency of an element is defined as the number of hydrogen atoms that combine with or are displaced by one atom of the element . Cl, monovalent; O, divalent; N, trivalent; tetravalent C; variable valency P (3 , 5). It is never a useful concept despite of physical reality, so more common & artificial concept is oxidation state (oxidation number) .

Oxidation Number :

It is the charge (real or imaginary) which an atom appears to have when it is in combination. It may be a whole no. or fractional. For an element may have different values. It depends on nature of compound in which it is present. There are some operational rules to determine oxidation number.

Stock's Notation :

Generally used for naming compounds of metals , some non-metals also. eg. Cr_2O_3 Chromium (III) oxide and P_2O_5 Phosphorous (V) oxide .

Oxidation :

Addition of oxygen , removal of hydrogen , addition of electro-negative element , removal of electro-positive element, loss of electrons, increase in oxidation number (de-electronation) .

Reduction :

Removal of oxygen, addition of hydrogen, removal of electronegative element, addition of electro-positive element, gain of electrons, decrease in oxid. no. (electronation).

Redox Reactions :   A reaction in which oxidation & reduction occur simultaneously .

Oxidising Agents (oxidants / oxidisors):

They oxidise others, themselves are reduced & gain electrons. eg. O_2, O_3, HNO_3, MnO_2, H_2O_2, halogens, $KMnO_4$, $K_2Cr_2O_7$, KIO_3, $Cl(SO_4)_3$, $FeCl_3$, $NaOCl$, hydrogen ions.
[Atoms present in their higher oxidation state.]

Reducing Agents (reductants / reducers):

They reduce others, themselves get oxidised & lose electrons. H_2, molecule is weak but Nascent hydrogen is powerful . C, CO, H_2S, SO_2, $SnCl_2$, Sodium thio Sulphate, Al, Na, CaH_2, $NaBH_4$, $LiAlH_4$
[Atoms present in their lower oxidation state].

Both Oxidising & Reducing Agents : SO_2 , H_2O_2 , O_3 , NO_2 , etc .

Balancing Of Equations :

(i) Ion-electron method **(ii)** Oxidation number method

[Concept involved that in any chemical reaction electrons cannot be produced so no. of electrons in both the sides should be same]

Oxidation Half Reaction : $\qquad$ $Na \longrightarrow Na^+ + e^-$.

*Reduction Half Reaction :* $\qquad$ $F_2 + 2e^- \longrightarrow 2\,F^-$.

COMMON OXIDATION AND REDUCTION PARTS

OXIDATION PARTS	REDUCTION PARTS
$Fe^{2+} \longrightarrow Fe^{3+}$	$Fe^{3+} \longrightarrow Fe^{2+}$
$Zn \longrightarrow Zn^{2+}$	
$X^- \longrightarrow X_2$	$X_2 \longrightarrow X^-$
$S^{2-} \longrightarrow S$	$Cr_2O_7^{2-} \longrightarrow Cr^{3+}$
$H_2O_2 \longrightarrow O_2$	$NO_3^- \longrightarrow NO$
$SO_3^{2-} \longrightarrow SO_4^{2-}$	$MnO_4^- \longrightarrow Mn^{2+}$ (neutral med.)
$C_2O_4^{2-} \longrightarrow CO_2$	$MnO_4^- \longrightarrow MnO_2$ (Basic med.)
$S_2O_3^{2-} \longrightarrow S_4O_6^{2-}$	$SO_4^{2-} \longrightarrow SO_2$
$I_2 \longrightarrow IO_3^-$	$MnO_2 \longrightarrow Mn^{2+}$

Types Of Redox Reduction :

Intermolecular redox, disproportion, Intra molecular redox .

Disproportion:

In such reactions the oxidising and reducing agents(atom) are the same .

$$\underset{\text{reduction}}{\overset{\text{oxidation}}{H_2O_2 + H_2O_2 \longrightarrow 2\,H_2O + O_2}}$$.
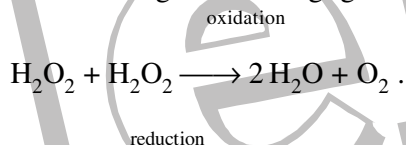
To identify whether a reaction is redox or not , find change in oxidation number or loss and gain of electrons. If there is no change in oxidation number , the reaction is not a redox reaction .

NOTE : To predict the product of reaction remember :

(a) Free halogen on reduction gives halide ion $(F_2 \rightarrow F^-)$

(b) Alkali metals on oxidation give metallic ion with + 1 oxidation state.

(c) Conc. HNO_3 on reduction gives NO_2 , while dilute HNO_3 can give NO, N_2, NH_4^+ or other products depending on the nature of reducing agent and on dilution.

(d) In acid solution $KMnO_4$ is reduced to Mn^{2+} while in neutral or alkaline , it gives MnO_2 or K_2MnO_4 .

(e) H_2O_2 on reduction gives water and on oxidation gives oxygen.

(f) Dichromate ion in acid solution is reduced to Cr^{3+} .

Nature of oxides based on oxidation number :

Lowest oxidation state	$\longrightarrow$	Basic	(MnO)
Intermediate oxidation state	$\longrightarrow$	Amphoteric	(Mn_3O_4 , MnO_2)
Highest oxidation state	$\longrightarrow$	Acidic	(Mn_2O_7)

Metathesis Reactions :

Never redox reactions . In these two compounds react to form two new compounds and no change in oxidation number occur . eg.

(i) $Pb\,(NO_3)_2 + K_2CrO_4 \longrightarrow Pb\,CrO_4 + 2\,KNO_3$ $\quad$ (ii) $HCl + NaOH \longrightarrow NaCl + H_2O$
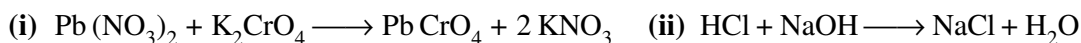
Rules For Assigning Oxidation Number :
(i)   Oxidation number of free elements or atoms is zero .
(ii) Oxidation number of allotropes is zero .
(iii) Oxidation number of atoms in homo-nuclear molecules is zero .
(iv) Oxidation number of mono-atomic ions is equal to the algebric charge on them .
(v)   Oxidation number of F in compounds is - 1 .
(vi) Oxidation number of H in its compounds is + 1 , except in metalhydrides where it is - 1 .
(vii) Oxidation number of O is - 2 in its compounds , but in F_2O it is + 2 and in peroxides it is - 1 and - 0.5 in KO_2 .
(viii) Oxidation number of alkali metals in their compounds + 1 .
(ix) Oxidation number of alkaline earth metals in their compounds is + 2 .
(x)   Oxidation number of an ion is equal to its charge .
(xi) Oxidation number of a molecule as a whole is zero .
(xii) The sum of oxidation number of all the atoms in a molecule should be zero and in an ion equal to its charge .

Average Oxidation Number : Find Oxidation Number of Fe in Fe_3O_4

Fe_3O_4 is FeO. Fe_2O_3.

O. N. of Fe in FeO is + 2   ;   O. N. of Fe in Fe_2O_3 is + 3 .

Therefore average O. N. of three Fe atoms $= \dfrac{+2+2 \times (+3)}{3} = +\dfrac{8}{3}$.

EQUIVALENT CONCEPT

(A) Volumetric analysis: This mainly involve titrations based chemistry. It can be divided into two major category.   (I) Non-redox system   (II) Redox system
(I) Non – redox system: This involve following kind of titrations:
1.   Acid-Base titrations
2.   Back titration
3.   Precipitation titration
4.   Double indicator acid base titration

Titrimetric Method of Analysis : A titrimetric method of analysis is based on chemical reaction such as.

$$aA + tT \longrightarrow Product$$

Where 'a' molecules of "analysis", A, reacts with t molecules of reagent T.
T is called Titrant normally taken in buret in form of solution of known concentration. The solution of titrant is called "standard solution".

The addition of titrant is added till the amount of T, chemically equivalent to that of 'A' has been added. It is said equivalent point of titration has been reached. In order to know when to stop addition of titrant, a chemical substance is used called indicator, which respond to appearance of excess of titrant by changing colour precisely at the equivalence point. The point in the titration where the indicator changes colour is termed the 'end point'. It is possible that end point be as close as possible to the equivalence point.

The term titration refer's to process of measuring the volume of titrant required to reach the end point. For many years the term volumetric analysis was used rather than titrimetric analysis. However from a rigorons stand point the term titrimetric is preferable because volume measurement may not be confirmed to titration. In certain analysis, for example one might measure the volume of a gas.
We can adopt mole method in balanced chemical reactions to relate reactant and products but it is more easier to apply law of equivalents in volumetric calculations because it does not require knowledge of balanced chemical reactions involved in sequence.

Law of equivalents refers to that, equivalents of a limiting reactant is equal to equivalent of other reactant reacting in a chemical reaction or equal to equivalents of products formed. *n* factor here we mean a conversion factor by which we divide molar mass of substance to get equivalent mass and it depends on nature of substance which vary from one condition to another condition.

We can divide n-factor calculations in two category.

(A) when compound is not reacting.

(B) when compound is reacting.

Acid-Base titration

To find out strength or concentration of unknown acid or base it is titrated against base or acid of known strength. At the equivalence point we can know amount of acid or base used and then with the help of law of equivalents we can find strength of unknown.

Meq of acid at equivalence point = Meq of base at equivalence point

Back titration

Back titration is used in volumetric analysis to find out excess of reagent added by titrating it with suitable reagent. It is also used to find out percentage purity of sample. For example in acid-base titration suppose we have added excess base in acid mixture. To find excess base we can titrate the solution with another acid of known strength.

Precipitation titration :

In ionic reaction we can know strength of unknown solution of salt by titrating it against a reagent with which it can form precipitate. For example NaCl strength can be known by titrating it against $AgNO_3$ solution with which it form white ppt. of AgCl.

Meq. of NaCl at equivalence point = meq of $AgNO_3$ used = meq of AgCl formed

Double indicator acid-base titration:

In the acid-base titration the equivalence point is known with the help of indicator which changes its colour at the end point. In the titration of polyacidic base or polybasic acid there are more than one end point for each step neutralization. Sometimes one indicator is not able to give colour change at every end point. So to find out end point we have to use more than one indicator. For example in the titration of Na_2CO_3 against HCl there are two end points.

$$Na_2CO_3 + HCl \longrightarrow NaHCO_3 + NaCl$$

$$NaHCO_3 + HCl \longrightarrow H_2CO_3 + NaCl$$
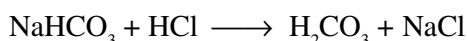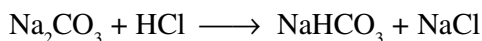
When we use phenophthalein in the above titration it changes its colour at first end point when $NaHCO_3$ is formed and with it we can not know second end point. Similarly with methyl orange it changes its colour at second end point only and we can not know first end point. It is because all indicator changes colour on the basis of pH of medium. So in titration of $NaHCO_3$, $KHCO_3$ against acid phenolphthalein can not be used.

So we can write with phenolpthalein, if total meq of $Na_2CO_3 = 1$ then

½ meq of Na_2CO_3 = meq of HCl

with methyl orange,

meq of Na_2CO_3 = meq of HCl

n-factor in non-redox system

Titration	Indicator	pH Range	n factor
Na_2CO_3 against acid	Phenolphthalein	8.3 – 10	1
K_2CO_3	Methyl orange	3.1 – 4.4	2

of products formed in reaction.

Note: When we carry out dilution of solution, meq eq, milli mole or mole of substance does not change because they represent amount of substance, however molar concentration may change.

Solubilities of some important salt's :

1. **Chloride :**
   $AgCl$ – White ppt.
   Hg_2Cl_2 – White ppt.   All other chlorides are soluble in water.
   $PbCl_2$ – White ppt.
   $CuCl$ – Insolution ppt.
   $BiOCl$ – White ppt.
   $SbOCl$ – White ppt.
   Hg_2OCl_2 – White ppt.

2. **Bromide :**
   $AgBr$ – Pate yellow ppt.
   $PbBr_2$ – White ppt.   All other bromides are soluble in water
   Hg_2Br_2 – White ppt.
   $CuBr$ – White ppt.

3. **Iodide :**
   AgI – Yellow ppt.
   PbI_2 – Yellow ppt.
   Hg_2I_2 – Green ppt.
   HgI_2 – Red ppt.
   CuI – White ppt.
   BI_3 – Black ppt.

4. **Some important oxides and hydroxises :**
   Ag_2O – Brown ppt.
   $Pb(OH)_2$ – White ppt.
   $Pb(OH)_4$ – White ppt.
   Hg_2O – Black ppt.
   HgO – Yellow ppt.
   Cu_2O – Red ppt.
   CuO – Black ppt.
   $Cu(OH)_2$ – Blue ppt.
   $Cd(OH)_2$ – White ppt.
   $Fe(OH)_2$ – White ppt.
   $Fe(OH)_3$ – Red ppt.
   $Sn(OH)_2$ – White ppt.
   $Sn(OH)_4$ – White ppt.
   $Al(OH)_3$ – White gelatenons
   $Cr(OH)_3$ – Grey-Green
   $Co(OH)_2$ – Pink
   $Co(OH)_3$ – Brownish black
   $Ni(OH)_2$ – Green
   $Ni(OH)_3$ – Black
   $Mn(OH)_2$ – White
   $MnO(OH)_2$ – Brown

$Zn(OH)_2$ – White
$Mg(OH)_2$ – White

Carbonates :   Except Alkali metals and NH_4^+ all other carbonates are insoluble.

$Ag_2CO_3 \longrightarrow$ White ppt. $\longrightarrow Ag_2O + CO_2$
$3HgO.HgCO_3 \longrightarrow$ basic murcuric carbonate White ppt.
$CuCO_3 \longrightarrow$ Green ppt.
$CaCO_3 \longrightarrow$ White ppt.

Sulphites (SO_3^{2-}) :   Except Alkali metal and Ammonium, all other sulphite are generally insoluble.

Examples : Ag_2SO_3
$PbSO_3$
$BaSO_3 \longrightarrow$ White ppt.
$CaSO_3$

Thiosulphates :   Mostly soluble except

$Ag_2S_2O_3 \longrightarrow$ White ppt. $[Ag(S_2O_3)_2]^{3-}$ soluble
$PbS_2O_3 \longrightarrow$ White ppt.
$BaS_2O_3 \longrightarrow$ White ppt.

Thiocynate (SCN⁻) : $Hg(SCN)_2$ – White ppt. (Pharaoh's serpent)
$Ag(SCN)$ – White ppt.
$Cu(SCN)_2$ – Black ppt.
$Cu(SCN)$ – White ppt.
$Fe(SCN)_3$ – Red complex.
$[Co(SCN)_4]^{2-}$ – Blue complex
$Co[Hg(SCN)_4]$ – Blue ppt.

Cynaides(CN⁻) :   Except Alkali metal Alkaline earth metal cyanides are soluble in water.
$Hg(CN)_2$ – soluble in water in undissociated form
$Ag(CN)$ – White ppt. $[Ag(CN)_2]^-$ soluble
$Pb(CN)_2$ – White ppt.
$Fe(CN)_3$ – Brown ppt. $[Fe(CN)_6]^{3-}$ soluble
$Co(CN)_2$ – Brown ppt. $[Co(CN)_6]^{4-}$ soluble
$Ni(CN)_2$ – Green $[Ni(CN)_4]^{2-}$ soluble

Sulphides :   Except Alkali metals and ammonium salt's all other sulphides are insoluble. Some insoluble sulphides with unusual colour are
$CdS \longrightarrow$ Yellow
$MnS \longrightarrow$ Pink
$ZnS \longrightarrow$ White
$SnS \longrightarrow$ Brown
$SnS_2 \longrightarrow$ Yellow
$As_2S_3 \longrightarrow$ Yellow
$Sb_2S_3 \longrightarrow$ Orange

Chromates : $Ag_2CrO_4 \longrightarrow$ Red ppt.
$PbCrO_4 \longrightarrow$ Yellow ppt.
$BaCrO_4 \longrightarrow$ Yellow ppt.
$FeCrO_4 \longrightarrow$ Green ppt.
Dichromates are generally soluble.
MnO_4 – Permangnates are generally soluble.

Phosphates:	Are generally insoluble :
	$Ag_3PO_4 \longrightarrow$ Yellow ppt.
	$AlPO_4 \longrightarrow$ Yellow ppt.
	$ZrO(HPO_4) \longrightarrow$ White ppt.
	$Mg(NH_4)PO_4 \longrightarrow$ White ppt.
	$(NH_4)_3[P Mo_{12}O_{40}] \longrightarrow$ Canary yellow ppt.

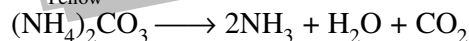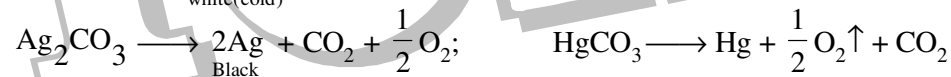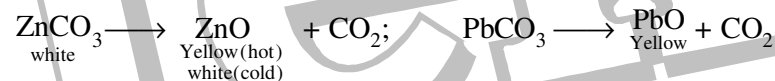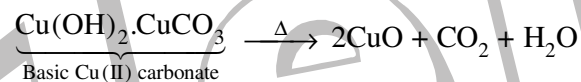*Phosphite (HPO_4^{2-}):* Except Alkali metals all other phosphites are insoluble

Hypo phosphite: All hypophosphites are soluble in water.
All Acetate are soluble except $Ag(CH_3COO)$
All formates are soluble except $Ag(HCOO)$
Tatarate,Citrate,Salicylate,Succinate of Silver-are all insoluble white ppt.

Some Important ppt.: KH (Tartarate) $\longrightarrow$ White ppt.
NH_4H(Tartarate) $\longrightarrow$ White ppt.
$K_2[PtCl_6] \longrightarrow$ White ppt.
$K_3[Co(NO_2)_6] \longrightarrow$ Yellow ppt.
$(NH_4)_3 [Co(NO_2)_6] \longrightarrow$ Yellow ppt.
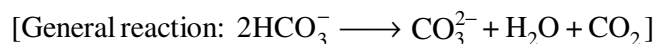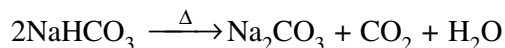$(NH_4)_2 [PtCl_6] \longrightarrow$ Yellow ppt.

HEATING EFFECTS

Heating effect of carbonate & bicarbonate salts

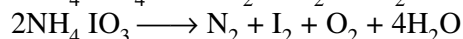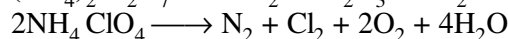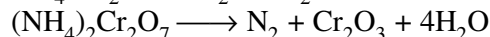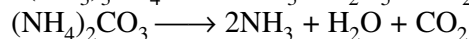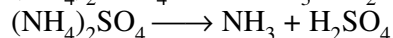All carbonates except (Na, K, Rb, Cs) decompose on heating giving CO_2

$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$
$$MCO_3 \longrightarrow MO + CO_2 \text{ [M = Be, Mg, Ca, Sr, Ba]}$$

$$\underbrace{Cu(OH)_2.CuCO_3}_{\text{Basic Cu(II) carbonate}} \xrightarrow{\Delta} 2CuO + CO_2 + H_2O$$

$$\underset{\text{white}}{ZnCO_3} \longrightarrow \underset{\substack{\text{Yellow(hot)}\\ \text{white(cold)}}}{ZnO} + CO_2; \qquad PbCO_3 \longrightarrow \underset{\text{Yellow}}{PbO} + CO_2$$

$$\underset{\text{Yellow}}{Ag_2CO_3} \longrightarrow \underset{\text{Black}}{2Ag} + CO_2 + \frac{1}{2}O_2; \qquad HgCO_3 \longrightarrow Hg + \frac{1}{2}O_2\uparrow + CO_2$$

$$(NH_4)_2CO_3 \longrightarrow 2NH_3 + H_2O + CO_2$$
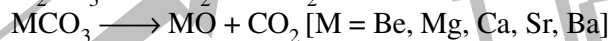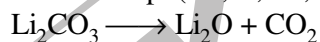
All bicarbonates decompose to give carbonates and CO_2. eg.

$$2NaHCO_3 \xrightarrow{\Delta} Na_2CO_3 + CO_2 + H_2O$$

[General reaction: $2HCO_3^- \longrightarrow CO_3^{2-} + H_2O + CO_2$]

Heating effect of ammonium salts

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O; \qquad NH_4NO_3 \longrightarrow N_2O + 2H_2O$$
$$(NH_4)_2Cr_2O_7 \longrightarrow N_2 + Cr_2O_3 + 4H_2O$$
$$2NH_4ClO_4 \longrightarrow N_2 + Cl_2 + 2O_2 + 4H_2O$$
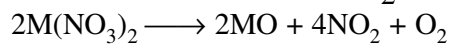$$2NH_4IO_3 \longrightarrow N_2 + I_2 + O_2 + 4H_2O$$

[If anionic part is oxdising in nature, then N_2 will be the product (some times N_2O).]

$$(NH_4)_2HPO_4 \longrightarrow HPO_3 + H_2O + 2NH_3$$
$$(NH_4)_2SO_4 \longrightarrow NH_3 + H_2SO_4$$
$$2(NH_3)_3PO_4 \longrightarrow 2NH_3 + P_2O_5 + 3H_2O$$
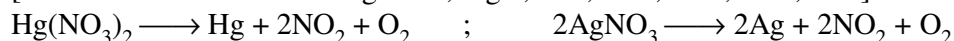$$(NH_4)_2CO_3 \longrightarrow 2NH_3 + H_2O + CO_2$$

[If anionic part weakly oxidising or non oxidising in nature then NH_3 will be the product.]

Heating effect of nitrate salts
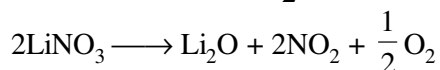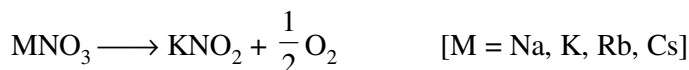
$$MNO_3 \longrightarrow KNO_2 + \frac{1}{2}O_2 \qquad [M = Na, K, Rb, Cs]$$

$$2LiNO_3 \longrightarrow Li_2O + 2NO_2 + \frac{1}{2}O_2$$
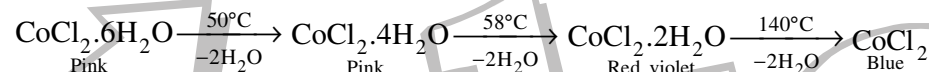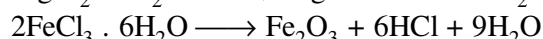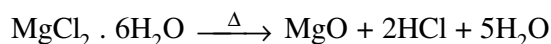
$$2M(NO_3)_2 \longrightarrow 2MO + 4NO_2 + O_2$$

[M = all bivalent metal's ions eg. $Zn^{+2}, Mg^{+2}, Sr^{+2}, Ca^{+2}, Ba^{+2}, Cu^{+2}, Pb^{+2}$]

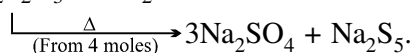$$Hg(NO_3)_2 \longrightarrow Hg + 2NO_2 + O_2 \qquad ; \qquad 2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$$

Heating effect of Halides salts

$$2FeCl_3 \longrightarrow 2FeCl_2 + Cl_2 \qquad ; \qquad AuCl_3 \longrightarrow AuCl + Cl_2$$

$$Hg_2Cl_2 \longrightarrow HgCl_2 + Hg \qquad ; \qquad NH_4Cl \longrightarrow NH_3 + HCl$$

$$PbX_4 \longrightarrow PbX_2 + X_2 \qquad [X = Cl, Br, SCN^-]$$

Heating effect of hydrated chloride salts

$$MgCl_2 . 6H_2O \xrightarrow{\Delta} MgO + 2HCl + 5H_2O$$

$$2FeCl_3 . 6H_2O \longrightarrow Fe_2O_3 + 6HCl + 9H_2O$$

$$2AlCl_3 . 6H_2O \longrightarrow Al_2O_3 + 6HCl + 9H_2O$$

$$\underset{Pink}{CoCl_2.6H_2O} \xrightarrow[-2H_2O]{50°C} \underset{Pink}{CoCl_2.4H_2O} \xrightarrow[-2H_2O]{58°C} \underset{Red\ violet}{CoCl_2.2H_2O} \xrightarrow[-2H_2O]{140°C} \underset{Blue}{CoCl_2}$$

Heating effect of hydrated Sulphate salts

$$\underset{Blue\ vitriol}{CuSO_4.5H_2O} \xrightarrow[-4H_2O]{100°C} \underset{Bluish\ White}{CuSO_4.H_2O} \xrightarrow[-H_2O]{220°C} \underset{White}{CuSO_4} \xrightarrow{>800°C} CuO + SO_2 + \frac{1}{2}O_2$$

$$\xrightarrow{750°C} \underset{Black}{CuO + SO_3}$$

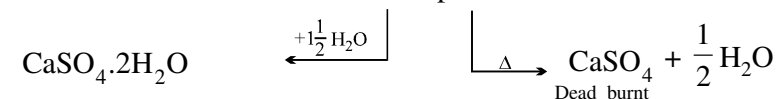$$\underset{Green\ Vitriol}{FeSO_4.7H_2O} \xrightarrow[-7H_2O]{300°C} FeSO_4 \xrightarrow{\Delta} Fe_2SO_3 + SO_2 + SO_3 \text{ (very important)}$$

$$Fe_2(SO_4)_3 \xrightarrow{\Delta} Fe_2O_3 + 3SO_3$$

$$\underset{epsom\ salt}{MgSO_4.7H_2O} \xrightarrow[-7H_2O]{\Delta} MgSO_4 \downarrow [Same\ as\ ZnSO_4]$$

$$\underset{gypsum}{CaSO_4.2H_2O} \xrightarrow{120°C} (CaSO_4.\frac{1}{2}H_2O) + 1\frac{1}{2}H_2O$$

$$\text{Plaster of pairs}$$

$$CaSO_4.2H_2O \xleftarrow{+1\frac{1}{2}H_2O} \qquad \xrightarrow{\Delta} \underset{Dead\ burnt}{CaSO_4} + \frac{1}{2}H_2O$$

$$Na_2S_2O_3.5H_2O \xrightarrow{220°C} Na_2S_2O_3 + 5H_2O$$

$$\xrightarrow[\text{(From 4 moles)}]{\Delta} 3Na_2SO_4 + Na_2S_5.$$

$$ZnSO_4.7H_2O \xrightarrow{70°C} ZnSO_4.6H_2O \xrightarrow{70°-200°C} ZnSO_4.H_2O \xrightarrow{>200°C} ZnSO_4$$

$$\downarrow \Delta >800°C$$

$$ZnO + SO_2 + \frac{1}{2}O_2$$

$$2NaHSO_3 \longrightarrow Na_2S_2O_5 + H_2O \begin{array}{l} \xrightarrow{\Delta} Na_2SO_3 + SO_2 \\ \longrightarrow Na_2S + Na_2SO_4 \end{array}$$
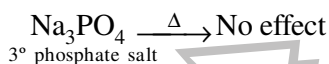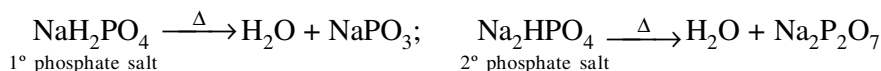
$$2NaHSO_4 \xrightarrow{\Delta} Na_2SO_4 + H_2O + SO_3$$

Heating effect of Oxide salts

$$2Ag_2O \xrightarrow[300°C]{\Delta} 4Ag + O_2 \qquad ; \qquad \underset{\text{yellow}}{HgO} \xrightarrow[400°C]{\Delta} \underset{\text{red}}{HgO} \xrightarrow[\substack{\text{strong} \\ \text{heating}}]{\Delta} Hg + \frac{1}{2}O_2$$

$$PbO_2 \xrightarrow{\Delta} PbO + \frac{1}{2}O_2 \qquad ; \qquad \underset{\text{Red lead}}{Pb_3O_4} \underset{340°C}{\overset{>470°C}{\rightleftharpoons}} \underset{\text{Litharge}}{6PbO} + O_2$$

$$3MnO_2 \xrightarrow{900°C} Mn_3O_4 + O_2 \qquad ; \qquad \underset{\text{white}}{ZnO} \underset{\text{Cold}}{\overset{\text{Hot}}{\rightleftharpoons}} \underset{\text{yellow}}{ZnO}$$

$$2CrO_5 \xrightarrow{} Cr_2O_3 + \frac{1}{2}O_2 \quad ; \qquad 2CrO_3 \xrightarrow{420°C} Cr_2O_3 + \frac{3}{2}O_2$$

$$I_2O_5 \xrightarrow{} I_2 + \frac{5}{2}O_2$$
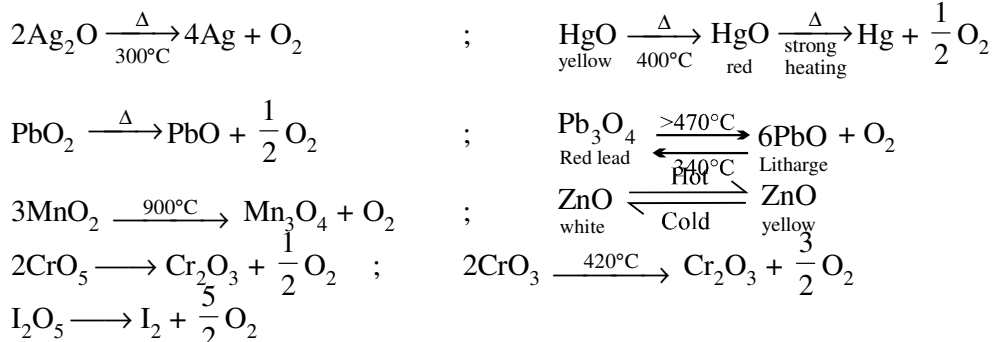
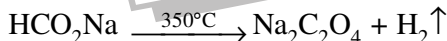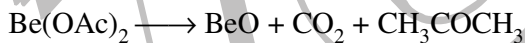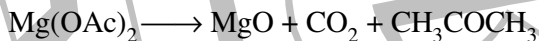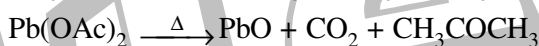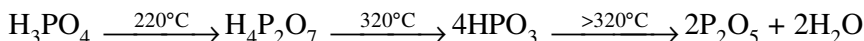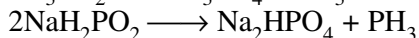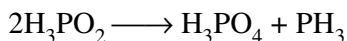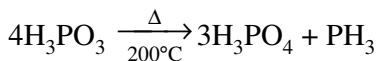**Heating effect of dichromate & chromate salts**

$$(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O; \quad K_2Cr_2O_7 \xrightarrow{\Delta} 2K_2CrO_4 + Cr_2O_3 + \frac{7}{2}O_2$$
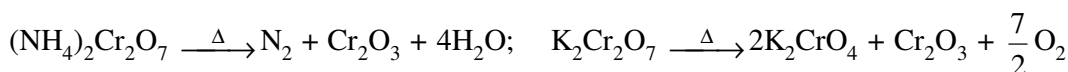
Heating effect of phosphate salts

$$\underset{\text{1° phosphate salt}}{NaH_2PO_4} \xrightarrow{\Delta} H_2O + NaPO_3; \qquad \underset{\text{2° phosphate salt}}{Na_2HPO_4} \xrightarrow{\Delta} H_2O + Na_2P_2O_7$$

$$\underset{\text{3° phosphate salt}}{Na_3PO_4} \xrightarrow{\Delta} \text{No effect}$$

$$Na(NH_4)HPO_4.4H_2O \xrightarrow[-4H_2O]{\Delta} NaNH_4HPO_4 \xrightarrow{\text{High temp.}} NaPO_3 + NH_3 + H_2O$$

$$2Mg(NH_4)PO_4 \xrightarrow{\Delta} Mg_2P_2O_7 + 2NH_3 + H_2O$$

Heating effects of acetate, formate, oxalate salts

$$CH_3CO_2K \xrightarrow{\Delta} K_2CO_3 + CH_3COCH_3 \qquad\qquad Na_2C_2O_4 \xrightarrow{} Na_2CO_3 + CO$$

$$Pb(OAc)_2 \xrightarrow{\Delta} PbO + CO_2 + CH_3COCH_3 \qquad SnC_2O_4 \xrightarrow{\Delta} SnO + CO_2 + CO$$

$$Mg(OAc)_2 \xrightarrow{} MgO + CO_2 + CH_3COCH_3 \qquad FeC_2O_4 \xrightarrow{} FeO + CO + CO_2$$

$$Be(OAc)_2 \xrightarrow{} BeO + CO_2 + CH_3COCH_3 \qquad Ag_2C_2O_4 \xrightarrow{\Delta} 2Ag + 2CO_2$$

$$Ca(OAc)_2 \xrightarrow{} CaCO_3 + CH_3COCH_3 \qquad\quad HgC_2O_4 \xrightarrow{} Hg + 2CO_2$$

$$Ba(OAc)_2 \xrightarrow{} BaCO_3 + CH_3COCH_3$$

$$HCO_2Na \xrightarrow{350°C} Na_2C_2O_4 + H_2\uparrow$$

$$2HCOOAg \xrightarrow{\Delta} HCOOH + 2Ag + CO_2 \qquad\qquad (HCOO)_2Hg \xrightarrow{} HCOOH + Hg + CO_2$$

Heating effect of Acids

$$2HNO_3 \xrightarrow{\Delta} H_2O + 2NO_2 + \frac{1}{2}O_2$$

$$H_2SO_4 \xrightarrow{444°C} H_2O + SO_3; \qquad\qquad H_2SO_4 \xrightarrow{>800°C} H_2O + SO_2 + \frac{1}{2}O_2$$
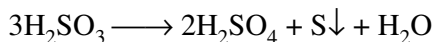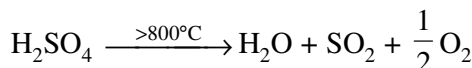
$$\left.\begin{array}{l} 3H_2SO_3 \xrightarrow{} 2H_2SO_4 + S\downarrow + H_2O \\ 3HNO_2 \xrightarrow{} HNO_3 + 2NO + H_2O \\ HClO_3 \xrightarrow{} HClO_4 + ClO_2 + H_2O \\ 3HOCl \xrightarrow{} 2HCl + HClO_3 \\[6pt] 4H_3PO_3 \xrightarrow{200°C} 3H_3PO_4 + PH_3 \\[6pt] 2H_3PO_2 \xrightarrow{} H_3PO_4 + PH_3 \\ 2NaH_2PO_2 \xrightarrow{} Na_2HPO_4 + PH_3 \end{array}\right\} \begin{array}{l} \text{Undergoes} \\ \text{dispropor-} \\ \text{-tionation} \\ \text{reaction} \end{array}$$

$$H_3PO_4 \xrightarrow{220°C} H_4P_2O_7 \xrightarrow{320°C} 4HPO_3 \xrightarrow{>320°C} 2P_2O_5 + 2H_2O$$

$$H_3BO_3 \xrightarrow{100°C} 4HBO_2 \xrightarrow{140°C} H_2B_4O_7 \xrightarrow[\text{hot}]{\text{Red}} 2B_2O_3 + H_2O$$

$$H_2C_2O_4 \xrightarrow{\Delta} H_2O + CO + CO_2$$

Some reactions of important oxidising agents

(I) *Potassium dichromate ($K_2Cr_2O_7$) :*

$Cr_2O_7^{2-}$ ion takes electrons in the acidic medium and is reduced to Cr^{3+} ion. Thus $Cr_2O_7^{2-}$ acts as an oxidising agent in acidic medium.

$$K_2Cr_2O_7 + 4H_2SO_4(dil.) \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3O$$

or $\qquad Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

(1) $\quad K_2Cr_2O_7 + 7H_2SO_4 + 6KI \longrightarrow 4K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3I_2$

or $\quad\; Cr_2O_7^{2-} + 14H^+ + 6I^- \longrightarrow 2Cr^{3+} + 7H_2O + 3I_2$

(2) $\quad K_2Cr_2O_7 + 7H_2SO_4 + 6FeSO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3Fe_2(SO_4)_3$

or $\quad\; Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

(3) $\quad K_2Cr_2O_7 + 4H_2SO_4 + 3H_2S \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 7H_2O + 3S$

or $\quad\; Cr_2O_7^{2-} + 8H^+ + 3H_2S \longrightarrow 2Cr^{3+} + 7H_2O + 3S$

(4) $\quad K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$

or $\quad\; Cr_2O_7^{2-} + 2H^+ + 3SO_2 \longrightarrow 2Cr^{3+} + 3MnO_4 + H_2O$

(5) $\quad K_2Cr_2O_7 + 4H_2SO_4 + 3Na_2SO_3 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 3Na_2SO_3 + 4H_2O$

or $\quad\; Cr_2O_7^{2-} + 8H^+ + 3SO_3^{2-} \longrightarrow 2Cr^{3+} + 3SO_4^{2-} + 4H_2O$

(6) $\quad K_2Cr_2O_7 + 14HCl \longrightarrow 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$

or $\quad\; Cr_2O_7^{2-} + 14H^+ + 6Cl^- \longrightarrow 2Cr^{3+} + 7H_2O + 3Cl_2$

(7) $\quad K_2Cr_2O_7 + H_2SO_4 + 4H_2O_2 \xrightarrow{\text{ether}} K_2SO_4 + 2CrO_5 + 5H_2O$

or $\quad\; Cr_2O_7^{2-} + 2H^+ + 4H_2O_2 \xrightarrow{\text{ether}} 2CrO_5 + 5H_2O$

(II) *Manganese dioxide (MnO_2) :*

In presence of excess of H^+ ions, MnO_2 acts as a stronge oxidising agent. In showing this behaviour Mn^{4+} changes to Mn^{2+} ion.

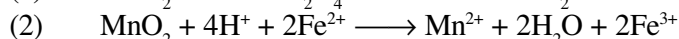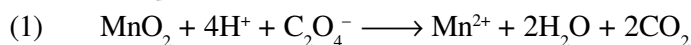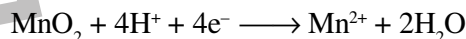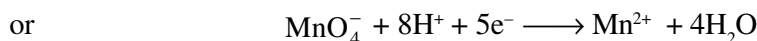$$MnO_2 + 4H^+ + 4e^- \longrightarrow Mn^{2+} + 2H_2O$$

(1) $\quad MnO_2 + 4H^+ + C_2O_4^- \longrightarrow Mn^{2+} + 2H_2O + 2CO_2$

(2) $\quad MnO_2 + 4H^+ + 2Fe^{2+} \longrightarrow Mn^{2+} + 2H_2O + 2Fe^{3+}$

(3) $\quad MnO_2 + 4H^+ + 2Cl^- \longrightarrow Mn^{2+} + 2H_2O + Cl_2$

(III) *Potassium permangate ($KMnO_4$) :*

(A) **In acidic medium:** The reduction of MnO_4^- ion into Mn^{2+} ion san be represented by the following ionic equation :

$$2MnO_4^- + 4H^+ \longrightarrow Mn^{2+} + 2H_2O + 5O$$

or $\qquad MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$

(1) *KI to I_2 ($I^- \to I_2$)*

$2KMnO_4 + 8H_2SO_4 + 10KI \longrightarrow 6K_2SO_4 + 2MnSO_4 + 8H_2O + 5I_2$
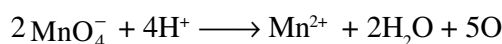
or $\quad 2MnO_4^- + 16H^+ + 10I^- \longrightarrow 2Mn^{2+} + 8H_2O + 5I_2$
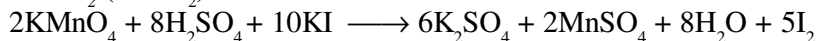
(2) *Ferrous salts to ferric salts* ($Fe^{2+} \to Fe^{3+}$)

$2KMnO_4 + 8H_2SO_4 + 10FeSO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5Fe_2(SO_4)_3$

or $\quad MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow 2Mn^{2+} + 4H_2O + 5Fe^{3+}$
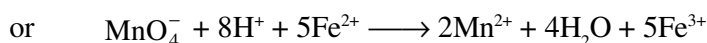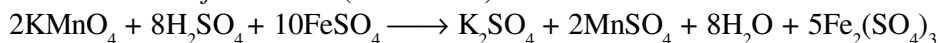
(3)   *Oxalic acid* ($H_2C_2O_4$) *or oxalate* ($C_2O_4^{2-}$) *to* CO_2

$$2KMnO_4 + 8H_2SO_4 + 5H_2C_2O_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 10CO_2$$

or $$2\,MnO_4^- + 16H^+ + 5C_2O_4^- \longrightarrow 2Mn^{2+} + 8H_2O + 5CO_2$$

(4)   *H_2S to S* ($S^{2-} \rightarrow S°$)

$$2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5S$$

or $$2\,MnO_4^- + 16H^+ + 5S^{2-} \longrightarrow 2Mn^{2+} + 8H_2O + 5S$$

(5)   *Nitrite to nitrate* ($NO_2^- \rightarrow NO_3^-$)

$$2KMnO_4 + 3H_2SO_4 + 5KNO_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5KNO_3$$

or $$2\,MnO_4^- + 6H^+ + 5NO_2^- \longrightarrow 2Mn^{2+} + 3H_2O + 5NO_3^-$$

(6)   *Arsenite* AsO_3^{3-} *(As = +3) to arsenate,* AsO_4^{3-} *(As = +5)*

$$2KMnO_4 + 3H_2SO_4 + 5Na_3AsO_3 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5Na_3AsO_4$$

or $$2\,MnO_4^- + 6H^+ + 5AsO_3^{3-} \longrightarrow 2Mn^{2+} + 3H_2O + 5AsO_4^{3-}$$

(7)   *Sulphite,* SO_3^{2-} *(S = +4) to sulphate,* SO_4^{2-} *(S = +6)*

$$2KMnO_4 + 3H_2SO_4 + 5Na_2SO_3 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5Na_2SO_4$$

or $$2\,MnO_4^- + 6H^+ + 5SO_3^{2-} \longrightarrow 2Mn^{2+} + 3H_2O + 5SO_4^{2-}$$

(8)   *Halogen acid, HX (X = −1) to the corresponding halogen,* $X_2(X = 0)$ ($X^- \rightarrow X_2$)
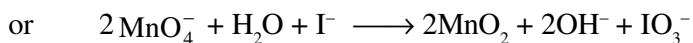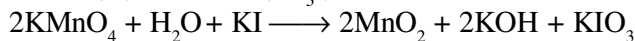
$$2KMnO_4 + 3H_2SO_4 + 10HCl \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5Cl_2$$

or $$2\,MnO_4^- + 16H^+ + 10Cl^- \longrightarrow 2Mn^{2+} + 3H_2O + 5Cl_2$$

(9)   *H_2O_2 (O = −1) to* O_2 *(O = 0)*

$$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$$

or $$2\,MnO_4^- + 6H^+ + 5H_2O_2 \longrightarrow 2Mn^{2+} + 8H_2O + 5H_2O$$

(10)   *SO_2 (S = +4) to* H_2SO_4 *(S = +6)* ($SO_2 \rightarrow SO_4^{2-}$)

$$2KMnO_4 + 2H_2O + 5SO_2 \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$$

or $$2\,MnO_4^- + 2H_2O + 5SO_2 \longrightarrow 2Mn^{2+} + 5SO_4^{2-}$$

(11)   *Hydrazine,* N_2H_4 *(N = −2) to* $N_2(N = 0)$

$$4KMnO_4 + 6H_2SO_4 + 5N_2H_4 \longrightarrow 2K_2SO_4 + 4MnSO_4 + 16H_2O + 5N_2$$

or $$4\,MnO_4^- + 12H^+ + 5N_2H_4 \longrightarrow 2Mn^{2+} + 16H_2O + 5N_2$$

(12)   *Hydrazoic acid,* HN_3 *(N = −1/3) to* $N_2(N = 0)$

$$2KMnO_4 + 3H_2SO_4 + 10HN_3 \longrightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 15N_2$$

or $$2\,MnO_4^- + 6H^+ + 5HN_3 \longrightarrow 2Mn^{2+} + 8H_2O + 15N_2$$

(13)   *Nitric oxide, NO (N = +2) to* HNO_3 *(N = +5)*

$$6KMnO_4 + 9H_2SO_4 + 10NO \longrightarrow 3K_2SO_4 + 6MnSO_4 + 4H_2O + 10HNO_3$$

or $$3\,MnO_4^- + 9H^+ + 5NO \longrightarrow 3Mn^{2+} + 2H_2O + 5HNO_3$$

(14)   *Potassium ferrocyanide,* $K_4[Fe(CN)_6]$ *to potassium ferricyanide,* $K_3[Fe(CN)_6]$

$$2KMnO_4 + 3H_2SO_4 + 10K_4[Fe(CN)_6] \longrightarrow K_2SO_4 + 2MnSO_4 + 2H_2O + 10K_3[Fe(CN)_6] + 10KOH$$

or $$MnO_4^- + 8H^+ + 5[Fe(CN)_6]^{4-} \longrightarrow Mn^{2+} + 4H_2O + 5[Fe(CN)_6]^{3-}$$

(15)   *Sodium thiosulphate,* $Na_2S_2O_3$ *(S = +3) to sodium dithionate,* $Na_2S_2O_6$ *(S = +5)*

$$6KMnO_4 + 9H_2SO_4 + 5Na_2S_2O_3 \longrightarrow 3K_2SO_4 + 6MnSO_4 + 9H_2O + 5Na_2S_2O_6$$

or $$6\,MnO_4^- + 18H^+ + 5S_2O_3^{2-} \longrightarrow 6Mn^{2+} + 9H_2O + 5S_2O_6^{2-}$$
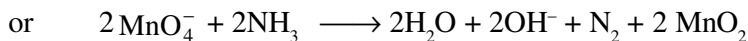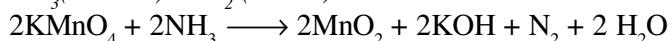
(B) **In alkaline medium:** In alkaline solution MnO_4^- ion is reduced to colourless & insoluble MnO_2 according to the following equations:
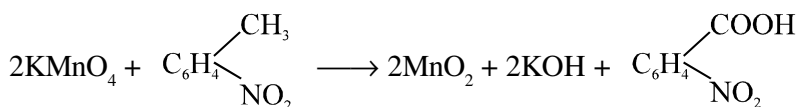
$$2\,MnO_4^- + H_2O \xrightarrow{\text{alkali}} 2MnO_2 + 2OH^- + 3O$$

or
$$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$$
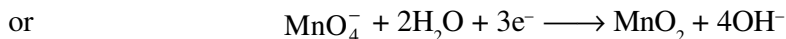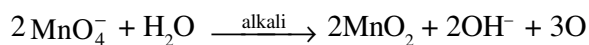
(1) *Iodides(I^-) to iodates (IO_3^-)*
$$2KMnO_4 + H_2O + KI \longrightarrow 2MnO_2 + 2KOH + KIO_3$$

or
$$2\,MnO_4^- + H_2O + I^- \longrightarrow 2MnO_2 + 2OH^- + IO_3^-$$

(2) *$NH_3(N = -3)$ to N_2 $(N = 0)$*
$$2KMnO_4 + 2NH_3 \longrightarrow 2MnO_2 + 2KOH + N_2 + 2\,H_2O$$

or
$$2\,MnO_4^- + 2NH_3 \longrightarrow 2H_2O + 2OH^- + N_2 + 2\,MnO_2$$

(3) *Nitrotoluene to nitrobenzoic acid*

Nitrotoluene   Nitrobenzoic acid

or
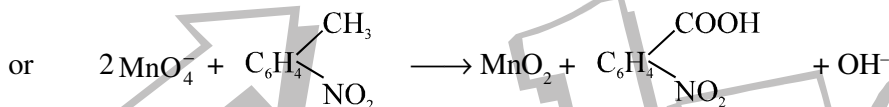
(4) *Ethylene $(H_2C = CH_2)$ to ethylene glycol $(HO–CH_2–CH_2–OH)$*
$$2KMnO_4 + 4H_2O + 3H_2C{=}CH_2 \longrightarrow 2MnO_2 + 2KOH + 3HO–CH_2–CH_2–OH$$

or
$$2\,MnO_4^- + 4H_2O + 3H_2C{=}CH_2 \longrightarrow 2MnO_2 + 2OH^- + 3HO–CH_2–CH_2–OH$$

(C) **In neutral medium:** In neutral solution, $KMnO_4$ is directly reduced to MnO_2
$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3O$$

or
$$2\,MnO_4^- + H_2O \longrightarrow 2OH^- + 2MnO_2 + 3O$$

or
$$MnO_4^- + 2H_2O + 3e^- \longrightarrow 2MnO_2 + 4OH^-$$
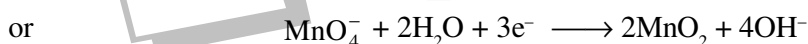
(1) *Manganous salt (e.g. $MnSO_4$) to insoluble MnO_2 $(Mn^{2+} \longrightarrow Mn^{4+}O_2)$*
$$2KMnO_4 + 4H_2O + 3MnSO_4 + H_2SO_4 \longrightarrow 5MnO_2 + 3H_2SO_4 + K_2SO_4 + 2H_2O$$

or
$$2\,MnO_4^- + 10H_2O + 3Mn^{2+} \longrightarrow 5MnO_2 + 8H_2O + 4H^+$$
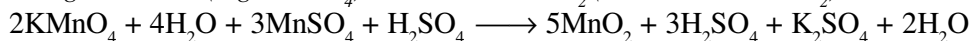
(2) *Sodium thiosulphate, $Na_2S_2O_3$ $(S = +2)$ to Na_2SO_4 $(S = +6)$ $[S_2O_4^{2-} \longrightarrow SO_4^{2-}]$*
$$8KMnO_4 + H_2O + 3Na_2S_2O_3 \longrightarrow 8MnO_2 + 2KOH + 3Na_2SO_4 + 3K_2SO_4$$

or
$$8\,MnO_4^- + H_2O + 3S_2O_3^{2-} \longrightarrow 8MnO_2 + 2OH^- + 6SO_4^{2-}$$
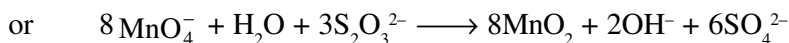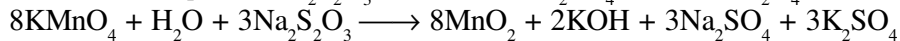
(3) *Nitrogen dioxide, NO_2 $(N = +4)$ to HNO_3 $(N = +5)$ $[NO_2 \longrightarrow NO_3^-]$*
$$2KMnO_4 + 4H_2O + 6NO_2 \longrightarrow 2KOH + 2MnO_2 + 2MnO_2 + 6HNO_3$$

or
$$MnO_4^- + H_2O + 3NO_2 \longrightarrow MnO_2 + 3NO_3^- + 2H^+$$
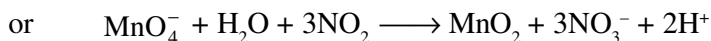
THE ATLAS

STOICHIOMETRY

↓

1. Mole - definition and meaning
2. Gram - atomic mass
3. Gram- molecular weight
4. Relative atomic mass
5. Isotopic abundance
6. Average atomic mass

↓

CHEMICAL CALCULATION USING
MOLE CONCEPT BASED ON
BALANCED CHEMICAL REACTION

THEORETICAL
STOICHIOMETRY

↓

1. Stoichiometric proportion
2. Non stoichiometric proportion
3. Concept of limiting reagent

EXPERIMENTAL
STOICHIOMETRY
ANALYSIS

Gravimetric

Titrimetic
Method

↓

Reaction in
aqueous solution
1. Acid Base
2. Redox
3. Precipitation
4. Complex titrimetric

Gas Analysis

↓

Reaction
involving
gaseous
reactants and
products

GLOSSARY

Aliquot. A portion of the whole, usually a simple fraction. A portion of a sample withdraw from a volumetric flask with a pipet is called an aliquot.

Analytical concentration. The total number of moles per litre of a solute regardless of any reactions that might occur when the solute dissolves. Used synonymously with formality.

Equivalent. The amount of a substance which furnishes or reacts with 1 mol of H^+ (acid-base), 1 mol of electrons (redox), or 1 mol of a univalent cation (precipitation and complex formation).

Equivalent weight. The weight in grams of one equivalent of a substance.

Equivalence point. The point in a titration where the number of equivalents of titrant is the same as the number of equivalents of analyte.

End point. The point in a titration where an indicator changes color.

Formula weight. The number of formula weights of all the atoms in the chemical formula of a substance.

Formality. The number of formula weights of solute per litre of solution; synonymous with analytical concentration.

Indicator. A chemical substance which exhibits different colors in the presence of excess analyte or titrant.

Normality. The number of equivalents of solute per litre of solution.

Primary standard. A substance available in a pure form or state of known purity which is used in standardizing a solution.

Standardization. The process by which the concentration of a solution is accurately ascertained.

Standard solution. A solution whose concentration has been accurately determined.

Titrant. The reagent (a standard solution) which is added from a buret to react with the analyte.

EASY RIDE

Acid Base Titration

Q1. A small amount of $CaCO_3$ completely neutralized 52.5 mL of N/10 HCl and no acid is left at the end. After converting all calcium chloride to $CaSO_4$, how much plaster of paris can be obtained?

Q2. How many ml of 0.1 N HCl are required to react completely with 1 g mixture of Na_2CO_3 and $NaHCO_3$ containing equimolar amounts of two?

Q3. 10 g $CaCO_3$ were dissolved in 250 ml of M HCl and the solution was boiled. What volume of 2 M KOH would be required to equivalence point after boiling? Assume no change in volume during boiling.

Q4. 125 mL of a solution of tribasic acid (molecular weight = 210) was neutralized by 118mL of decinormal NaOH solution and the trisodium salt was formed. Calculate the concentration of the acid in grams per litre.

Q5. Upon heating one litre of N/2 HCl solution, 2.675g of hydrogen chloride is lost and the volume of solution shrinks to 750 ml. Calculate (i) the normality of the resultant solution (ii) the number of milli-equivalents of HCl in 100 mL of the original solution.

Q6. For the standardization of a $Ba(OH)_2$ solution, 0.2g of potassium acid phthalate (m.wt. 204.2g) weighed which was then titrated with $Ba(OH)_2$ solution. The titration requires 27.80mL $Ba(OH)_2$ solution. What is the molarity of base? The reaction products include $BaC_8H_4O_4$ as only Ba containing species.

Q7. A definite amount of NH_4Cl was boiled with 100mL of 0.8N NaOH for complete reaction. After the reaction, the reactant mixture containing excess of NaOH was neutralized with 12.5mL of 0.75N H_2SO_4. Calculate the amount of NH_4Cl taken.

Q8. H_3PO_4 is a tri basic acid and one of its salt is NaH_2PO_4. What volume of 1 M NaOH solution should be added to 12 g of NaH_2PO_4 to convert it into Na_3PO_4?

Q9. Calculate the number of gm. of borax, $Na_2B_4O_7.10H_2O$, per litre of a solution of which 25cc required 15.6 cc of N/10 hydrochloric acid for naturalization, methyl orange being used as indicator. In aqueous solution, borax hydrolyses according to the equation:
$$Na_2B_4O_7 + 7H_2O = 2NaOH + 4H_3BO_3$$
The liberated boric acid is a weak acid and is without effect on methyl orange.

Q10. 25mL of a solution of Na_2CO_3 having a specific gravity of 1.25g ml^{-1} required 32.9 mL of a solution of HCl containing 109.5g of the acid per litre for complete neutralization. Calculate the volume of 0.84N H_2SO_4 that will be completely neutralized by 125g of Na_2CO_3 solution.

Q11. A solution containing 4.2 g of KOH and $Ca(OH)_2$ is neutralized by an acid. It consumes 0.1 equivalent of acid, calculate the percentage composition of the sample.

Q12. 5gm of a double sulphate of iron and ammonia was boiled with an excess of sodium hydroxide solution and the liberated ammonia was passed into 50cc of normal sulphuric acid. The excess of acid was found to require 24.5cc of normal sodium hydroxide for naturalization. Calculate the percentage of ammonia (expressed as NH_3) in the double salt.

Q13. 0.5 g of fuming H_2SO_4 (oleum) is diluted with water. The solution requires 26.7 ml of 0.4 N NaOH for complete neutralization. Find the % of free SO_3 in the sample of oleum.

Q14. 1.64 g of a mixture of $CaCO_3$ and $MgCO_3$ was dissolved in 50 mL of 0.8 M HCl. The excess of acid required 16 mL of 0.25 M NaOH for neutralization. Calculate the percentage of $CaCO_3$ and $MgCO_3$ in the sample.

Q15. 1.5 g of chalk were treated with 10 ml of 4N – HCl. The chalk was dissolved and the solution made to 100 ml 25 ml of this solution required 18.75 ml of 0.2 N – NaOH solution for complete neutralisation. Calculate the percentage of pure $CaCO_3$ in the sample of chalk?

Q16. 2.013g of a commercial sample of NaOH containing Na_2CO_3 as an impurity was dissolved to give 250ml solution. A 10ml portion of this solution required 20ml of 0.1N H_2SO_4 for complete neutralization. Calculate % by weight of Na_2CO_3.

Q17. Exactly 50 ml of Na_2CO_3 solution is equivalent to 56.3 ml of 0.102 N HCl in an acid-base neutralisation. How many gram $CaCO_3$ would be precipitated if an excess of $CaCl_2$ solution were added to 100 ml of this Na_2CO_3 solution.

Q18. 6g mixture of NH_4Cl and NaCl is treated with 110mL of a solution of caustic soda of 0.63N. The solution was then boiled to remove NH_3. The resulting solution required 48.1mL of a solution of 0.1N HCl. What is % composition of mixture?

Q19. Calculate the number of gm(a) of hydrochloric acid, (b) of potassium chloride in 1 litre of a solution, 25cc of which required 21.9cc of N/10 sodium hydroxide for naturalization and another 25cc after the addition of an excess of powdered chalk, required 45.3cc of N/10 silver nitrate for the complete precipitation of the chloride ion.

Q20. 2.5 gm of a mixture containing $NaHCO_3$, Na_2CO_3 and NaCl is dissolved in 100 ml water and its 50 ml portion required 13.33 ml 1.0 N HCl solution to reach the equivalence point. On the other hand its other 50 ml portion required 19 ml 0.25 M NaOH solution to reach the equivalence point. Determine mass % of each component? ($Na_2CO_3 = 36.38\%$, $NaHCO_3 = 31.92\%$, $NaCl = 31.7\%$)

Redox Titration

Q21. It requires 40.05 ml of 1M Ce^{4+} to titrate 20ml of 1M Sn^{2+} to Sn^{4+}. What is the oxidation state of the cerium in the product.

Q22. A volume of 12.53 ml of 0.05093 M SeO_2 reacted with exactly 25.52 ml of 0.1M $CrSO_4$. In the reaction, Cr^{2+} was oxidized to Cr^{3+}. To what oxidation state was selenium converted by the reaction.

Q23. A 1.0g sample of H_2O_2 solution containing x % H_2O_2 by mass requires x cm^3 of a $KMnO_4$ solution for complete oxidation under acidic conditions. Calculate the normality of $KMnO_4$ solution.

Q24. Metallic tin in the presence of HCl is oxidized by $K_2Cr_2O_7$ to stannic chloride, $SnCl_4$. What volume of deci-normal dichromate solution would be reduced by 1g of tin.

Q25. Calculate the mass of oxalic acid which can be oxidized by 100ml of M MnO_4^- solution, 10ml of which is capable of oxidizing 50ml of 1N I$^-$ of I_2.

Q26. Exactly 40ml of an acidified solution of 0.4M iron(II) ion of titrated with $KMnO_4$ solution. After addition of 32ml $KMnO_4$, one additional drop turns the iron solution purple. Calculate the concentration of permangnate solution.

Q27. The iodide content of a solution was determined by the titration with Cerium(IV) sulfate in the presence of HCl, in which I$^-$ is converted to ICl. A 250ml sample of the solution required 20ml of 0.058N Ce^{4+} solution. What is the iodide concentration in the original solution in gm/lt.

Q28. Potassium acid oxalate $K_2C_2O_4 \cdot 3HC_2O_4 \cdot 4H_2O$ can be oxidized by MnO_4^- in acid medium. Calculate the volume of 0.1M $KMnO_4$ reacting in acid solution with one gram of the acid oxalate.

Q29. 5g sample of brass was dissolved in one litre dil. H_2SO_4. 20 ml of this solution were mixed with KI, liberating I_2 and Cu$^+$ and the I_2 required 20 ml of 0.0327 N hypo solution for complete titration. Calculate the percentage of Cu in the alloy.

Q30. 1.44g pure FeC_2O_4 was dissolved in dil. HCl and solution diluted to 100 mL. Calculate volume of 0.01M $KMnO_4$ required to oxidize FeC_2O_4 solution completely.

Q31. 0.84 g iron ore containing x percent of iron was taken in a solution containing all the iron in ferrous condition. The solution required x ml of a dichromatic solution for oxidizing the iron content to ferric state. Calculate the strength of dichromatic solution.

Q32. 0.5M $KMnO_4$ solution completely reacts with 0.05M FeC_2O_4 solution under acidic conditions where the products are Fe^{3+}, CO_2 and Mn^{2+}. The volume of FeC_2O_4 used is 125 ml. What volume of $KMnO_4$ was used.

Q33. A solution is made by mixing 200 ml of 0.1M $FeSO_4$, 200 gm of 0.1M $KMnO_4$ and 600 ml 1M $HClO_4$. A reaction occurs in which Fe^{2+} is converted to Fe^{3+} & MnO_4^- to Mn^{2+} in acid solution. Calculate the concentration of each ion.

Q34. To 100ml of $KMnO_4$ solution containing 0.632 gm of $KMnO_4$, 200 ml of $SnCl_2$ solution containing 2.371 gm is added in presence of HCl. To the resulting solution excess of $HgCl_2$ solution is added all at once. How many gms of Hg_2Cl_2 will be precipitated.   (Mn = 55; K = 39; Sn = 118.7; Hg = 201)

Q35. A 1.0 g sample of Fe_2O_3 solid of 55.2% purity is dissolved in acid and reduced by heating the solution with zinc dust. The resultant solution is cooled and made upto 100.0 mL. An aliquot of 25.0 mL of this solution requires 17.0 mL of 0.0167 M solution of an oxidant for titration. Calculate the number of moles of electrons taken up by the oxidant in the reaction of the above titration.

Q36. A mixture of FeO and Fe_2O_3 is reacted with acidified $KMnO_4$ solution having a concentration of 0.2278 M, 100 ml of which was used. The solution was then titrated with Zn dust which converted Fe^{3+} of the solution to Fe^{2+}. The Fe^{2+} required 1000 ml of 0.13 M $K_2Cr_2O_7$ solution. Find the % of FeO & Fe_2O_3

Q37. 2 gms of FeC_2O_4 are made to react in acid solution with 0.25 M $KMnO_4$ solution. What volume of $KMnO_4$ solution would be required. The resulting solution is treated with excess of NH_4Cl and NH_4OH solution. The precipitated $Fe(OH)_3$ is filtered off, washed and ignited. What is the mass of the product obtained. (Fe = 56)

Q38. The neutralization of a solution of 1.2 g of a substance containing a mixture of $H_2C_2O_4 \cdot 2H_2O$, $KHC_2O_4 \cdot H_2O$ and different impurities of a neutral salt consumed 18.9 ml of 0.5 N NaOH solution. On titration with $KMnO_4$ solution, 0.4 g of the same substance needed 21.55 ml of 0.25 N $KMnO_4$. Calculate the % composition of the substance.

Q39. A 1.0 g sample containing $BaCl_2 \cdot 2H_2O$ was dissolved and an excess of K_2CrO_4 solution added. After a suitable period, the $BaCrO_4$ was filtered, washed and redissolved in HCl to convert CrO_4^{2-} to $Cr_2O_7^{2-}$. An excess of KI was added, and the liberated iodine was titrated with 84.7 mL of 0.137 M sodium thiosulphate. Calculate the percent purity of $BaCl_2 \cdot 2H_2O$.

Q40. A sample of Mg was burnt in air to give a mix of MgO and Mg_3N_2. The ash was dissolved in 60meq HCl and the resulting solution was back titrated with NaOH. 12 meq of NaOH were required to reach end point. An excess of NaOH was then added and the solution distilled. The NH_3 released was then trapped in 10 meq of second acid solution. Back titration of this solution required 6 meq of the base. Calculate the % of Mg burnt to the nitride.

Double titration

Q41. A solution contains Na_2CO_3 and $NaHCO_3$. 20ml of this solution required 4ml of 1N – HCl for titration with Ph indicator. The titration was repeated with the same volume of the solution but with MeOH.10.5 ml of 1 – N HCl was required this time. Calculate the amount of Na_2CO_3 & $NaHCO_3$.

Q42. A solution contains a mix of Na_2CO_3 and NaOH. Using Ph as indicator 25ml of mix required 19.5 ml of 0.995 N HCl for the end point. With MeOH, 25 ml of the solution required 25ml of the same HCl for the end point. Calculate gms/L of each substance in the mix .

Q43. 200ml of a solution of mixture of NaOH and Na_2CO_3 was first titrated with Ph and $\frac{N}{10}$ HCl. 17.5 ml of HCl was required for end point. After this MeOH was added and 2.5 ml of some HCl was again required for next end point. Find out amounts of NaOH and Na_2CO_3 in the mix.

Q44. What is the concentration of a solution of orthophosphoric acid(gm H_3PO_4 per litre), 25cc of which required 18.8cc of N sodium hydroxide for naturalization in the presence of phenolphthalein as indicator?

Q45. 2gm of mixture of hydrated sodium carbonate $Na_2CO_3 . 10H_2O$, and sodium bicarbonate was dissolved in water and made up to 250 cc. 25 cc of this solution was titrated, using methyl orange as indicator, and 22.5cc of 0.087N HCl were required for naturalization. Calculate the percentage of sodium bicarbonate in the mixture.

Q46. A solution contains Na_2CO_3 and $NaHCO_3$. 10ml of this requires 2ml of 0.1M H_2SO_4 for neutralisation using Ph indicator. MeOH is then added when a further 2.5 ml of 0.2 M H_2SO_4 was needed. Calculate strength of Na_2CO_3 and $NaHCO_3$.

Q47. A sample containing Na_2CO_3 & NaOH is dissolved in 100ml solution. 10ml of this solution requires 25ml of 0.1N HCl when Ph is used as indicator. If MeOH is used as indicator 10ml of same solution requires 30ml of same HCl. Calculate % of Na_2CO_3 and NaOH in the sample.

Q48. What is the concentration of a solution of sodium carbonate (expressed as gm. of anhydrous sodium carbonate per litre), 25cc of which required 18.3cc of 0.12N sulphuric acid for neutralization, phenolphthalein being used as an indicator?

Q49. When the salt, $KNaC_4H_4O_6 . 4H_2O$ (molecular weight 282) is ignited, there is a residue of sodium carbonate and potassium carbonate. A gram of this salt gave a residue which required 63.8cc of N/10 hydrochloric acid for neutralization, methyl orange being used as indicator. Calculate the percentage purity of the salt.

Q50. Calculate (i) the number of gm. of anhydrous sodium carbonate, (ii) the number of gm. of sodium bicarbonate, present together in one litre of a solution. 25cc of this solution required 11.8cc of N/10 hydrochloric acid for naturalization when phenolphthalein was used as indicator and 31.0cc of N/10 hydrochloric acid when methyl orange was used as indicator.

Back Titration

Q51. 50gm of a sample of $Ca(OH)_2$ is dissolved in 50ml of 0.5N HCl solution. The excess of HCl was titrated with 0.3N – NaOH. The volume of NaOH used was 20cc. Calculate % purity of $Ca(OH)_2$.

Q52. One gm of impure sodium carbonate is dissolved in water and the solution is made up to 250ml. To 50ml of this made up solution, 50ml of 0.1N – HCl is added and the mix after shaking well required 10ml of 0.16N – NaOH solution for complete titration. Calculate the % purity of the sample.

Q53. What amount of substance containing 60% NaCl, 37% KCl should be weighed out for analysis so that after the action of 25 ml of 0.1N $AgNO_3$ solution, excess of Ag^+ is back titrated with 5 ml of NH_4SCN solution? Given that 1 ml of NH_4SCN = 1.1 ml of $AgNO_3$.

Q54. 5g of pyrolusite (impure MnO_2) were heated with conc. HCl and Cl_2 evolved was passed through excess of KI solution. The iodine liberated required 40 mL of $\frac{N}{10}$ hypo solution. Find the % of MnO_2 in the pyrolusite.

Q55. 1.64 g of a mixture of $CaCO_3$ and $MgCO_3$ was dissolved in 50 mL of 0.8 M HCl. The excess of acid required 16 mL of 0.25 M NaOH for neutralization. Calculate the percentage of $CaCO_3$ and $MgCO_3$ in the sample.

Q56. A mixture of $CaCl_2$ and NaCl weighing 2.385g was dissolved in water and treated with a solution of sodium oxalate which produces a precipitate of calcium oxalate. The precipitate was filtered from the mixture and then dissolved in HCl to give oxalic acid which when titrated against 0.2M $KMnO_4$ consumed 19.64 mL of the latter. What was percentage by mass of $CaCl_2$ in the original sample?

Q57. An acid solution of a $KReO_4$ sample containing 26.83 mg of combined rhenium was reduced by passage through a column of granulated zinc. The effluent solution, including the washings from the column, was then titrated with 0.10 N $KMnO_4$. 11.45 mL of the standard permanganate was required for the re-oxidation of all the rhenium to the perrhenate ion, ReO_4^-. Assuming that rhenium was only element reduced. What is the oxidation state to which rhenium was reduced by the Zn column.
(Atomic mass of Re = 186.2)

Q58. H_2O_2 is reduced rapidly by Sn^{2+}, the products being Sn^{4+} & water. H_2O_2 decomposes slowly at room temperature to yield O_2 & water. Calculate the volume of O_2 produced at 20°C & 1.00 atm when 200 g of 10.0 % by mass H_2O_2 in water is treated with 100.0 ml of 2.00 M Sn^{2+} & then the mixture is allowed to stand until no further reaction occurs.

Q59. A mixture containing As_2O_3 and As_2O_5 required 20.1 ml of 0.05N iodine for titration. The resulting solution is then acidified and excess of KI was added. The liberated iodine required 1.1113g hypo $(Na_2S_2O_3 . 5H_2O)$ for complete reaction. Calculate the mass of the mixture. The reactions are
$$As_2O_3 + 2I_2 + 2H_2O \rightarrow As_2O_5 + 4H^+ + 4I^-$$
$$As_2O_5 + 4H^+ + 4I^- \rightarrow As_2O_3 + 2I_2 + 2H_2O$$

Q60. A sample of $MnSO_4 . 4H_2O$ is strongly heated in air which gives Mn_3O_4 as residue.
(i) The residue is dissolved in 100 ml of 0.1N $FeSO_4$ containing H_2SO_4.
(ii) The solution reacts completely with 50ml of $KMnO_4$ solution.
(iii) 25 ml of $KMnO_4$ solution used in step (ii) requires 30 ml of 0.1N $FeSO_4$ solution for the complete reaction.
Find the weight of $MnSO_4.4H_2O$ in the sample.

PROFICIENCY TEST

Q.1 *Fill in the blanks with appropriate items :*

1. The number of water molecules in 0.5 mol of barium chloride dihydrate is _____.

2. 20ml of 0.1 M $H_2C_2O_4 \cdot 2H_2O$ (oxalic acid) solution contains oxalic acid equal to _____ moles.

3. The volume of 1.204×10^{24} molecules of water at 4°C is _____.

4. 0.2 mol of ozone (O_3) at N.T.P. will occupy volume _____ L.

5. The balancing of chemical equation is based upon _____.

6. 2 gm of hydrogen will have same number of H atoms as are there in _____ g hydrazine (NH_2–NH_2).

7. The mass of x atoms of element = $\dfrac{.........x}{N_A}$.

8. The moles of x atoms of a triatomic gas = $\dfrac{x}{N_A} \times$ _____.

9. The amount of Na_2SO_4 which gives 9.6 gm of SO_4^{2-} is _____.

10. The 44 mg of certain substance contain 6.02×10^{20} molecules. The molecular mass of the substance is _____.

11. The mass of 1×10^{22} molecules of $CuSO_4 \cdot 5H_2O$ is _____.

12. The atomic mass of iron is 56. The equivalent mass of the metal in $FeCl_2$ is _____ and that in $FeCl_3$ is _____.

13. The sulphate of a metal M contains 9.87% of M. The sulphate is isomorphous with $ZnSO_4 \cdot 7H_2O$. The atomic mass of M is _____.

14. A binary compound contains 50% of A (at. mass = 16) & 50% B (at. mass = 32). The empirical formula of the compound is _____.

15. 10.6 g of Na_2CO_3 react with 9.8 g of H_2SO_4 to form 16 g of Na_2SO_4 & 4.4 g CO_2. This is in accordance with the law of _____.

16. 3 g of a salt (m. wt. 30) are dissolved in 250 ml of water. The molarity of solution is _____.

17. 0.5 mole of $BaCl_2$ are mixed with 0.2 mole of Na_3PO_4 the maximum number of mole of $Ba_3(PO_4)_2$ formed are _____.

18. The Eq. weight of Na_2HPO_4 when it reacts with excess of HCl is _____.

19. The mole fraction of solute in 20% (by weight) aqueous H_2O_2 solution is _____.

20. A metallic oxide contains 60% of the metal. The Eq. weight of the metal is _____.

21. The number of gm of anhydrous Na_2CO_3 present in 250 ml of 0.25 N solution is _____.

22. _____ ml of 0.1 M H_2SO_4 is required to neutralize 50 ml of 0.2 M NaOH solution.

23. The number of mole of water present in 90 g H_2O are _____.

24. The concentration of K^+ ion in 0.2 M $K_2Cr_2O_7$ solution would be _____.

25. 280 ml of sulphur vapour at NTP weight 3.2 g . The Mol. formula of the sulphur vapour is _____.

Q.2 *True or False Statements :*

1. Equal volumes of helium and nitrogen under similar conditions have equal number of atoms.

2. The smallest particle is a substance which is capable in independent existence is called an atom.

3. The number of formula units in 0.5 mole of KCl is 6.02×10^{23}.

4. 22.4 L of ethane gas at S.T.P. contains H atoms as are present in 3 gram molecules of dihydrogen.

5. Molarity of pure water is 55.5.

6. A 20% solution of KOH (density = 1.02 g/ml) has molarity = 3.64.

7. In a mixture of 1 g C_6H_6 & 1 g C_7H_8, the mole fraction of both are same.

8. 1 mole of $C_{12}H_{22}O_{11}$ contains 22 hydrogen atoms.

9. $KClO_4$ & $KMnO_4$ are isomorphous in nature.

10. Mass of 3.01×10^{23} molecules of of methane is 8 gm.

11. A hydrocarbon contains 86% C. 448 ml of the hydrocarbon weighs 1.68 g at STP. Then the hydrocarbon is an alkene.

12. 6.023×10^{54} e^{-s} weigh one kg.

13. An oxide of metal M has 40% by mass of oxygen. Metal M has relative atomic mass of 24. The empirical formula of the oxide is MO.

14. 5 g of a crystalline salt when rendered anhydrous lost 1.8 g of water. The formula weight of the anhydrous salt is 160. The number of molecules of water of crystallisation in the salt is 5.

15. Number of valence e^{-s} in 4.2 g of N^{3-} is 24 N_A.

16. The equivalent mass of $KMnO_4$ in alkaline medium is molar mass divided by five.

17. The equivalent mass of $Na_2S_2O_3$ in its reaction with I_2 is molar mass divided by two.

18. In a reaction, H_2MoO_4 is changed to MoO_2^+. In this case, H_2MoO_4 acts as an oxidising agent.

19. $KBrO_3$ acts as a strong oxidising agent. It accepts 6 electrons to give KBr.

20. 0.1 M sulphuric acid has normality of 0.05 N.

21. The reaction, $2H_2O_2 \longrightarrow 2H_2O + O_2$ is not an example of a redox reaction.

22. The disproportionation reaction,
$$2Mn^{3+} + 2H_2O \longrightarrow MnO_2 + Mn^{+2} + 4H^+$$
is an example of a redox reaction.

23. The oxidation number of hydrogen is always taken as + 1 in its all compounds.

24. The increase in oxidation number of an element implies that the element has undergone reduction.

25. The oxidation state of oxygen atom in potassium super oxide is $-\dfrac{1}{2}$.

MIDDLE GAME

Q1. A sample of calcium carbonate contains impurities which do not react with a mineral acid. When 2 grams of the sample were reacted with the mineral acid, 375 ml of carbon dioxide were obtained at 27°C and 760 mm pressure. Calculate the % purity of the sample of $CaCO_3$?

Q2. One gram of an alloy of aluminium and magnesium when heated with excess of dil. HCl forms magnesium chloride, aluminium chloride and hydrogen. The evolved hydrogen collected over mercury at 0°C has a volume of 1.2 litres at 0.92 atm pressure. Calculate the composition of the alloy.

Q3. 10 gm of a mixture of anhydrous nitrates of two metal A & B were heated to a constant weight & gave 5.531 gm of a mixture of the corresponding oxides. The equivalent weights of A & B are 103.6 & 31.8 respectively. What was the percentage of A in the mixture.

Q4. 50ml of a solution, containing 0.01 mole each Na_2CO_3, $NaHCO_3$ and NaOH was titrated with N-HCl. What will be the titre readings if
(a) only Ph is used as indicator.
(b) only MeOH is used as indicator from the beginning.
(c) MeOH is added after the first end point with Ph.

Q5. Chrome alum $K_2SO_4 . Cr_2(SO_4)_3 . 24 H_2O$ is prepared by passing SO_2 gas through an aqueous solution of $K_2Cr_2O_7$ acidified with dilute sulphuric acid till the reduction is complete. The alum is crystallized followed by filtration/centrifugation. If only 90% of the alum can be recovered from the above process, how much alum can be prepared from 10kg of $K_2Cr_2O_7$? Give the number of moles of electrons supplied by SO_2 for reducing one mole of $K_2Cr_2O_7$.

Q6. 25 mL of a solution containing HCl was treated with excess of M/5 KIO_3 and KI solution of unknown concentration where I_2 liberated is titrated against a standard solution of 0.021M $Na_2S_2O_3$ solution whose 24 mL were used up. Find the strength of HCl and volume of KIO_3 solution consumed.

Q7. A 10g sample of only CuS and Cu_2S was treated with 100 mL of 1.25 M $K_2Cr_2O_7$. The products obtained were Cr^{3+}, Cu^{2+} and SO_2. The excess oxidant was reacted with 50 mL of Fe^{2+} solution. 25 ml of the same Fe^{2+} solution required 0.875M acidic $KMnO_4$ the volume of which used was 20 mL. Find the % of CuS and Cu_2S in the sample.

Q8. A substance of crude copper is boiled in H_2SO_4 till all the copper has reacted. The impurities are inert to the acid. The SO_2 liberated in the reaction is passed into 100 mL of 0.4 M acidified $KMnO_4$. The solution of $KMnO_4$ after passage of SO_2 is allowed to react with oxalic acid and requires 23.6 mL of 1.2 M oxalic acid. If the purity of copper is 91%, what was the weight of the sample.

Q9.. A 1.87gm. sample of chromite ore($FeO.Cr_2O_3$) was completely oxidized by the fusion of peroxide. The fused mass was treated with water and boiled to destroy the excess of peroxide. After acidification the sample was treated with 50ml. of 0.16M Fe^{2+}. In back titration 2.97 ml of 0.005 M barium dichromate was required to oxidize the excess iron (II). What is the percentage of chromite in the sample?

Q10. 0.6213 g of sample contains an unknown amount of As_2O_3. The sample was treated with HCl resulting in formation of $AsCl_3(g)$ which was distilled into a beaker of water. The hydrolysis reaction is as follows

$$AsCl_3 + 2H_2O \rightarrow HAsO_2 + 3H^+ + 3Cl^-.$$

The amount of $HAsO_2$ was determined by titration with 0.04134 M I_2, requiring 23.04 mL to reach the equivalence point. The redox products in the titration were H_3AsO_4 and I^-. Find the amount of $KMnO_4$ needed to oxidize As in As_2O_3 to its maximum possible oxidation state in acidic medium.

Q11. A sample of steel weighing 0.6 gm and containing S as an impurity was burnt in a stream of O_2, when S was converted to its oxide SO_2. SO_2 was then oxidized to SO_4^{--} by using H_2O_2 solution containing 30ml of 0.04 M NaOH. 22.48 ml of 0.024 M HCl was required to neutralize the base remaining after oxidation. Calculate the % of S in the sample.

Q12. Sulfur dioxide is an atmospheric pollutant that is converted to sulfuric acid when it reacts with water vapour. This is one source of acid rain, one of our most pressing environmental problems. The sulfur dioxide content of an air sample can be determined as follows. A sample of air is bubbled through an aqueous solution of hydrogen peroxide to convert all of the SO_2 to H_2SO_4

$$H_2O_2 + SO_2 \longrightarrow H_2SO_4$$

Titration of the resulting solution completes the analysis. In one such case, analysis of 1550 L of Los Angeles air gave a solution that required 5.70 ml of 5.96×10^{-3} M NaOH to complete the titration. Determine the number of grams of SO_2 present in the air sample.

Q13. 1.4 g of a complex $[Co(NH_3)_x] Cl_3$ was treated with 50 mL of 2N NaOH solution and boiled. Ammonia gas evolved was passed through 50 mL of 1N H_2SO_4. After the reaction was over, excess acid required 37.2 mL of 0.5 N NaOH. Calculate

(i) The percentage of ammonia in the sample.   (ii) The value of x in the formula.

Q14. 3.3 gm of a sample of Anhydrous $CuSO_4$ was dissolved in water and made to 250ml. 25 ml of this solution after taking usual precautions was treated with a little excess of KI solution. A white ppt. of Cu_2I_2 and iodine was evolved. The iodine so evolved required 24.6 ml of hypo solution containing 20gm of $(Na_2S_2O_3 \cdot 5H_2O)$ per litre. What is the purity of $CuSO_4$ solution.

Q15. A certain sample of coal contained some iron pyrite (FeS_2) – a pollution causing impurity. When the coal was burned iron(II) was oxidised and SO_2 was formed. The SO_2 was reacted with NaOH when sodium sulphite and water was formed. On a particular fay 10^3 kg of coal was burned and it required 4 litres of 5M NaOH for the treatment of SO_2. What was the percentage of pyrite in the coal. What was the percentage of sulphur in the coal.

Q16. Calculate the % of MnO_2 in a sample of pyrolusite ore, 1.5 g which was made to react with 10 g. of Mohr's salt $(FeSO_4.(NH_4)_2SO_4. 6H_2O)$ and dilute H_2SO_4. MnO_2 was converted Mn^{2+}. After the reaction the solution was diluted to 250 ml and 50 ml of this solution, when titrated with 0.1 N $K_2Cr_2O_7$, required 10 ml of the dichromate solution.

Q17. Chlorine dioxide (ClO_2), has been used as a disinfectant in air conditioning systems. It reacts with water according to the reaction: $ClO_2 + H_2O \longrightarrow HClO_3 + HCl$

In an experiment, a 10.0 L sealed flask containing ClO_2 and some inert gas at 300 K and 1.0 atmosphere pressure is opened in a bath containing excess of water and all ClO_2 is reacted quantitatively. The resulting solution requried 200 mL 0.9 M NaOH solution for naturalization. Determine mole fraction of ClO_2 in the flask.

Q18. Consider the following reactions: $XeF_2 + F_2 \longrightarrow XeF_6$

and $XeF_6 + (-CH_2-CH_2)_n \longrightarrow (-CH_2-CH_2-)_n \longrightarrow (-CH_2-CH_2-) + HF + XeF_4$

Determine mass of F_2 (g) required for preparation of 1.0 kg fluorinated polymer.

Q19. 2.0 g of a sample containing NaCl, NaBr and some inert impurity is dissolved in enough water and treated with excess of $AgNO_3$ solution. A 2.0 g of precipitate was formed. Precipitate on shaking with aqueous NaBr gain 0.76 g of weight. Determine mass percentage of NaCl in the original sample.

Q20. 2.725 g of a mixture of $K_2C_2O_4$, KHC_2O_4 and $H_2C_2O_4 \cdot 2H_2O$ is dissolved in 100 mL H_2O and its 10mL portion is titrated with 0.1 N HCl solution. 20 mL acid was required to reach the equivalence point. In another experiment, 10mL portion of the same stock solution is titrated with 0.1 N KOH solution. 20 mL of base was required to reach the equivalence point. Determine mass percentage of each component in the mixture.

Q21. A 0.127 g of an unsaturated oil was treated with 25 mL of 0.1 M ICl solution. The unreacted ICl was then treated with excess of KI. Liberated iodine required 40 mL 0.1 M hypo solution. Determine mass of I_2 that would have been required with 100.0 g oil if I_2 were used in place of ICl.

Q22. The CO in a 20.3 L sample of gas was converted to CO_2 by passing the gas over iodine pentoxide heated to 150^0C. $I_2O_5(s) + 5CO(g) \longrightarrow 5CO_2(g) + I_2(g)$. The iodine distilled at this temperature and collected in a vessel containing 8.25 ml of 0.011 M $Na_2S_2O_3$. The excess $Na_2S_2O_3$ was back titrated with 2.16 ml of 0.00947 M I_2 solution. Calculate the number of milligrams of CO per litre of the sample.

Q23. The chromate ion may be present in waste from a chrome plating plant. It is reduced to insoluble chromium hydroxide by dithionate ion in basic medium $S_2O_4^{2-} + Cr_2O_4^{2-} \longrightarrow SO_3^{2-} + Cr(OH)_3$. 100 ml of water require 387 gm of $Na_2S_2O_4$. Calculate molarity and normality of CrO_4^{2-} in waste water. Also express concentration in ppm of Na_2CrO_4.

Q24. A gas mixture was passed at the rate of 2.5 L/min. through a solution of NaOH for a total of 64 minutes. The SO_2 in the mixture was retained as sulphite ion: $SO_2(g) + 2OH^- \longrightarrow SO_3^{2-} + H_2O$. After acidification with HCl, the sulphite was titrated with 4.98 mL of 0.003125 M KIO_3.
$IO_3^- + SO_3^- + HCl \longrightarrow ICl_2^- + SO_4^{2-} + H_2O$. If density of the mixture is 1.2 gm/lt, calculate concentration of SO_2 in ppm.

Q25. The arsenic in a 1.223 gm sample of a pesticide was converted to H_3AsO_4 by suitable treatment. The acid was then neutralized and exactly 40 ml of 0.08 M $AgNO_3$ was added to precipitate the arsenic quantitavely as Ag_3AsO_4. The excess Ag^+ in the filterate required 11.27 ml of 0.1 M KSCN as $Ag^+ + SCN^- \longrightarrow AgSCN$ (s) Calculate the percent As_2O_3 in the sample.($As_2O_3 = 198$)

Q26. 5 gm of bleaching powder was suspended in water and volume made up to half a litre. 20 ml of this suspension when acidified with acetic acid and treated with excess of potassium iodide solution liberated iodine which required 20 ml of a decinormal hypo solution for titration. Calculate percentage of available chlorine in bleaching powder.

Q27. 25 mL of a 0.107M H_3PO_4 was titated with a 0.115M solution of a NaOH solution to the end point identified by the colour change of the indicator, bromocresol green. This required 23.1 mL. The titration was repeated using phenolphthalein indicator. This time, 25 mL of same H_3PO_4 solution required 46.8 mL of same NaOH solution. What is the coefficient 'n' in the equation
$$H_3PO_4 + nOH^- \rightarrow nH_2O + [H_{(3-n)}PO_4]^{n-} \text{ for each reaction?}$$

Q28. 1 gm sample of $KClO_3$ was heated under such conditions that a part of it decomposed according to the equation   (1) $2KClO_3 \longrightarrow 2 KCl + 3O_2$
and remaining underwent change according to the equation. (2) $4KClO_3 \longrightarrow 3 KClO_4 + KCl$
If the amount of O_2 evolved was 146.8 ml at S.T.P., calculate the % of weight of $KClO_4$ in the residue.

Q29. Methyl t-butyl ether (MTBE) is a carbon-based compound that has replaced lead - containing materials as the principal antiknock ingredient in gasoline. Today's gasoline contains about 7% MTBE by mass. MTBE is produced from isobutene by the following reaction:
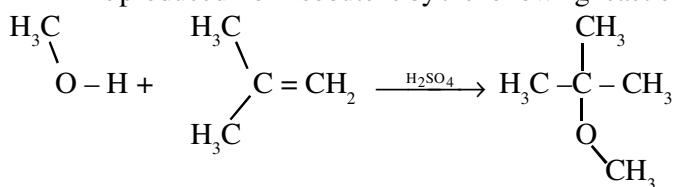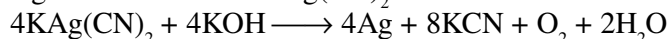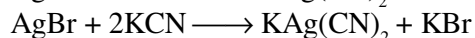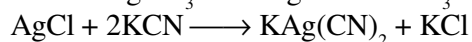

Methanol   Isobutene   MTBE
 CH_4O C_4H_8 $C_5H_{12}O$
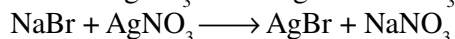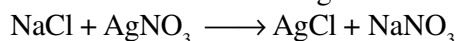
Approximately 2 billion pounds of MTBE are produced each year at a cost of about 10 ¢ per pound. Assume that you are a chemist working for a company that sold 750 million pounds of MTBE last year.
(a) If the synthesis has a reaction yield of 86%, how much isobutene was used to produce the MTBE?

(b) You have improved the synthesis of MTBE so that the yield of the reaction increases from 86% to 93%. If the company uses the same mass of isobutene for next year's production, how many pounds of MTBE will the company sell if it uses your new process?

(c) Assuming that the price of MTBE does not change, how much more money will the company make next year because of your work?

Q30. A mixture of NaCl and NaBr weighing 3.5084 gm was dissolved and treated with enough $AgNO_3$ to precipitate all of the chloride and bromide as AgCl and AgBr. The washed precipitate was treated with KCN to solubilize the silver and the resulting solution was electrolyzed. The equations are :

$$NaCl + AgNO_3 \longrightarrow AgCl + NaNO_3$$
$$NaBr + AgNO_3 \longrightarrow AgBr + NaNO_3$$
$$AgCl + 2KCN \longrightarrow KAg(CN)_2 + KCl$$
$$AgBr + 2KCN \longrightarrow KAg(CN)_2 + KBr$$
$$4KAg(CN)_2 + 4KOH \longrightarrow 4Ag + 8KCN + O_2 + 2H_2O$$

After the final step was complete, the deposit of metallic silver weighed 5.5028 gm. What was the composition of the initial mixture.

Q31. Phosphorus is essential for plant growth, and it is often the limiting nutrient in aqueous ecosystems. However, too much phosphorus can cause algae to grow at an explosive rate. This process, known as eutrophication, robs the rest of the ecosystem of essential oxygen, often destroying all other aquatic life. One source of aquatic phosphorus pollution is the HPO_4^{2-} used in detergents in sewage plants. The simplest way to remove HPO_4^{2-} is to treat the contaminated water with lime, CaO, which generates Ca^{2+} and OH^- ions in water. The phosphorus precipitates as $Ca_5(PO_4)_3OH$.

(a) Write the balanced equation for CaO dissolving in water.

(b) Write the balanced equation for the precipitation reaction.

(c) How many kilograms of lime are required to remove all the phosphorus from a 1.00×10^4 L holding tank filled with contaminated water that is 0.0156 M in HPO_4^{2-}?

Q32. It was desired to neutralize a certain solution prepared by mixing KCl and hydrobromic acid. Titration of 10ml of this solution with 0.1M $AgNO_3$ solution required 50ml of the latter for the complete precipitation of the halides. The resulting precipitate when filtered, washed and dried weighed 0.771 gm. How much 0.1M NaOH must have been used for the neutralization of 10ml of the solution.

Q33. The element Se, dispersed in a 5.0 ml sample of detergent for dandruff control, was determined by suspending the sample in warm, ammonical solution that contain 45.0 ml of 0.020 M $AgNO_3$.

$$6Ag^+ + 3Se(s) + 6NH_3 + 3H_2O \longrightarrow 2Ag_2Se(s) + Ag_2SeO_3(s) + 6NH_4^+$$
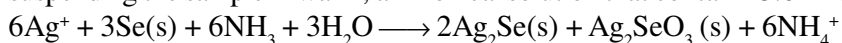
The mixture was next treated with excess nitric acid which dissolves the Ag_2SeO_3 but not the Ag_2Se. The Ag^+ from the Ag_2SeO_3 and excess $AgNO_3$ consumed 16.74 ml of 0.0137 N KSCN in a Volhard titration. How many milligrams of Se were contained per millilitre of sample.

Q34. In the presence of fluoride ion, Mn^{2+} can be titrated with MnO_4^-, both reactants being converted to a complex of Mn(III). A 0.545 g sample containing Mn_3O_4 was dissolved and all manganese was converted to Mn^{2+}. Titration in the presence of fluoride ion consumed 31.1 ml of $KMnO_4$ that was 0.117 N against oxalate.

(a) write a balanced chemical equation for the reaction, assuming that the complex is MnF_4^-.

(b) what was the % of Mn_3O_4 in the sample?

Q35. $CuSO_4$ reacts with KI in an acidic medium to liberate I_2 $2CuSO_4 + 4KI \longrightarrow Cu_2I_2 + 2K_2SO_4 + I_2$. Mercuric periodate $Hg_5(IO_6)_2$ reacts with a mixture of KI & HCl according to the following equation:

$$Hg_5(IO_6)_2 + 34KI + 24 HCl \longrightarrow 4K_2HgI_4 + 8I_2 + 24 KCl + 12 H_2O$$

The liberated iodine is titrated against $Na_2S_2O_3$ solution; 1 ml of which is equivalent to 0.0499 gm of $CuSO_4 \cdot 5H_2O$. What volume in ml of $Na_2S_2O_3$ solution will be required to react with the I_2 liberated from 0.7245 gm of $Hg_5(IO_6)_2$?

Given Mol. wt. of $Hg_5(IO_6)_2 = 1448.5$ gm/mol; Mol. wt. of $CuSO_4 \cdot 5H_2O = 249.5$ gm/mol

ANSWER KEY

EASY RIDE
Acid Base Titration

Q1. 0.381 g   Q2. V = 157.8 ml   Q3. V = 25 mL   Q4. 6.608 g/litre   Q5. (i) 0.569N, (ii) 50

Q6. 0.0176M   Q7. 3.78g   Q8. 200 mL   Q9. 11.92 g/litre   Q10. 470 mL

Q11. KOH = 35%, $Ca(OH)_2$ = 65%   Q12. 8.67   Q13. 20.72 %

Q14. $MgCO_3$ = 52.02%, $CaCO_3$ = 47.98 %   Q15. 83.33   Q16. 2.63%   Q17. 0.575 gm

Q18. % of NH_4Cl = 57.5%, % of NaCl = 42.5%

Q19. 3.198 g HCl/litre, 6.974 g KCl/litre

Q20. 0.06gm; 0.0265gm

Redox Titration

Q21. + 3   Q22. zero   Q23. 0.588 N   Q24. 337 mL   Q25. 22.5gm   Q26. 0.1M

Q27. 0.254gm/lt   Q28. V = 31.68 ml   Q29. 41.53%   Q30. 600 L MnO_4^- solution

Q31. 0.15 N   Q32. 7.5 ml   Q33. Fe^{3+} = 0.02M; MnO_4^- = 0.016 M; H^+ = 0.568 M; Mn^{2+} = 0.004M;

SO_4^{2-} = 0.02M; K^+ = 0.02M, ClO_4^- = 0.6M

Q34. 1.176 gm   Q35. 6.07 ≈ 6   Q36. FeO = 13.34%; Fe_2O_3 = 86.66%

Q37. 33.33 ml ; 1.486 gm   Q38. $H_2C_2O_4 \cdot 2H_2O$ = 14.35%, $KHC_2O_4 \cdot H_2O$ = 81.71%

Q39. 94.38%   Q40. 27.27%

Double titration

Q41. 0.424 gm; 0.21gm   Q42. 23.2 gm, 22.28gm   Q43. 0.06gm; .0265gm

Q44. 36.85 g/litre   Q45. 56.7%   Q46. 4.24 g/L; 5.04 g/L   Q47. 39.85%; 60.15%

Q48. 9.31 g/litre   Q49. 90.0%   Q50. (i) 5.003 g/litre, (ii) 2.486 g/litre

Back Titration

Q51. 1.406%   Q52. 90.1%   Q53. 0.1281 g   Q54. 0.174g; 3.48%

Q55. $MgCO_3$ = 52.02% , $CaCO_3$ = 47.98%   Q56. 45.7% $CaCl_2$ Q57. –1

Q58. 4.67L   Q59. 0.25g   Q60. 1.338gm

PROFICIENCY TEST

Q.1

1.	6.02×10^{23}	2.	2×10^{-3} mol	3.	36 ml	4.	4.48 L
5.	Laws of conservation of mass			6.	16 gm	7.	GAM
8.	1/3	9.	14.2 gm	10.	44 g mol^{-1}	11.	4.13 g
12.	44.8 L	13.	24.3	14.	A_2B	15.	Conservation of mass
16.	0.4	17.	0.1	18.	M/2	19.	0.1168
20.	12	21.	3.3125 g	22.	50	23.	5
24.	0.4 M	25.	S_8				

Q.2

1.	False	2.	False	3.	False	4.	True
5.	True	6.	True	7.	False	8.	False
9.	True	10.	True	11.	True	12.	False
13.	True	14.	True	15.	False	16.	False
17.	False	18.	True	19.	True	20.	False
21.	False	22.	True	23.	False	24.	False
25.	True						

MIDDLE GAME

Q1. 76.15%   Q2. Al = 0.546 g; Mg = 0.454 g   Q3. 51.6%   Q4. 20ml, 40ml, 20ml

Q5. 30.55kg, 6 electrons   Q6. $V_{KIO_3} = 0.42$ mL, [HCl] = 0.02N, 0.73 gm/lt

Q7. 57.4% CuS, 42.6% Cu_2S Q8. 5 gm   Q9. 15.8%   Q10. 0.06 gm

Q11. 1.7613%   Q12. 1.087×10^{-3}gm   Q13. (a) 38.13%; (b) x = 6

Q14. 95.9%   Q15. 60%, 320gm   Q16. 59.48%   Q17. 44.335%

Q18. 3.04 kg   Q19. 33.15%   Q20. 27.9%, 50.92%, 21.18%   Q21. 100g

Q22. 0.2424 mg/lt   Q23. 0.0445 N; 0.0148 M; 2400 ppm   Q24. 10.375ppm

Q25. 5.594% As_2O_3 Q26. 35.5% available Cl_2

Q27. For Bromocresol, n = 1; For Phenolphthalein n = 2   Q28. 49.8%

Q29. (a) 2.52×10^{11} gm; (b) 811 million pounds; (c) 6.1 million dollars

Q30. NaCl = 67%; NaBr = 33%   Q31. 14.56 Kg   Q32. 12.02 ml   Q33. 7.95mg/ml

Q34. 40.77%   Q35. 40 ml $Na_2S_2O_3$ solution.

ANSWERS OF STOICHIOMETRY: MOLE II
EX: MIDDLE GAME

Q1.76.15%   Q2. Al = 0.546 g; Mg = 0.454 g   Q3. 51.6%   Q4. 20ml, 40ml, 20ml

Q5. 30.55kg, 6 electrons   Q6. V_{KIO_3} = 0.42 mL, [HCl] = 0.02N, 0.73 gm/lt

Q7. 57.4% CuS, 42.6% Cu_2S Q8. 5 gm   Q9. 15.8%   Q10. 0.06 gm

Q11. 1.7613%   Q12. 1.087×10^{-3}gm   Q13. (a) 38.13%; (b) x = 6

Q14. 95.9%   Q15. 60%, 320gm   Q16. 59.48%   Q17. 44.335%

Q18. 3.04 kg   Q19. 33.15%   Q20. 27.9%, 50.92%, 21.18%   Q21.100g

Q22. 0.2424 mg/lt   Q23. 0.0445 N; 0.0148 M; 2400 ppm   Q24. 10.375ppm

Q25. 5.594% As_2O_3 Q26. 35.5% available Cl_2

Q27. For Bromocresol, n = 1; For Phenolphthalein n = 2   Q28. 49.8%

Q29. (a) 2.52×10^{11} gm; (b) 811 million pounds; (c) 6.1 million dollars

Q30. NaCl = 67%; NaBr = 33%   Q31. 14.56 Kg   Q32. 12.02 ml   Q33. 7.95mg/ml

Q34. 40.77%   Q35. 40 ml $Na_2S_2O_3$ solution.