d AND f BLOCK ELEMENTS

1 INTRODUCTION

The d-block of the periodic table contains the elements of the groups 3-12 in which the d orbitals are progressively filled in each of the four long periods. The elements constituting the f -block are those in which the 4 f and 5 f orbitals are progressively filled in the latter two long periods; these elements are formal members of group 3 from which they have been taken out to form a separate f-block of the periodic table. The names transition metals and inner transition metals are often used to refer to the elements of d-and f-blocks respectively. There are mainly three series of the transition metals, 3d series (Sc to Zn), 4d series (Y to Cd) and 5d series (La to Hg, omitting Ce to Lu). The fourth 6d series which begins with Ac is still incomplete. The two series of the inner transition metals, (4f and 5f) are known as lanthanoids and actinoids respectively. Strictly speaking, a transition element is defined as the one which has incompletely filled d orbitals in its ground state or in any one of its oxidation states. Zinc, cadmium and mercury of group 12 have full d 10 configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals. However, being the end members of the three transition series, their chemistry is studied along with the chemistry of the transition metals.

2 TRANSITION ELEMENTS: INTRODUCTION

2.1. DEFINITION & ELECTRONIC CONFIGURATIONS OF ATOMS

The elements lying between s and p-block elements of the periodic table are collectively known as ***transition*** or ***transitional elements (T.E.'s)***: These elements either in their atomic state or in any of their common oxidation state have partly filled (n-1)d orbitals of (n-1)th main shell. In these elements the differentiating electron enters (n-1)d orbitals of (n-1)th main shell and as such these are called ***d-block elements.***

The valence shell configurations of these elements can be represented by $(n\text{-}1)d^{1-10}.ns^{0,\,1,\,2}$. The configurations clearly show that strictly, according to the definition of d-block elements, Cu, Ag and Au should be excluded from d-block elements, since these elements, both in their atomic state [with configuration $(n\text{-}1)d^{10}ns^{1}$] and in their +1 oxidation state [with configuration $(n\text{-}1)d^{10}$], do not have partly filled (n-l)d-orbitals. Similarly Zn, Cd and Hg which both in their atomic state $[(n\text{-}1)d^{10}ns^{2}]$ and in +2 oxidation $[(n\text{-}1)d^{10}]$ do not contain partly filled (n-1)d orbitals, should also be excluded from d-block elements. Similar is the case with Pd atom with configuration $4d^{10}5s^{0}$. Yet, in order to maintain a rational classification of elements, these elements (viz Cu, Ag, Au, Zn, Cd, Hg and Pd) are also generally studied with d-block elements.

All the d-block elements are classified into four series *viz* 3d, 4d, 5d and 6d series corresponding to the filling of 3d, 4d, 5d and 6d orbitals of (n-1)th main shell. Each of 3d, 4d and 5d series has ten elements while 6d series has at present only one element *viz* Ac_{80} whose valence shell configuration is $6d^{1}\,7s^{2}$.

2.2. IRREGULARITIES IN CONFIGURATIONS

The irregularities in the observed configurations of Cr ($3d^5 4s^1$), Cu ($3d^{10} 4s^1$), Mo ($4d^5 5s^1$), Pd ($4d^{10} 5s^0$), Ag ($4d^{10} 5s^1$) and Au ($5d^{10} 6s^1$) are explained on the basis of the concept that half-filled and completely filled d-orbitals are realtively more stable than other d-orbitals.

On the basis of the above concept it is, however, not easy to explain the irregularities found in the observed electronic configurations of the atoms of other elements, since one has to consider the net effect of so many other factors such as (i) nuclear electronic attraction (ii) shielding of one electron by several other electrons (iii) inter-electronic repulsion (iv) the exchange-energy forces etc. All these factors play an important part together in determining the final stability of an electronic configuration of an atom. It is not easy to explain why unlike Cr($3d^5 As^1$) and Mo($4d^5$ $5s^1$) should have the idealised electronic configuration ($4f^{14} 5d^4 6s^2$).

The properties of transition elements of any given period are not so much different from one another as those of the same period of non-transition elements. The reason of this fact lies in the electronic configuration of transition elements. We know that electronic configurations of transition elements is invariably $(n-1)d^{1-10}\ ns^{0 \text{ or } 1 \text{ or } 2}$ which indicates that (i) the electronic configurations of transition elements differ from one another only in the number of electrons in d orbitals in the (n-1)th shell and (ii) the number of electrons in the outermost shell, ns, is invariably 1 or 2.

3 PHYSICOCHEMICAL PROPERTIES

3.1. METALLIC CHARACTERS

All the transition elements are metals, since the number of electrons in the outermost shell is very small, being equal to 2. They are hard, malleable and ductile. They exhibit all the three types of structures: face centred cubic (fcc), hexagonal close packed (hcp) and body centred cubic (bcc). Metals of VIII and IB Groups are softer and more ductile than other metals. It appears that covalent and metallic bonding both exist in the atoms of transition metals. The presence of unfilled d-orbitals favours covalent bonding. These metals are good conductors of heat and electricity.

3.2. MELTING AND BOILING POINTS

The transition elements have very high melting and boiling points as compared to those of s and p block elements. Zn, Cd and Hg have relatively low values. The reason for these low values is that these metals have completely filled d-orbitals with no unpaired electron that may be available for covalent bonding amongst the atoms of these metals. The formation of covalent bonding occurs in the rest of the d-block elements on account of the presence of unfilled d-orbitals.

Although melting and boiling points show no definite trends in the three transition series, the metals having the highest melting and boiling points are towards the middle of each transition series.

3.3. ATOMIC (COVALENT) AND IONIC RADII

It will be seen atomic and ionic radii values decrease generally, on moving from left to right in the period. This is due to the fact that an increase in the nuclear charge tends to attract the electron cloud inwards. The atomic radii for the elements from Cr to Cu are, however, very close to one another. This is due to the fact that simultaneous addition of electron to 3d-level exercise the reverse effect by screening the outer 4s-electrons from the inward pull of the nucleus. As a result of these two opposing effects, the atomic radii do not alter much on moving from Cr to Cu. The ionic radii of M^{2+} and M^{3+} ions follow the same trends as their atomic radii. The radii of M^{2+}

ions, although somewhat smaller than that of Ca^{2+} ion (0.99Å) are comparable with it. Thus MO oxides of the transition element should be similar to CaO in many ways, although somewhat less basic and less soluble in water. Similarly the hydration energies of M^{2+} ions should be similar to but somewhat greater than that of Ca^{2+} ion. This is borne out by facts, since the hydration energy of Ca^{2+} ion is 395 kcal and the observed values of hydration energies for the elements Ti^{2+} … Cu^{2+} are between 446 kcal and 597 kcal.

The radii of M^{3+} ions are slightly greater than that of Ga^{3+} ion (0.62Å). Thus M_2O_3 oxides of transitional elements should be similar but slightly less acidic (more basic) than Ga_2O_3 and the hydration energies of M^{3+} ions should be less than 1124 kcal which is the hydration energy of Ga^{3+} ion. The observed values of hydration energies for the series Sc^{3+} … Fe^{3+} are between 947 kcal and 1072 kcal.

3.4. IONISATION POTENTIALS

The first ionisation potentials of transitional elements lie between the values of those of s- and p-block elements. The first ionisation potentials of all the transition elements lie between 5 to 10 electron volts. In case of transition elements the addition of the extra electron in the (n-1) d level provides a screening effect which shields the outer ns electrons from the inward pull of positive nucleus on the outer ns electrons. Thus the effects of the increasing nuclear charge and the shielding effect created due to the expansion of (n-1)d orbital oppose each other. On account of these counter effects, the ionisation potentials increase rather slowly on moving in a period of the first transition series.

First ionisation potentials: It is evident that the values for the first four 3d block elements (Sc, Ti, V and Cr) differ only slightly from one another. Similarly the values for Fe, Co, Ni and Cu also are fairly close to one another. The value of I_I for Zn is considerably higher. This is due to the extra-stability of $3d^{10}$ level which is completely filled in Zn-atom.

Second ionisation potentials: The second ionisation potentials are seen to increase more or less regularly with the increase of atomic number. The value of I_{II} for Cr and Cu are higher than those of their neighbours. This is due to the fact that the electronic configurations of Cr^+ and Cu^+ ions have extra stable $3d^5$ and $3d^{10}$ levels.

There is a sudden fall in the values of ionisation potentials in going from II B (Zn-group elements) to IIIA sub-group. This sudden fall is expalined on the basis that in case of IIIA group elements the electron to be removed is from a 4p-orbital which is incompletely filled, while in case of the II B group elements, the electron to be removed is from 4s-orbital which is completely filled. Thus more energy will be required to remove an electron from a filled 4s-orbital on comparison to that used to remove an electron from a 4p-orbital which is incompletely filled.

Electropositive character of transitional elements as compared to that of alkali metals and alkaline earth metals: The values of first ionisation potentials of transitional elements in most cases lie between those of s-and p-block elements. Thus the transitional elements are less electropositive than the elements of I A and II A groups. Thus, although the transitional elements do form ionic compounds, yet they do not form ionic compounds so readily as the alkali and alkaline earth metals do. Also, unlike the alkali and alkaline earth metals, the transitional elements also have a tendency to form the covalent compounds under certain conditions. Generally the compounds in which the transitional elements show a smaller valency are ionic, while those in which a higher valency is exhibited are covalent in character.

3.5. OXIDATION STATES

One of the most important property that distinguishes transition elements from s-and p-block elements is that they show variable oxidation states. s-and p-block elements have oxidiation states either equal to their group number, G or equal to (8-G). The transition elements on the other hand exhibit variable oxidation states.

This unique property is due to the fact that the energy levels of 3d, 4d and 5d orbitals are fairly close to those of 4s, 5s and 6s orbitals respectively and, therefore, in addition to ns electrons and variable number of (n-1) d electrons are also lost in getting various oxidation states.

i) ***Minimum oxidation state:*** All the transition elements with the exception of Cr, Cu, Ag, Au and Hg which have a minimum oxidation state of +1 exhibit a minimum oxidation state of +2. In most cases this +2 oxidation state arises due to the loss of two s-electrons.

ii) ***Maximum oxidation state:*** Each of the elements in groups III B to VII B can show the maximum oxidation state equal to its group number. Thus, Cr in group VIB shows a maximum oxidation state of +6 in $Cr_2O_7^{2-}$ ion. Most of the elements in VIII group show a maximum oxidation state equal to + 6. However, **Ru** and **Os** have a maximum oxidation state equal to +8 which is the highest oxidation state shown by any element.

iii) ***Relative stability of various oxidation states:*** The relative stabilities of various oxidation states of 3d-series elements can be correlated with the extra stability of $3d^0$, $3d^5$ and $3d^{10}$ configurations to some extent. Thus Ti^{4+} ($3d^0$) is more stable than Ti^{3+} ($3d^1$) and similarly Mn^{2+} ($3d^5$) is more stable than Mn^{4+} ($3d^4$). It may, however, be pointed out that such a generalisation for the relative stability of various oxidation states of 4d and 5d series elements is often rather difficult to realise.

The higher oxidation state of 4d and 5d series elements are generally more stable than those of the elements of 3d series, e.g., Mo, Te (4d series elements) and W, Re (5d-series elements) form the oxyanions: $Mo^{VI}O_4^{2-}$, $Tc^{VII}O_4^-$, $W^{VI}O_4^{2-}$, $Re^{VII}O_4^-$ which are stable and in which the transition elements concerned show their maximum oxidation states. The corresponding oxyanions of Cr and Mn namely $Cr^{VI}O_4^{2-}$ and $Mn^{VII}O_4^-$ are strong oxidising agents.

Furthermore, the highest oxidation states of second and third row elements are encountered in compounds containing the more electronegative elements *viz.* F, O and Cl. Thus for the compounds $Ru^{VIII}O_4$, $Os^{VIII}O_4$, $W^{VI}Cl_6$ and $Pt^{VI}F_6$ there are no analogs being formed by the first row elements. The lower oxidation states particularly +2 and +3 are important in the chemistry of aquated and complex ions of the 3d-series (i.e. first row) elements but these ions are not very important in the chemistry of second (i.e. 4d series) and third (5d-series) row elements. In short it may be said that in going down a sub-group the stability of the higher oxidation states increases while that of lower oxidation states decreases.

iv) ***Formation of ionic and covalent compounds:*** Transition elements cannot form ionic compounds in higher oxidation states because the loss of more than three electrons is prevented by the higher attractive force exerted (on the electrons) by the nucleus. Higher oxidation states of these metals are not formed by the actual loss of electrons but due to the formation of new hybrid orbitals involving (n-1)d, ns and np orbitals.

The transition elements form ionic bonds in the lower oxidation states and the ionic character of the bond decreases with the increase in the oxidation state. With this decrease in the ionic character of the bond the basic character of the oxides decreases, e.g. MnO (oxidatioin states of Mn = +2) is basic, MnO_2 (Mn + +4) is amphoteric and MnO_3 (Mn = +6) is acidic.

3.6. COLOUR

Ionic and covalent compounds of transition elements are usually markedly coloured, in contrast to compounds of the s and p block elements which are often white and are generally not strongly coloured. Colour is associated with in complete electron shells and the ability to promote an electron from one energy level to other. Exactly the right amount of energy to do this is obtained by absorbing the light of a particular wave length. In the transition elements, d-electrons are promoted to a higher energy level within the d-shell. This corresponds to a fairly small energy difference, and so light is absorbed in the visible region. If red light is absorbed then the transmitted light contains an excess of the other colours of the spectrum-particularly blue, so that the compound appears blue, for example Cu^{2+}'.

Illustration 1: ***Why Zn^{+2} salts are white while Ni^{2+} salts are blue***

Solution: Zn^{+2} has completely filled d-orbitals ($3d^{10}$) while Ni^{2+} has incompletely filled d-orbitals ($3d^8$)

3.7. COMPLEX FORMATION

The transition elements have an unparallel tendency to form coordination compounds with Lewis Base, i.e., with groups which are able to donate an electron pair. These groups are called ligands. A ligand may be a neutral molecule such as NH_3 or ion such as Cl^- or CN^- etc.

$Co^{3+} + 6(NH_3) \longrightarrow [Co(NH_3)_6]^{3+}$

$Fe^{2+} + 6CN^- \longrightarrow [Fe(CN)_6]^{4-}$

The reason transition elements are good in forming complexes are:

i) Small size and high effective nuclear charge

ii) Availability of low lying vacant d–orbitals which can accept lone pair of electrons donated by a ligand.

3.8. CATALYTIC PROPERTIES

Transition metals and their compounds are known to act as good catalyst due to the following reasons:

i) Due to the their variable oxidation state, they form unstable intermediate compounds and provide a new path with lower activation energy for the reaction (Intermediate compound formation theory)

ii) In some cases the finely divided metals or their compounds provide a large surface area for adsorption and the adsorbed reactants react faster due to the closer contact(Adsorption theory)

1. $TiCl_3$	Used as Ziegler – Natta catalyst
2. V_2O_5	Converts SO_2 to SO_3 in the contact process for making H_2SO_4
3. MnO_2	Used as a catalyst to decompose $KClO_3$ to give O_2
4. Fe	Used in Haber – Bosch process for making NH_3
5. $FeCl_3$	Production of CCl_4 from CS_2 and Cl_2
6. $FeSO_4$ & H_2O_2	Fenton's reagent
7. $PdCl_2$	Wacker process for the following conversion $C_2H_2 + H_2O + PdCl_2$ to $\rightarrow CH_3CHO + 2HCl + Pd$
8. Pd	For hydrogenation (Phenol → Cyclohexanol)
9. Pt/PtO	Adam catalyst used for reduction
10. Pt	$SO_2 \rightarrow SO_3$ contact process
11. Pt	Cleaning car exhaust fumes
12. Cu	In manufacture of $(CH_3)_2SiCl_2$

13. Cu/V	Oxidation of cyclohexanol
14. $CuCl_2$	Deacon process or making Cl_2 from HCl
15. Ni	Raneynickel

3.9. MAGNETIC PROPERTIES

When a substance is placed in a magnetic field of strength H, the intensity of the magnetic field in the substance may be greater than or less than H.

If the field in the substance is greater than H, the substance is paramagnetic. Thus paramagnetic materials attract lines of force and if it is free to move, a paramagnetic material will move from a weaker to a stronger part of the field. Paramagnetism arises as a result of unpaired electron in the atom. If the field in the substance is less than H, the substance is diamagnetic. They tend to repel lines of force and move from a strong to weaker part of a magnetic field. In diamagnetic substance, electrons are paired up.

It should be noted that Fe,Co and Ni are ferromagnetic. Ferromagnetic materials may be regarded as special case of paramagnetism in which the moments of individuals atoms become aligned and all point in the same direction. It is also possible to get antiferromagnetism by pairing the moments of adjacent atoms which point in opposite directions. It occurs in salts of Fe^{3+}, Mn^{2+} etc.

Paramagnetism is expressed in terms of magnetic moment, which is related to the number of unpaired electrons as follows

$\mu = \sqrt{n(n+2)}$ B.M.

n = number of unpaired electrons

B.M. = Bohr Magneton, unit of magnetic moment

More the magnetic moment more is the paramagnetic behaviour

Illustration 2: ***Calculate the magnetic moments of Fe^{2+} and Fe^{3+}***

Solution: In Fe^{2+} there are 4 unpaired electrons.

$\mu = \sqrt{4(4+2)} = \sqrt{4\times 6} = \sqrt{24} = 4.89$ B.M.

In Fe^{3+} there are 5 unpaired electrons.

$\mu = \sqrt{5(5+2)} = \sqrt{5\times 7} = \sqrt{35} = 5.91$ B.M.

Illustration3: ***Why does Mn (II) show maximum paramagnetic character amongst the bivalent ions of the first transition series?***

Solution: Mn^{+2} has maximum number of unpaired electrons.

3.10. FORMATION OF ALLOYS

As the transition elements have similar atomic sizes hence in the crystal lattice, one metal can be readily replaced by another metal giving solid solution and smooth alloys. The alloys so formed are hard and have often high melting point.

3.11. INTERSTITIAL COMPOUND

Transition metals form no. of interstitial compounds, in which they take up atoms of small size e.g. H, C and N in the vacant spaces in the their lattices. The presence of these atoms results in decrease in malleability and ductility of the metals but increases their tensile strength.

3.12 COMPOUNDS OF IRON

Ferrous sulphate (Green vitriol), $FeSO_4.7H_2O$

It is commonly known as hara Kasis.

a) **Preparation**

- i) By dissolving scrap Fe in dil. H_2SO_4
- ii) From Kipp's waste which contains ferrous sulphate with some free H_2SO_4; the latter is neutralised with scrap iron forming $FeSO_4$ and hydrogen.
- iii) By the action of air and water on iron pyrites. The solution is treated with scrap iron to remove H_2SO_4 and to reduce Fe^{3+} sulphate Fe^{2+} sulphate.

b) **Properties**

- i) Hydrated and anhydrous $FeSO_4$ are green and white in colour respectively. It is isomorphous with epsom salt, $MgSO_4.7H_2O$ and $ZnSO_4.7H_2O$. It effervesces on exposure to air.
- ii) Light green crystals of $FeSO_4$ lose water and turn brown on exposure to air, due to oxidation.
- iii) On heating at 300°C it gives anhydrous $FeSO_4$ which on further heating gives Fe_2O_3 and SO_2.
- iv) Like other ferrous salts, it takes up HNO_3 forming brown coloured double compound, $Fe(NO)SO_4$, nitroso ferrous sulphate (Ring test for nitrates).
- v) It decolourises acidified potassium permanganate and turns acidified dichromate green (reducing character).
- vi) It forms double salts with sulphates of alkali metals with general formula $R_2SO_4.FeSO_4.6H_2O$. With ammonium sulphate, it forms a double salt known as ferrous ammonium sulphate or Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$. It does not effervesce. It ionises in solution to gives Fe^{2+}, NH_4^+ and SO_4^{2-} ions.

Ferric oxide, Fe_2O_3

- i) It occurs in nature as haematite.
- ii) Fe_2O_3 is a red powder, insoluble in H_2O and not acted upon by air or H_2O
- iii) It is amphoteric in nature and reacts with acids and alkalies.
- iv) It is reduced to iron by H_2,C and CO.
- v) It is used as a catalyst in the oxidation of CO to CO_2 in the **Bosch process**.

Ferric chloride, $FeCl_3$

a) Preparation

- i) Hydrated ferric chloride ($FeCl_3.6H_2O$) can be prepared by dissolving iron, $Fe(OH)_3$ or ferric oxide in dil. HCl.
- ii) Reaction of Fe with dry Cl_2 gives anhydrous $FeCl_3$,

b) Properties

- i) Anhydrous salt is yellow, deliquescent compound and highly soluble in H_2O.
- ii) Its aqueous solution is acidic due to hydrolysis.
- iii) On heating it gives $FeCl_2$ and Cl_2.
- iv) It oxidizes H_2S to S, SO_2 to H_2SO_4, $SnCl_2$ to $SnCl_4$ and $Na_2S_2O_3$ to $Na_2S_4O_6$.

3.13. COPPER, SILVER AND GOLD

a) These metals are commonly called as coinage or currency metals. Their general electronic configuration is $(n-1)\ d^{10}\ ns^1$. These show variable valencies +1, +2 and +3.

b) Gradation in properties

- i) The nobility increases from copper to gold.

ii) The affinity of oxygen also decreases from Cu to Au.
iii) Copper forms a large number of salts followed by silver followed by gold.
iv) The ease with which the salts of these elements are reduced increases from Cu to Au.

Compounds of Copper

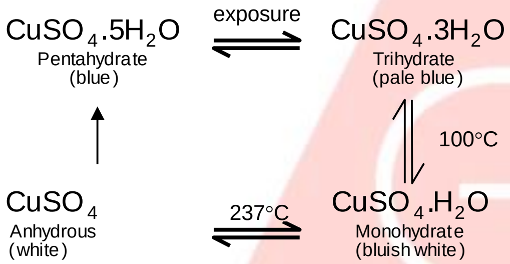
i) Copper sulphate, cupric sulphate or blue vitriol, $CuSO_4.5H_2O$.

Preparation

i) By treating copper scrap or turnings, cuprous oxide, cupric oxide or malachite with H_2SO_4.
ii) By roasting copper pyrites, $CuFeS_2$ in air.

Properties

i) It has 5 molecules of H_2O of crystallisation; all of which can be removed on heating, to form colourless $CuSO_4$ (again coloured with H_2O).
ii) At high temperature it forms cupric oxide.



iii) It forms double salts with alkali sulphates, e.g. $K_2SO_4.CuSO_4.6H_2O$
iv) When treated with NH_4OH, it first forms precipitate of cupric hydroxide copper (II) sulphate **(Schweitzer's reagent)**, used for dissolving cellulose in the manufacture of aritifical silk.
v) It reacts with KCN forming a complex compound $K_3[Cu(CN)_4]$.
vi) It liberates iodine from soluble iodides.

Uses in the preparation of **Bordeaux mixture** ($CuSO_4$ solution + lime) which is used to kill moulds and fungi on wines.

Compounds Silver

Silver Nitrate (Lunar caustic) $AgNO_3$

a) Preparation

i) By dissolving Ag in warm dil. HNO_3.

b) Properties

i) It is very soluble in H_2O and when comes in contact with organic substances (e.g. skin, clothes, etc.) it produces burning sensation and reduced to metallic silver which is white like the moon Luna hence its name Lunar caustic.
ii) On heating above its melting point it decomposes to silver.
iii) When treated with soluble halides, it forms the corresponding silver halide.
iv) When treated with alkali, it forms silver oxide which in case of NH_4OH dissolves to form complex ion.
v) It reacts with iodine and gives $AgIO_3$ and AgI (when $AgNO_3$ is in excess) or HIO_3 and AgI (when I_2 is in excess).
vi) With a very dilute solution of $Na_2S_2O_3$, it gives white precipitate which quickly changes to yellow, brown and finally black due to the formation of silver sulphide. With conc. solution of sodium thiosulphate, it does not give any precipitate.

c) **Uses** – in volumetric analysis, photography and in silvering of mirrors.

d) **Silvering of mirrors** – The process is based on the reduction of an ammonical solution of silver nitrate by some reducing agent like glucose, formaldehyde, tartarate, etc.

Silver Bromide, AgBr

a) **Preparation:** by adding $AgNO_3$ solution to soluble bromide solution

b) **Properties**

  i) It is insoluble in water and conc. acid but soluble in excess of strong solution of ammonia (cf. AgCl is soluble in dilute solution of NH_4OH, AgI is insoluble in NH_4OH solution).

  ii) Silver halides, are also soluble in KCN and hypo solutions

  iii) On heating, it melts to red liquid

  iv) It is used as the light sensitive material in photographic films. It is the most sensitive AgX to photo-reduction.

3.14. ZINC, CADMIUM AND MERCURY

a) These are the elements of group 12 having electronic configuration $(n-1)\ d^{10}\ ns^2$ and +2 oxidation state. In these elements the d-subshell is full, hence these are regarded as non-transition elements which is evident from the following characteristics.

  i) They do not show variable valency except mercury

  ii) Many of their compounds are white.

  iii) Their melting and boiling points are very low.

b) Unique structure of mercurous ion – Unlike Zn and Cd, Hg exhibits +1 as well as +2 oxidation state. Thus mercurous ion exists are Hg_2^{2+} and not as Hg^+.

c) Structure of mercurous ion – It consists of two atoms linked by a covalent and $(-Hg-Hg-)^{2+}$ and explains the diamagnetic character of mercurous ion were Hg^+ (presence of an unpaired electron in 6s orbital) and mercurous salt should have been paramagnetic.

d) Anomalous behaviour of mercury,

  i) It is liquid at ordinary temperature while Zn and Cd are solids.

  ii) It is less electropositive than hydrogen and therefore does not displace hydrogen from acids while Zn and Cd does.

  iii) It does not form hydroxide or peroxide, while Zn and Cd do so

  iv) Mercuric oxide, on heating, gives metallic mercury and oxygen while oxides of Zn and Cd are stable towards heat.

  v) $HgCl_2$ is covalent while zinc and cadmium chlorides are ionic. With NH_3, $HgCl_2$ gives a white ppt. of $Hg(NH_2)Cl$, while Zn and Cd salts from complex ions, $[M(NH_3)_4]^{2+}$.

4 INNER TRANSITION ELEMENTS

The f-block elements are known as inner transition elements because they involve the filling for inner sub-shells (4f or 5f)

Lanthanides: It consists of elements that follows lanthanum and involve the filling of 4 subshell

4.1. SOME IMPORTANT PROPERTIES OF LANTHANIDES

1. ***Electronic Configuration :***

   $[Xe]\ 4f^{n+1}\ 5d^{\circ}\ 6s^2$ or $[Xe]\ 4f^n\ 5d^1\ 6s^2$

2. ***Oxidation State:*** Lathanides exhibit the oxidation state of +3. Some of them also exhibit the oxidation state of +2 and +4.

3. ***Colouration:*** Many of the lanthanides ions are coloured in solid state as well as in solutions. The colour is due to the *f-f transition* since they have partly filled f-orbitals.
4. ***Lanthanide Contraction:*** The steady decrease in the size of lanthanide ions (M^{3+}) with the increase in atomic no. is called lanthanide contraction.
   Causes: As we move down the group from left to right in a lanthanide series, the atomic no. increases and for every proton in the nucleus the extra electron goes to 4f orbital. The 4f orbital is too diffused to shield the nucleus effectively, thus there is a gradual increase in the effective nuclear charge experienced by the outer electrons. Consequently , the attraction of the nucleus for the electrons in the outermost shell increases with the increase of atomic number, thus size decreases.

4.2. CONSEQUENCE OF LANTHANIDE CONTRACTION

1. ***Separation of Lanthanides:*** Due to the similar sizes of the lanthanides, it is difficult to separate them but due to lanthanide contraction their properties slightly vary (such as ability to form complexes). The variation in the properties is utilized to separate them.
2. ***Basic Strength of Hydroxide:*** Due to the lanthanide contraction, size of M^{3+} ions decreases and there is increase in covalent character in M–OH and hence basic character decreases.
3. ***Similarity of second and third transition series:*** The atomic radii of second row transition elements are almost similar to those of the third row transition elements because the increase in size on moving down the group from second to third transition elements is cancelled by the decrease in size due to the lanthanide contraction.

4.3. ACTINIDES

INTRODUCTION: It consists of elements that follow Actinium and involve the filling of 5f subshell. The actinoids are radioactive elements and the earlier members have relatively long half-lives, the latter ones have half-life values ranging from a day to 3 minutes for lawrencium (Z =103). The latter members could be prepared only in nanogram quantities. These facts render their study more difficult.

GENERAL CHARACTERISTICS AMND COMPARISON WITH LANTHANIDES: The actinoid metals are all silvery in appearance but display a variety of structures. The structural variability is obtained due to irregularities in metallic radii which are far greater than in lanthanoids.

The actinoids are highly reactive metals, especially when finely divided. The action of boiling water on them, for example, gives a mixture of oxide and hydride and combination with most non metals takes place at moderate temperatures. Hydrochloric acid attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers; alkalies have no action.

The magnetic properties of the actinoids are more complex than those of the lanthanoids. Although the variation in the magnetic susceptibility of the actinoids with the number of unpaired 5 f electrons is roughly parallel to the corresponding results for the lanthanoids, the latter have higher values. It is evident from the behaviour of the actinoids that the ionisation enthalpies of the early actinoids, though not accurately known, but are lower than for the early lanthanoids. This is quite reasonable since it is to be expected that when 5f orbitals are beginning to be occupied, they will penetrate less into the inner core of electrons. The 5f electrons, will therefore, be more effectively shielded from the nuclear charge than the 4f electrons of the corresponding lanthanoids. Because the outer electrons are less firmly held, they are available for bonding in the actinoids.

A comparison of the actinoids with the lanthanoids, with respect to different characteristics as discussed above, reveals that behaviour similar to that of the lanthanoids is not evident until the second half of the actinoid series. However, even the early actinoids resemble the lanthanoids in showing close similarities with each other and in gradual variation in properties which do not entail change in oxidation state.

The lanthanoid and actinoid contractions, have extended effects on the sizes, and therefore, the properties of the elements succeeding them in their respective periods. The lanthanoid contraction is more important because the chemistry of elements succeeding the actinoids are much less known at the present time

ELECTRONIC CONFIGURATION: All the actinoids are believed to have the electronic configuration of $7s^2$ and variable occupancy of the 5f and 6d subshells. The fourteen electrons are formally added to 5f, though not in thorium (Z = 90) but from Pa onwards the 5f orbitals are complete at element 103. The irregularities in the electronic configurations of the actinoids, like those in the lanthanoids are related to the stabilities of the f^0 , f^7 and f^{14} occupancies of the 5f orbitals. Thus, the configurations of Am and Cm are $[Rn]\ 5f^7 7s^2$ and $[Rn]\ 5f^7 6d^1 7s^2$. Although the 5f orbitals resemble the 4f orbitals in their angular part of the wave-function, they are not as buried as 4f orbitals and hence 5f electrons can participate in bonding to a far greater extent.

OXIDATION STATE: There is a greater range of oxidation states, which is in part attributed to the fact that the 5f, 6d and 7s levels are of comparable energies. The known oxidation states of actinoids are listed in Table 8.11. The actinoids show in general +3 oxidation state. The elements, in the first half of the series frequently exhibit higher oxidation states. For example, the maximum oxidation state increases from +4 in Th to +5, +6 and +7 respectively in Pa, U and Np but decreases in succeeding elements (Table 8.11). The actinoids resemble the lanthanoids in having more compounds in +3 state than in the +4 state. However, +3 and +4 ions tend to hydrolyse. Because the distribution of oxidation states among the actinoids is so uneven and so different for the former and later elements, it is unsatisfactory to review their chemistry in terms of oxidation states.

IONIC SIZES: The general trend in lanthanoids is observable in the actinoids as well. There is a gradual decrease in the size of atoms or M^{3+} ions across the series. This may be referred to as the actinoid contraction (like lanthanoid contraction). The contraction is, however, greater from element to element in this series resulting from poor shielding by 5f electrons.

5 APPLICATIONS OF d & f BLOCK ELMENTS

- ➔ Iron and steels are the most important construction materials. Their production is based on the reduction of iron oxides, the removal of impurities and the addition of carbon and alloying metals such as Cr, Mn and Ni. Some compounds are manufactured for special purposes such as TiO for the pigment industry and MnO_2 for use in dry battery cells.
- ➔ The battery industry also requires Zn and Ni/Cd. The elements of Group 11 are still worthy of being called the coinage metals, although Ag and Au are restricted to collection items and the contemporary UK ‘copper’ coins are copper-coated steel.
- ➔ The ‘silver’ UK coins are a Cu/Ni alloy. Many of the metals and/or their compounds are essential catalysts in the chemical industry. V_2O_5 catalyses the oxidation of SO_2 in the manufacture of sulphuric acid. $TiCl_4$ with $A1(CH_3)_3$ forms the basis of the Ziegler catalysts used to manufacture

polyethylene (polythene). Iron catalysts are used in the Haber process for the production of ammonia from N_2/H_2 mixtures.

- Nickel catalysts enable the hydrogenation of fats to proceed. In the Wacker process the oxidation of ethyne to ethanal is catalysed by $PdCl_2$. Nickel complexes are useful in the polymerisation of alkynes and other organic compounds such as benzene.
- The photographic industry relies on the special light-sensitive properties of AgBr**.**