Notes of Inorganic chemistry

B.Sc - II nd yr (4th Sem)

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CHEMISTRY OF LANTHANIDE ELEMENTS

* Lanthanide :-

The series involving the filling of 4f - orbitals following lanthanum, La (z = 57) is called lanthanide.

The elements present in the series are called lanthanides.

Their are fourteen elements in this series starting with cerium (z = 58) and ending with lutetium, Lu (z = 71)

These lanthanides are also sometimes refferred to as lanthanons.

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The important general characteristics of lanthanides are discussed below a table :-

Atomic No.	Name	Symbol	Electronic configuration	Density (g/ml)	Oxidation state	Colour	(B.M)
57	Lanthanum	La	$[Xe]\ 4f^0\ 5d^1\ 6s^2$	6.17	+3	Colourless	0
58	Cerium	Ce	$[Xe]\ 4f^2\ 5d^0\ 6s^2$	6.77	+3, +4	Colourless	2.54
59	Praseodymium	Pr	$[Xe]\ 4f^3\ 5d^0\ 6s^2$	6.78	+3, +4	Green	3.58
60	Neodymium	Nd	$[Xe]\ 4f^4\ 5d^0\ 6s^2$	7.00	+2, +3, +4	Lilac	3.62
61	Promethium	PM	$[Xe]\ 4f^5\ 5d^0\ 6s^2$	7.20	+3	Pink	2.68
62	Samarium	Sm	$[Xe]\ 4f^6\ 5d^0\ 6s^2$	5.93	+2, +3	Yellow	0.84
63	Europium	Eu	$[Xe]\ 4f^7\ 5d^0\ 6s^2$	5.24	+2, +3	Pale pink	3.60
64	Gadolinium	Gd	$[Xe]\ 4F^7\ 5d^1\ 6s^2$	7.95	+3	Colourless	7.94
65	Terbium	Tb	$[Xe]\ 4f^9\ 5d^0\ 6s^2$	8.33	+3, +4	Pale pink	9.72
66	Dysprosium	Dy	$[Xe]\ 4f^{10}\ 5d^0\ 6s^2$	8.56	+3, +4	Yellow	10.65
67	Holmium	Ho	$[Xe]\ 4f^{11}\ 5d^0\ 6s^2$	8.76	+3	Pale yellow	10.60
68	Erbium	Er	$[Xe]\ 4f^{12}\ 5d^0\ 6s^2$	9.16	+3	Pink	9.57
69	Thulium	Tm	$[Xe]\ 4f^{13}\ 5d^0\ 6s^2$	9.35	+2, +3	Pale green	7.63
70	Ytterbium	Yb	$[Xe]\ 4f^{14}\ 5d^0\ 6s^2$	7.01	+2, +3	Colourless	4.50
71	Lutetium	Lu	$[Xe]\ 4f^{14}\ 5d^1\ 6s^2$	9.74	+3	Colourless	0

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* Physical Properties :-

i.) Ionisation energies :-

The lanthanides have fairly low Ionisation energies. The first Ionisation energies are of the order of 560 KJ Mol^{-1} and second Ionisation energies are of the order of 1150 KJ Mol^{-1}

ii.) Melting and boiling points :-

Lanthanides have fairly high melting and boiling points. However, the melting and boiling points do not show any regular trend as we move from La to Lu in the series. Therefore, melting and boiling points of Eu and Yb are low as compared to the values for the lanthanide elements.

iii.) Density :-

The Density of lanthanides are low which range between

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6.7 to 9.74 g cm^{-3}. However, there is no definite trend in the density values of lanthanides with increase in atomic number.

v.) Electronegativity values :-

The electronegativity values of lanthanides are quite close to those of alkali and alkaline earthmetals. Therefore, lanthanides are expected to form Ionic compound.

* Oxidation states :-

The common oxidation states of all the lanthanides +3.

i.) Ce and Tb exhibit +4 oxidation states. Ce^{4+} : $[Xe]4f^{0}$
Tb^{4+} : $[Xe]4f^{7}$.

ii.) Eu and Yb exhibit +2 oxidation states. Eu^{2+} : $[Xe]4f^{7}$
Yb^{2+} : $[Xe]4f^{14}$

iii.) La, Gd and Lu exhibit only +3 oxidation states.

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* Colour and Spectral Properties :-

Pure lanthanide metals are silvery white but most of the tripositive ion are coloured both in solid state and in aquous solution. The colour of lanthanide metal ions depend upon the number of unpaired electrons in f-orbitals. This anomalous behaviour about the colours of lanthanide metal ions due to absorption certain wavelength in visible region. The absorption depends upon the energy required to excite an electron from one energy level to other i,e f-f-transition. Some colourless ions such as Ce^{3+} and Yb^{3+} show strong absorption in ultra-violet region. As a result, the absorption bands are usually sharp.

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* Magnetic Properties :-

The magnetic property of a substance due to presence of paired or unpaired electrons.

Dimagnetic substance :- The substance has all the electrons in paired state it is called as as dimagnetic substance.

Paramagnetic substance :- The substance containing one or more un-paired electrons, it is called as paramagnetic substance.

⇒ The magnetic behaviour of a substance can be expressed in terms of the magnetic moment. The value of magnetic moment depends upon the number of un-paired electrons. The larger number of unpaired electrons, the higher is the magnetic moment.

Thus the moment of lanthanide ions can be calculated from

$$\mu = g\sqrt{J(J+1)}$$

where g is lande splitting factor for the electron and is

$$g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$$

* Calculation of magnetic moment of Yb^{3+} ion :-

$Yb : [Xe]\ 4f^{14}\ 6s^2$

+3 +2 +1 0 -1 -2 +3

(↿↿↿↿↿↿↿)

$$S = \frac{1}{2} \times 1 = \frac{1}{2}$$

$$L = 3$$

$$J = (L+S) \text{ to } (L-S)$$

$$= \left(3+\frac{1}{2}\right) - \left(3-\frac{1}{2}\right)$$

$$= \frac{7}{2} \text{ to } \frac{5}{2}$$

$$J = \frac{7}{2}$$

since, $g = 1 + \frac{J(J+1) + S(S+1) - L(L+1)}{2J(J+1)}$

$$g = 1 + \frac{\frac{7}{2}\left(\frac{7}{2}+1\right) + \frac{1}{2}\left(\frac{1}{2}+1\right) - 3(3+1)}{2 \times \frac{7}{2}\left(\frac{7}{2}+1\right)}$$

$$g = \frac{8}{7}$$

$$\mu = \frac{8}{7}\sqrt{\frac{7}{2}\left(\frac{7}{2}+1\right)}$$

$$\boxed{\mu = 4.54 \text{ BM}}$$

$$\mu = \sqrt{n(n+2)} \quad \because n = 1$$

$$= \sqrt{1(1+2)}$$

$$= \sqrt{3}$$

$$\boxed{\mu_s = 1.73 \text{ B.M}}$$

* Lanthanide contraction :-

This small steady decrease in Ionic or atomic sizes of the lanthanide elements with increase in atomic number is called the lanthanide contration.

Consequences of lanthanide contraction :-

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i) Size of lanthanide ions :-
Their is regular decrease in the ionic radii of lanthanides.

ii) Electronegativity :-
There is slight regular increase in the electro-negativity of the trivalent ions.

iii) Electrode potential values :-
There is a small but smooth increase in standard electrode potential values. ε° for the process.

$$M^{3+} + 3e^- \longrightarrow M$$

* Reactivity of Lanthanides :-

All the lanthanides are highly electropositive metals and have almost similar chemical reactivity. The lanthanides are in general more reactive than d-block elements. some characteristics -

i) They tarnish readily on exposure to air.

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ii) All react with water slowly in cold but rapidly on heating liberating hydrogen and forming $Ln(OH)_3$

iii) All these combine with hydrogen at 200 - 300 °C giving LnH_3

iv) They also combine with halogens, oxygen and sulpher.

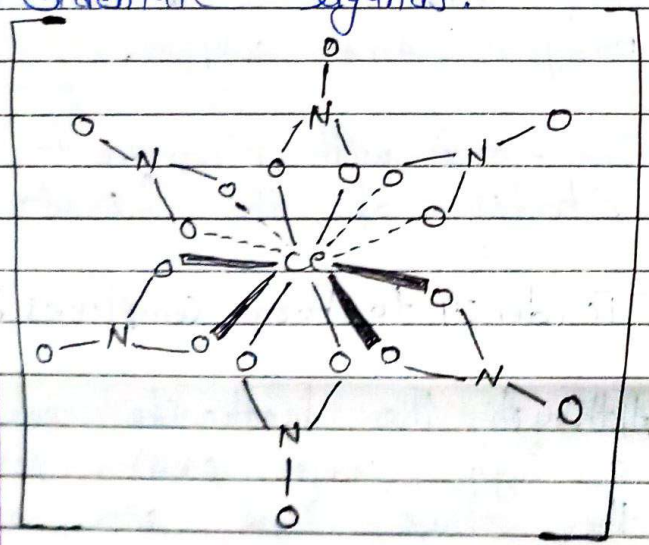
v) They react with nitrogen to form nitrides of the formula LnN.

* Tendency to Form Complexes :-

Although the lanthanide ions have a high charge (+3), yet they have large size of their ions. As a result, they have low charge density and therefore, they have very less tendency to form complexes.

However form complexes with chelating ligands such as acetylacetone, oximes, EDTA

Ce^{4+} ion forms stronger complex than Ce^{3+} ion. Ce^{4+} ion forms the dianionic complexes $[Ce(NO_3)_6]^{2-}$ in non-aqueous medium N_2O_4. In this complex coordination number of ce is 12. NO_3^- ion behaves as a bidentate ligands.



12-coordinated structure of $[Ce(NO_3)_6]^{2-}$

* OCCURRENCE OF LANTHIDES

i.) Monazite :-

It is the most important minerals containing lanthanides. It is essentially a lanthanide orthophosphate. Some monazite deposits contain appreciable amount of thorium ions also.

ii.) Bastnaesite :-

It is a mixed fluoro-carbonated with composition $M^{3+}CoF_6$ where M is La or Ln. Its large deposite are found in California, Sweden and new mexico.

iii) Cerite :-

It contains silicates of Ce, La, Pr and Nd and occur in sweden and Norway e.g. Githate, Xenotime, Gadolinite containing yttrium earths, Ce, Th.

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* ISOLATION OF LANTHANIDES

Monazite is the best known mineral containing the lanthanides. It is a mixture of phosphates $LnPO_4$ i,e lanthanium phosphate. It contains silicates of thorium, zirconium and titanium ions. The mineral is powdered and digested with hot conc^n sulphuric acid. as a result a phaste is obtained in which phosphates change into corresponding sulphates. The paste is separated by centrifugation and treated with cold water. The sulphates are more soluble in cold water pass into solution while silica, zircon are insoluble hence removed. The sol^n is neutralised with ammonium hydroxide [NH_4OH] so that thorium, zirconium and titanium are precipitated as

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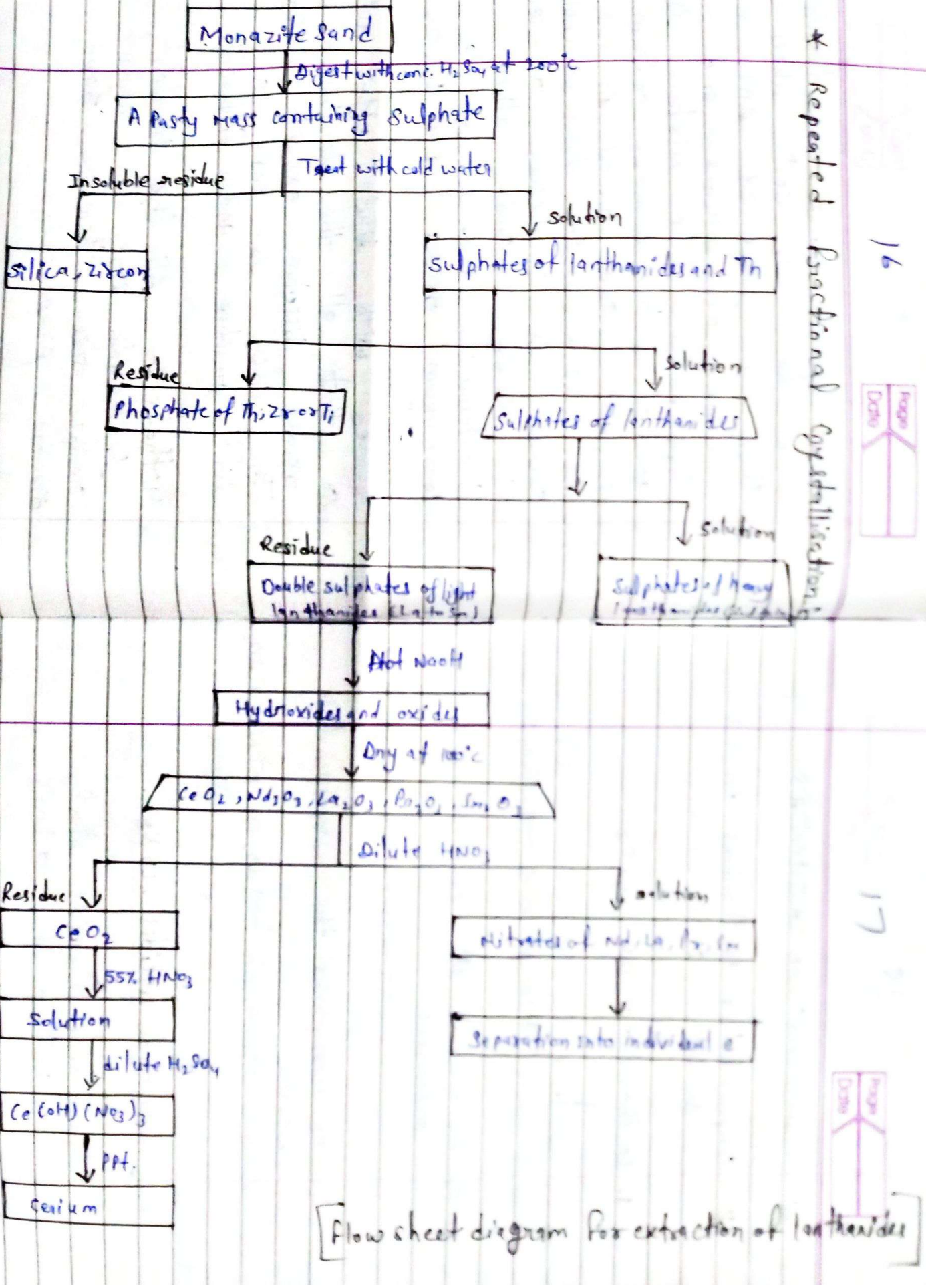
The double salts are treated with hot NaOH sol^n when they are converted into a mixture of oxides and hydroxides. The mixture is washed to remove sodium sulphate and dried in air at 373 K. In this process, cerium is completely oxidised to CeO_2 and other lanthanied are changed as lanthanium oxides i,e Ln_2O_3.

This mixture is then treated with dilute nitric acid so that all the lanthanum oxides dissolve except CeO_2. The CeO_2 is left as left residue and filtered.

Methods :- All the trivalent lanthanide ions have almost similar size, therefore have similar properties.



Flow sheet diagram for extraction of lanthanides

* Repeated fractional crystallisation

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* COMPOUNDS of LANTHANIDS

Compounds of lanthanides in +3 oxidation states :-

1. Lanthanide oxides, Ln_2O_3

i) Heating the lanthanides in air

$$4Ln + 3O_2 \rightarrow 2Ln_2O_3$$

ii) By heating the corresponding carbonates

$$Ln_2(CO_3)_3 \rightarrow Ln_2O_3 + 3CO_2$$

iii) By decomposing the corresponding nitrates

$$4Ln(NO_3)_3 \rightarrow Ln_2O_3 + 2NO_2 + 3O_2$$

2. Lanthanide halides, LnX_3.

Lanthanide fluoride, LnF_3

$$Ln^{3+} + 3F^- \rightarrow LnF_3$$

LnF_3 is insoluble in nature but fluorides of heavier lanthanide are soluble.

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3. Lanthanide nitrides :-

These are prepared by reacting lanthanides with nitrogen at high temp.

$$Ln + N_2 \xrightarrow[\text{light}]{\text{Heat}} LnN$$

LnN are hydrolysed with water

$$LnN + H_2O \rightarrow Ln(OH)_3 + NH_3$$

Compounds of lanthanides in +2 oxidation states :-

1.) Europium dicholoride, $EuCl_2$

It is prepared by reducing $EuCl_3$ with hydroden under pressure.

$$2EuCl_3 + H_2 \rightarrow 2EuCl_2 + 2HCl$$

The chemistry of Eu (II) is same as the chemistry of Ca (II) ion

e.g. →

i) Sulphates and carbonates are insoluble in water.

ii) Chlorides are insoluble in conc. HCl.

iii) Metals in liquid ammonia are also insoluble.

Compounds of lanthanides in +4 oxidation state. :-

Ce^{4+} compounds are used extensively as oxidising agent in quantitative analysis.

Cerium tetra fluoride - CeF_4

It is prepared by treating with CeF_3 with elemental fluorine at room temp.

$$2CeF_3 + F_2 \longrightarrow 2CeF_4$$

It is white compound.

Isolation of lanthanides. methods.

ii) Fractional precipitation :-

In a mixture of lanthanide salt, when a small amount of precipitating agent is added. the substance with low solubility product will precipitate most rapidly.

Ex Addition of solution of sodium hydroxide to the solution of lanthanide nitrates, precipitate of $Lu(OH)_3$ are obtain First. (low value solubility product) and precipitate of $La(OH)_3$ are obtain last (high value solubility product.) redissolving the precipitates and then precipitating agent a number of time possible have complete separation.

iii) Complex Formation :-

Complexing agent EDTA forms well known complex with lanthanide ion with small size of lanthanide ion. EDTA form stable complex.

e.g :- Lu^{3+} ion form most stable comple

with EDTA due to its small size
In acidic medium least stable
Salt complex with EDTA due to its
small size.
addition small amount of oxalic acid
will precipitate the lanthanide
ion e.g Ce^{3+}, Pr^{3+} and Nd^{3+}

(iv) Ion exchange Method :-

Ion exchange method is based upon
following Factors.

a) Size of hydrated lanthanide ion $[Ln^{3+}]$
increasing order of hydrous lanth
anide ion.

$Lu^{3+} < Yb^{3+} < ---- < La^{3+}$

Smaller in the size of lanthanide
ion more will be its hydration
therefore increasing order of size
hydrated ion

$La^{3+} < Ce^{3+} < ---- Lu^{3+}$

Smaller in the size of lanthanide
Hydrated ion more strongly
it is bound to the resin
eg. attachment of Lu^{3+} ion resin
will be least due to large size

of hydrated lutetium Lu^{3+}

ii) Exchange of protons :-

Synthetic re-
sin containing -COOH or $-SO_3H$ group
come in contact with lanthanide
ion $[Ln^{3+}]$ exchange of protons take
place as

$Ln^{3+} + 3H^+ - resin \rightarrow Ln[resin]_3 + 3H^+$ (prod
n)

Chemistry of Actinides Element:

Actinides:- The fourteen elements which follow actinium from thorium ($z=90$) to lawrencium ($z=103$) in the periodic table are called Actinides.

These are analogous to lanthanides and involve the filling of 5f orbitals. As in case of lanthanides, the name of the series is after the name of the preceding element actinium, with which these element closely resemble

These are called Actinons.

General characteristics of Actinides:-

The general electronic configuration of actinides may be writtern as $[Rn]\,5F^{1-14}\,6d^{0-1}\,7s^2$

Element	Symbol	Atomic number	Electronic- Configuration.
Actinium	Ac	89	$[Rn]\,6d^1 7s^2$
Thorium	Th	90	$[Rn]\,5f^1 6d^1 7s^2$
Protactinium	Pa	91	$[Rn]\,5f^2 6d^1 7s^2$
Uranium	U	92	$[Rn]\,5f^3 6d^1 7s^2$
Neptunium	Np	93	$[Rn]\,5f^4 6d^1 7s^2$
plutonium	Pu	94	$[Rn]\,5f^5 6d^1 7s^2$
Americium	Am	95	$[Rn]\,5f^7 6d^0 7s^2$
curium	Cm	96	$[Rn]\,5f^7 6d^1 7s^2$
Berkelium	Bk	97	$[Rn]\,5f^9 6d^0 7s^2$
californium	Cf	98	$[Rn]\,5f^{10} 6d^0 7s^2$
Einsteinium	Es	99	$[Rn]\,5f^{11} 6d^0 7s^2$
fermium	Fm	100	$[Rn]\,5f^{12} 6d^0 7s^2$
Mendelevium	Md	101	$[Rn]\,5f^{13} 6d^0 7s^2$
Nobelium	No	102	$[Rn]\,5f^{14} 6d^0 7s^2$
Lawrencium	Lr	103	$[Rn]\,5f^{19} 6d^1 7s^2$

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Physical Properties :-

(i) Melting and boiling points :-

The melting and boiling points of actinides are moderately high but they are considerably lower than those of transition - element.

(ii) Density :- The densities of actinides first increase and then decrease as shown in fig.

(iii) Heat of fusion and heat of Vaporisation :- The heat of fusion and vaporisation are measured only for a few elements. The heat vaporisation, in general decrease from Th to Am.

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3) Oxidation States :- Actinides show +2, +3, +4, +5 and +6 oxidation states. However, +3 oxidation state is most common among all the actinides.
The different oxidation states of actinide element are given in Table.

All the actinides have an oxidation state +3 like lanthanum But this is not always the most stable oxidation state in actinides.

The most stable oxidation state of the element upto uranium is the involving all the valence electrons.

for example, the most stable oxidation states of Th, Pa and U are
Th (+4), Pa (+5) and U (+6)

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(4) Ionic Radii and Actinide contraction:-

Like lanthanides, actinides also show actinide contraction. The size of the atom or ion of actinides decrease regularly along the series with the increase in atomic number from actinium to lawrencium.

This steady decrease in the ionic radii with the increase in atomic number is called actinide contraction.

The actinide contraction is due to the imperfect shielding of one 5f electron by another in the same subshell.

(5) Magnetic Properties:-

The magnetic properties of actinides are lesser than the theoretical predicted

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values. This is attributed to the fact that 5f electron of actinides are more exposed to crystal field and therefore are less effectively shielded.

6. Colour of Ions:-

Actinides ions are generally coloured. The colour of actinide ions depend upon the number of 5f-electrons. The ions containing no 5f-electrons, or seven 5f-e's are colourless.

Ac^{3+}	f^0	colourless
U^{3+}	f^3	red
Np^{3+}	f^4	blue or purple
Pu^{3+}	f^5	voilet
Am^{3+}	f^6	Pink
Cm^{3+}	f^7	colourless
Th^{4+}	f^0	colourless
Pa^{4+}	f^1	colourless
U^{4+}	f^2	green
Np^{4+}	f^3	Yellow-green
Pu^{4+}	f^4	Orange
Am^{4+}	f^5	Pink
Cm^{4+}	f^6	Pale-yellow.

The interpretation of f-f transitions of actinides are similar to those of f-f transitions of lanthanides. However, because the 5f e⁻s in actinides are more exposed than the 4f electron in lanthanides.

7) formation of complexes:-

Like lanthanides, actinides also form complexes. However, actinides have greater tendency to form complexes in comparison to lanthanides.

This is because of higher charge and smaller size of their ions.

The general tendency to complex formation is controlled by ionic size and charge and decrease.

$M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$

8. Reactivity:- The actinides are very reactive metals. The direct reactions of actinides with oxygen, halogens and acids are similar to those of lanthanides. They react with hydrogen to form non-stoichiometric hydrides.

9) compounds of Actinides:-

The actinide metals are electropositive and reactive. The reactivity increases with increase in atomic number.

Actinides form many compound with non metals.

Dioxides:-

$UO_2CO_3 \xrightarrow{Heat} UO_3 + CO_2$

$2UO_2(NO_3)_2 \cdot 6H_2O \rightarrow 2UO_3 + 4NO_2 + O_2 + 6H_2O$

$3UO_3 \xrightarrow{800-900^\circ C} U_3O_8 + \frac{1}{2}O_2$

Halides :- The actinides form halides range from AcX_6 to AcX_3

$AcX_6 + 2H_2O \longrightarrow AcO_2X_2 + 4HX$

occurrence and isolation of actinide elements :-

All the actinide elements have unstable nuclei and undergo radioactive decay. Among these, the half lives of ^{232}Th, ^{235}U, ^{238}U and possibly of ^{244}Pu are such that they have remained on the earth since the formation of solar system.

Let us briefly discuss the occurrence and isolation of U from its natural source and some other elements obtained from U.

The trihalides are known from actinide ranging from U → Cf :-

These compound show similar behaviour to lanthanide trihalides.

Complexes :-

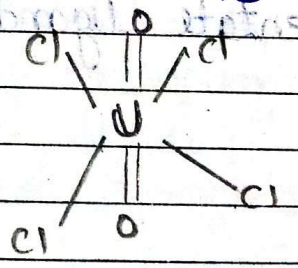
Like lanthanides, actinide also from complexes. Actinide have a greater tendency to from complex because of higher nucleas change and smaller size of their atom. Complex formed by actinide. For Eg :- M^{4+}, and Pu^{4+} from very strong anionic complexes.

The degree of complex formation in actinides decreases in the order.

$M^{4+} > MO_2^{2+} > M^{3+} > MO^{2+}$

for Eg :-

$[U^{VI}O_2Cl_4]^{2+}$, $[UO_2(OOCCH_3)_2I]_2$



Outchedral $[UO_2Cl_4]^{2-}$

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* Extraction by Organic solvents:- As mentioned above, the MO_2^{2+} ions can be extracted from nitrate solution into Organic solvents. The M^{4+} ions can be extracted into TBP in kerosens from 6m nitric acid solution. The M^{3+} can be extracted from 10 to 16 M nitric acid.

* Comparision of Lanthanide and Actinide series:-

(a) Points of similarities:-

i) Oxidation state of +3 is predominant in both the series.

ii) In both the series of orbitals are being progressively filled.

iii) Just like lanthanides contraction we have actinide contraction because 5f electrons have still poor shielding capacity as compared of 4f electron.

v) They have low electronegativities and are very reactive.

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vi) Actinides like lanthanides show ion-exchange behaviour.

(b) Points of differences:-

Inspite of a number of point of similarities b/w the two series there are some points of difference which arise mainly due to the difference in the nature of 4f and 5f orbitals in relation to the other nearby orbitals. The importants points of differences b/w lanthanides and actinides are listed in.

* Comparasion of d-block Elements with f-block Elements:-

The d-block elements donot resemble much with the elements of the f-block because the electrons enter penulimate shell in case of d-block elements and ante-penulimate shell in case of f-block elements. Therefor, d-orbitals project out and electron residing in them are strongly influenced

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by the nature of the ligands surrounding the metal atom or ion, i.e. d-electrons can interact strongly with their surrounding.

i) Size:-
The size of the atoms and ions of d-blocks elements are relatively smaller than those of the f-block elements

ii) Ionization of energies:-
The first ionization energy value of d-block elements are much higher as compared to those of f-blocks elements.

iii) Basic formation:-
The elements of d-block from complexes easily as oxides and hydroxide of d-blocks elements are less basic than those of f-block element

iv) Complex formation:-
The elements of d-block from complexes easily

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as compared to f-blocks elements. The latter mainly form metal chelates with strong chelating agents.

v) Reactions with unsaturated hydrocarbons:-
Both d- and f-blocks element react with unsaturated hydrocarbon such as $Lu(C_5H_6)_3$ olefins and cyclopentadines. The former form π-type of complexes while the latter form salts such as $Lu(C_5H_5)_3$ known as lanthanides cyclopentadienides.

vi) Magnetic moment values:-
In case of d-block elements especially for the first transition series magnetic properties are simple interpret and the magnetic cyclopentadienides. from spin only:-

Spin magnetic moment = $2\sqrt{s(s+1)}$.
Where, s = half no. of unpaired electrons. In case of f-blocks elements

the magnetic properties are quite difficult to interpret. Their magnetic moment values are calculated by taking into consideration spin as well as orbital contribution by using a more complex

$$\mu = \sqrt{4S(S+1) + L(L+1)}$$

vii) Electronic spectra:-

Electronic spectra of salts and complexes of d-blocks elements show broad bond, while those of f-block elements exhibit sharp almost line-like bonds.

Theory of Qualitative and Quantative Inorganic Analysis:-

* Qualitative analysis:→

Quantitative analysis deals with the identification of various constituents present in a given material. for Eg:- Zinc blends Contains zinc and sulphur.

i) Electropositive radical or cations:-
It is usualy a metallic part such as Na^+, Fe^{3+}, or Cu^{2+} non-metallic cation is NH_4^+.

ii) Electronegative radical or anion.
It is usually a non-metallic part such as Cl^-, CO_3^{2-}, NO_3^- etc.

a) Preliminary tests.
b) Wet tests for anions.
c) Wet tests for cations.

* Preliminary Tests:-

These tests give important clues regarding the identity of acid as well as basic present in a mixture some of the

Common tests are as follows:-

* Physical Examination:-

In this test, colour, smell, density and form of the mixture are examined as:-

a) Colours:-

Blue (Cu^{2+}), green (Ni^{2+}, Cu^{2+}), light green, deep green (Cr^{3+}), yellow or brown.

b) Smell:-

A pinch of the mixture moistened with water, is rubber b/w the fingers and its smell is noted as ammonical smell rotted eggs smell, vinegar smell.

c) Density:-

Heavy mixture (Pb^{2+}, Hg^{2+} or Ba^{2+}), light (Zn^{2+}, Ca^{2+}, or Mg^{2+} or Na^{+}).

d) Form:-

Form of the mixture whether it is crystalline or not give some information about the radicals as:

For Eg:- Amorphous.

2. Dry heating Test:-

Carbonates of most of the metals donot, mixture is heated in a dry test tube and the radicals are detected are form the information

a) Gas evolved:-

The evolution of these gases occurs due to decomposition of the salts on heating as:

$ZnCO_3 \longrightarrow ZnO + CO_2$

$NH_4Cl \longrightarrow NH_3 + HCl$

$MgCl_2 + H_2O \rightarrow MgO + 2HCl$

b) Water vapours:-

Appearance of water vapour on cooler portion of the test tube indicates hydrates salt such as: alums.

Eg:- Hydrated salt such as potash alum: $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$; $CuSO_4 \cdot 5H_2O$

c) Sublimate:-

Appearance of sublimate on coller portion of the test tube indicate as:

d) fusion:-
The salt melts as fuses on heating. The indicates the presence of alkali metal salt
Explanation:- Substance such as Iodine.

e) Swelling:-
Some salt's like alume borates, phosphates swell up on heating.
for Eg:-
$K_2SO_4.Al_2(SO_4)_3.24H_2O \rightarrow K_2SO_4.Al_2(SO_4)_3 + 24H_2O$

f) Decrepitation:-
Some salts like $Pb(NO_3)_2$, $Ba(NO_3)_2$. halides of Sodium and potassium on heating produce Creaking sound known as decrepitation.

(g) Colour of residue:-
from the colour of the residue left behind the following information is obtained

3) charcoal Cavity and Cobalt Nitrate Test:-
A pinch of the mixture is heated with fusion mixture (Na_2CO_3 and KNO_3) in a charcoal cavity and the changes which take place are noted as:-

Residue (hot)	Residue (cold)	
Yellow	White	Zn^{2+}
Reddish brown	Reddish brown	Cd^{2+}
Reddish brown	Yellow	Pb^{2+}
Orange	Yellow	Bi^{3+}

Eg:-
$PbO + C \rightarrow Pb + CO$
grey bead
$CuO + C \rightarrow Cu + CO$
Red scales

* Cobalt Nitrate test:-
If the residue in the charcoal cavity test is white it is moistened with a drop of cobalt nitrate and again heating.
Eg: $2Co(NO_3)_2 \rightarrow 2CoO + 4NO_2 + O_2$
$CaO + ZnO \rightarrow CoO.ZnO$
green.

$CoO + MgO \rightarrow CoO.MgO$
Pink.

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* 4. flame Test:-

A pinch of the mixture is treated with Conc. HCl and this paste is taken on a platinum wire and introduced into the non-luminous flame of Busen burner.

* 5. Borax Bead Test:-

This test is performed only on Coloured Salts. A hot platinum wire is dipped in borax and heated in the flame of Busen burner to form a transparent glassy bead. The hot bead is then touched with a Crystals of the coloured Salt and again introduced into the flame and following

$Na_2B_4O_7 \rightarrow 2NaBO_2 + B_2O_3$

$CuSO_4 + B_2O_3 \rightarrow Cu(BO_2)_2 + SO_3$

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6. Caustic Soda Test:-

A pinch of the mixture is heated with caustic soda (NaOH) Solution. The Solution of ammonia gas gives brown colour with Nessler's reagent according to the following reaction.

$NaCl + NaOH \rightarrow NaCl + NH_3 + H_2O$

$2K_2[HgI_4] + NH_3 + 3KOH \rightarrow H_2NHgO.HgI + 7KI + H_2O$

7. Dilute H_2SO_4 Test:-

A pinch of the Salt is treated with dilute Sulfuric acid when carbonates, bicarbonates, Sulpites, thisulphate and nirites get decomposed evolving specific gases.

$ZnCO_3 + H_2SO_4 \rightarrow ZnSO_4 + H_2O + CO_2$

$2KNO_2 + H_2SO_4 \rightarrow K_2SO_4 + H_2O + NO + NO_2$

8. $KMnO_4$ Test:-

A pinch of mixture is taken and warmed with dil. H_2SO_4 to expel gases released due to red^n with dil. H_2SO_4 and then $KMnO_4$ is added dropwise. The decolourination of $KMnO_4$ indicates the produced reagent.

$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$
$2NaCl + H_2SO_4 + O \rightarrow Na_2SO_4 + H_2O + Cl_2$

q. Conc. H_2SO_4 Test:-

Many salts particularly chlorides, bromides, iodides nitrate, acetates and oxalate get decomposed on heating with conc. H_2SO_4 only producing certain specific gases as:-

$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$

$\begin{matrix} COONa \\ | \\ COONa \end{matrix} + H_2SO_4 \rightarrow Na_2SO_4 + CO_2 + CO + H_2O$

* WET TESTS for acid Radicals:-

After having detected the acid radicals by preliminary tests, they are confirmed by tests known as confirmatory or wet tests.

a) Water Extract:-

About 2g of the mixture is shaken with distilled water and heated if need be.

in case the mixture competely dissolved in water, then its aqueous soln is used for wet tests otherwise it is filtered and filtrate is known as water Extract.

b) Sodium Carbonate Extract:-

If the mixture is not soluble in water, its Sodium carbonate extract is prepared by the following procedure

$FeS + Na_2CO_3 \rightarrow \underset{\text{residue}}{FeCO_3} + \underset{\text{soluble}}{Na_2S}$

i) Tests for Carbonate, CO_3^{2-}:-

i) Carbonates react with dil. H_2SO_4 producing CO_2 gas.

$ZnCO_3 + H_2SO_4 \rightarrow ZnSO_4 + H_2O + CO_2\uparrow$
$Ca(OH)_2 + CO_2 \rightarrow \underset{\text{Milkiness}}{CaCO_3} + H_2O$

ii) Tests for soluble Carbonates:-

a) $MgSO_4$ Test:-

$K_2CO_3 + MgSO_4 \rightarrow \underset{\text{White ppt.}}{MgCO_3\downarrow} + K_2SO_4$

b) CaCl Test:-

$CaCl_2 + Na_2CO_3 \rightarrow \underset{\text{White ppt.}}{MgCO_3\downarrow} + K_2SO_4$

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3) Tests for sulphides, S^{2-} :-

i) Sulphides react with dil. H_2SO_4 liberating H_2S gas.

$Na_2S + H_2SO_4 \rightarrow Na_2SO_4 + H_2S\uparrow$

ii) Lead Acetate test:-

Soluble sulphide react with lead acetate soln to produce black precipitate of lead sulphide.

$Na_2S + Pb(CH_3COO)_2 \rightarrow \underset{\text{Black}}{PbS\downarrow} + 2CH_3COONa$

iii) Sodium Nitroprusside Test:-

$Na_2S + Na_2[Fe(CN)_5NO] \rightarrow Na_4[Fe(CN)_5NOS]$

Sod. nitroprusside. violet or Pink

4. Tests for sulphites, SO_3^{2-} :-

i) $Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + SO_2\uparrow + H_2O$

ii) Potassium Dichromate Test:-

SO_2 gas turns acidified potassium dichromate solution green due to the reduction of dichromate to chromimum sulphate which is green.

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$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$

5. (oncentrated sulphuric acid test:-

When the given mixture is heated with conc. H_2SO_4 different gases are involved.

(i) F^-

$CaF_2 + H_2SO_4 \longrightarrow CaSO_4 + 2HF$

(ii) Presence of chromyl chloride is involved.

$K_2CrO_4 + H_2SO_4 \longrightarrow K_2SO_4 + CrO_3 + H_2O$

(iii) Br^-

$NaBr + H_2SO_4 \rightarrow NaHSO_4 + HBr$

(iv) $C_4H_6O_6^{2-}$ gives CO gas and carbon is set free.

$[CH(OH)COOK] + H_2SO_4 \longrightarrow C + CO\uparrow + CO_2\uparrow + 2H_2O + K_2SO_4$

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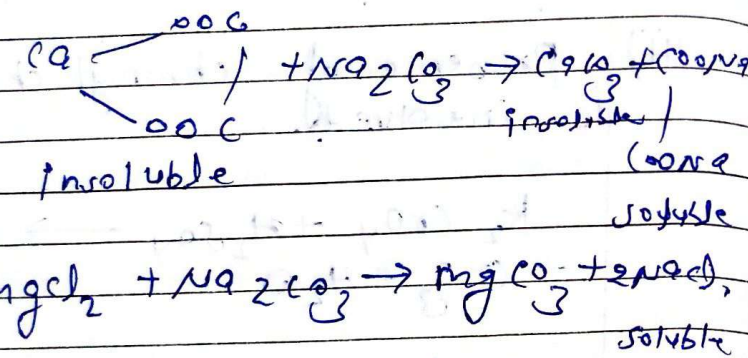
Preparation of the solutions:-

(i) water extract:-

About one gram of the powdered mixture is shaken with about 10 ml. distilled water and centrifuged.

(ii) Sodium carbonate extract:-



B. Individual acid radicals or anions

(1) Carbonate (CO_3^{2-})

(i) Carbonate react with dil. H_2SO_4.

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$ZnCO_3 + H_2SO_4 \longrightarrow ZnSO_4 + H_2O + CO_2$

Carbon dioxide turns lime water milky.

$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O$

milkiness

2. Bicarbonates (HCO_3^-)

(1) Bicarbonates react with dil H_2SO_4 to produce CO_2 gas.

$2NaHCO_3 + H_2SO_4 \rightarrow Na_2SO_4 + CO_2 + H_2O$

3. Nitrites (NO_2^-)

(1) when a mixture containing nitrite is heated with KI in the presence of dil H_2SO_4 iodine is liberated.

$2NaNO_2 + H_2SO_4 \longrightarrow Na_2SO_4 + 2HNO_2$

$2KI + 2HNO_2 + H_2SO_4 \rightarrow 2KHSO_4 + 2NO + 2H_2O + I_2$

4. Sulphites (S^{2-})

(1) Sulphides react with dilute H_2SO_4 liberating H_2S gas.

$Na_2S + H_2SO_4 \rightarrow Na_2SO_4 + H_2S$

(5) Sulphites (SO_3^{2-})

(1) sulphites react with dil. H_2SO_4 liberating SO_2 gas

$Na_2SO_3 + H_2SO_4 \rightarrow Na_2SO_4 + SO_2 + H_2O$

(6) Thiosulphites ($S_2O_3^{2-}$)

(1) Thiosulphates decolourise iodine solution.

$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

(colourless)

7. chlorides (Cl^-).

(1) To a portion of S.E add silver nitrate solution.

$NaCl + AgNO_3 \rightarrow AgCl + NaNO_3$

white ppt.

$AgCl + 2NH_4OH \rightarrow [Ag(NH_3)_2]Cl + 2H_2O$ soluble.

8. Bromides (Br^-)

(1) when $AgNO_3$ solution is added to S.E. pale yellow ppt. confirms Br^-

$AgNO_3 + NaBr \rightarrow AgBr + NaNO_3$

pale yellow.

9. Iodides (I^-)

(1) when $AgNO_3$ solution is added to S.E yellow ppt.

$NaI + AgNO_3 \rightarrow AgI + NaNO_3$

yellow ppt.

10. Nitrates (NO_3^-)

① on heating nitrates with conc H_2SO_4, brown

$2KNO_3 + H_2SO_4 \rightarrow K_2SO_4 + 2HNO_3$

(ii) Acetates (CH_3COO^-)

① Heat a little mixture with conc. H_2SO_4 : Evolution of acetic acid vapours, having vinegar like smell indicates the presence of CH_3COO^-

$2CH_3COONa + H_2SO_4 \rightarrow Na_2SO_4 + 2CH_3COOH$

12. oxalates ($C_2O_4^{2-}$)

① oxalates on heating with conc. H_2SO_4 give a mixture of CO and CO_2 gases

$Na_2C_2O_4 + H_2SO_4 \rightarrow Na_2SO_4 + H_2O + CO + CO_2$

13. Tartrates ($C_4H_4O_6^{2-}$)

① Tartrates on heating with conc. H_2SO_4 produce a mixture of CO and CO_2.

$K_2C_4H_4O_6 + H_2SO_4 \rightarrow K_2SO_4 + 2H_2O + CO + CO_2 + 2C$

charring.

14. sulphate (SO_4^{2-})

① sulphates react with barrium chloride solution to form a white ppt.

$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2NaCl$

white ppt.

15. Phosphates (PO_4^{3-})

① Acidify a portion of S.E with CH_3COOH and boil to expel CO_2 add NH_4OH and $CaCl_2$ solution.

$2Na_3PO_4 + 3CaCl_2 \rightarrow Ca_3(PO_4)_2 + 6NaCl$

white ppt.

16. Borates (BO_3^{3-})

① Heat the mixture with ethyl alcohol (1–2 ml) and conc. H_2SO_4 (1–2 ml) in a test tube.

$2NaBO_3 + 3H_2SO_4 \rightarrow 3Na_2SO_4 \rightarrow 2H_3BO_3$

$H_3BO_3 + 3C_2H_5OH \rightarrow (C_2H_5)BO_3$

$+ 3H_2O$

Ethyl borate

C. Typical combination of Acid Radicals or Anions:-

In a mixture containing more than one acid radicals sometimes there is interference in the detection of radicals.

① CO_3^{2-} in the presence of SO_3^{2-}

Carbonate cannot be tested in the presence of SO_3^{2-} both CO_2 and SO_2 cause and turn lime water milky.

$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O$

2: NO_2^- and NO_3^- in the presence of each other.

When a mixture is heated with conc. H_2SO_4 to detect NO_3^- ions, nitrite also decomposes to give NO_2

① When W.F is heated with urea (NH_2CONH_2) and dil. H_2SO_4 nitrites change to N_2 gas and get removed

$2NaNO_2 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_2$

$NH_2CONH_2 + 2HNO_2 \rightarrow N_2\uparrow + CO_2 + 3H_2O$

3. Nitrates (NO_3^-) in the presence of Bromides (Br^-) and iodides (I^-)

$2NaNO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_3$

$4HNO_3 \rightarrow 2H_2O + O_2 + 4NO_2$

light brown fumes

4. S^{2-}, SO_3^{2-}, $S_2O_3^{2-}$ and SO_4^{2-} in the presence of each other

These can be detected by the following methods:-
Add solid $CdCO_3$ to the s.E
A yellow ppt.

$$Na_2S + CdCO_3 \rightarrow CdS + Na_2CO_3$$
yellow PPt.

$$Na_2SO_4 + BaCl_2 \rightarrow BaSO_4 + 2NaCl$$
white ppt.

5. Cl^-, Br^- and I^- are present together.

The three radical can be detected from Na_2CO_3 extract. To s.E and dil H_2SO_4 and solid $NaNO_2$ boil the mixture.

$$NaI + H_2SO_4 \rightarrow NaHSO_4 + HI$$
$$2NaNO_2 + H_2SO_4 \rightarrow Na_2SO_4 + 2HNO_2$$
$$2HNO_2 + 2HI \rightarrow I_2\uparrow + 2NO + 2H_2O$$

6. oxalates ($C_2O_4^{2-}$) in the presence of carbonate (CO_3^{2-})

The mixture is treated with dil H_2SO_4 and heated until no more CO_2 gas is evolved by effervescence. A brisk effervescence with the evolution of CO_2 gas which turns lime water milky confirms oxalates.

$$Na_2C_2O_4 + H_2SO_4 \rightarrow Na_2SO_4 + H_2C_2O_4$$
$$MnO_2 + H_2SO_4 + H_2C_2O_4 \rightarrow MnSO_4 + 2H_2O + 2CO_2$$
$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$
lime water — milky

Complete