

## Transition Elements Including Lanthanides and Actinides

### Transition elements

A transition element may be defined as an element whose atom in the ground state or ion in common oxidation state has **incomplete sub-shell, has electron 1 to 9**. It is called transition element due to fact that it is lying between most electropositive (*s*-block) and most electronegative (*p*-block) elements and represent a transition from them. The **general electronic configuration** of these element is  $(n-1)^{1 \text{ to } 10} ns^{0 \text{ to } 2}$ .

The definition of transition metal excludes *Zn, Cd* and *Hg* because they have complete *d*-orbital. Their common oxidation state is  $Zn^{++}, Cd^{++}, Hg^{++}$ . They also do not show the characteristics of transition element. *Zn, Cd, Hg* are called non typical transition element. Some **exceptional electronic configuration of transition element** are :  $Cr = 3d^5 4s^1$ ,  $Nb = 4d^4 5s^1$ ,  $Pb = 4d^{10} 5s^0$ ,  $Ag = 4d^{10} 5s^1$ ,  $Cu = 3d^{10} 4s^1$ ,  $Mo = 4d^5 5s^1$ ,  $Ru = 4d^7 5s^1$ ,  $Pt = 5d^0 6s^1$ ,  $Au = 5d^{10} 6s^1$ . These irregularities can be explain on the basis of half filled and full filled stability of *d*-orbital.

**Classification** : Transition element are classified in following series :

- (1) First transition series ( $3d$ ) = 21 to 30 i.e. *Sc* to *Zn*.
- (2) Second transition series ( $4d$ ) = 39 to 48 i.e. *Y* to *Cd*.
- (3) Third transition series ( $5d$ ) = 57 *La* and 72 – 80 *Hf* to *Hg*.
- (4) Fourth transition series or  $6d$  series = 89 *Ac* and 104 – 112 *Rf*.

So there are 39 transition element at present in the periodic table.

### General characteristics (physico-chemical properties)

(1) **The atomic and ionic radii** : The atomic radii of transition element show following trends :

(i) They lie between those of '*s*' and '*p*' block element.

(ii) In a series the atomic radii first decrease up to middle then become constant and the end of the series show a slight increase.

Firstly moving L-R effective nuclear charge predominates, up to middle it is counter balanced by shielding and after due to electron - electron repulsion slight increase take place.

(iii) Down the group atomic radii increases down the 2<sup>nd</sup> transition series only then constant up to 3<sup>rd</sup> transition series then decreases due to lanthanide contraction.

(2) **Metallic character** : All transition elements are metals. The element having maximum unpaired electron, stronger is metallic bonding as *Cr, Mo* and *W*. They have relatively high densities they are malleable,

ductile and have high tensile strength, thermal and electrical conductivity and lusture. The metal having filled d-orbital are soft metal due to weak metallic bonding *Zn, Cd* and *Hg*.

(3) **Melting and Boiling Point** : They have strong metallic bonding and hence having high melting point. The m.pt first rises to a maximum and then fall as atomic number increases. *W* has highest melting point (3683 K) among transition element *Zn, Cd* and *Hg* having low melting point due to paired electron in a subshell. *Hg* is liquid at ordinary temperature.

(4) **Density** : Transition metals having high density due to strong metallic bonding. '*Os*' having density 22.6 gm  $\text{cm}^{-3}$  where as *Sc* has lowest density i.e. 3.2 gm/c.c.

(5) **Ionization energies** : The first ionisation energy of *d*-block element is higher than those of *s*-block element and lower than that of *p*-block element. The ionisation energy of *3d* and *4d* series is irregular due to irregular size. But due to poor shielding of *4f* electron the ionisation energy across *5d* series increase rapidly.

Element	<i>Sc</i>	<i>Ti</i>	<i>V</i>	<i>Cr</i>	<i>Mn</i>	<i>Fe</i>	<i>Co</i>	<i>Ni</i>	<i>Cu</i>	<i>Zn</i>
$IE_1$ (kj / mol)	631	656	650	652	717	762	758	736	745	905

(6) **Oxidation states** : Except first member (*Sc*) and last member of series *Zn* all metals show variable oxidation state due to vacant d- orbital.

Element	Outer electronic configuration	Oxidation state
<i>Sc</i>	$3d^1 4s^2$	+ 2, + 3
<i>Ti</i>	$3d^2 4s^2$	+ 2,+ 3,+ 4
<i>V</i>	$3d^3 4s^2$	+ 2,+ 3,+ 4,+ 5
<i>Cr</i>	$3d^5 4s^1$	+ 1,+ 2,+ 3,+ 4,+ 5,+ 6
<i>Mn</i>	$3d^5 4s^2$	+ 2,+ 3,+ 4,+ 5,+ 6,+ 7
<i>Fe</i>	$3d^6 4s^2$	+ 2,+ 3,+ 4,+ 5,+ 6
<i>Co</i>	$3d^7 4s^2$	+ 2,+ 3,+ 4
<i>Ni</i>	$3d^8 4s^2$	+ 2,+ 3,+ 4
<i>Cu</i>	$3d^{10} 4s^1$	+ 1,+ 2
<i>Zn</i>	$3d^{10} 4s^2$	+ 2

**The highest oxidation state** : The highest oxidation states are formed in fluorides and oxides, since fluorine and oxygen are the most electronegative element

(i) The highest oxidation state shown by any transition element is +8. Both *Os* and *Ru* show +8 oxidation state but the most stable oxidation state is *Os* is  $\text{OsO}_4$ .

(ii) The most common oxidation state of *3d* transition metal is +2 (except *Sc*) which show +3.

(iii) Mostly ionic bonds are formed in +2 and +3 oxidation state. But higher oxidation states give covalent bonds.

(iv) Higher oxidation state are stabilized by atom of high electronegativity like *O* or *F* where as lower oxidation state are stabilized by ligands which can accept electrons from the metal through  $\pi$  bonding.

(v) Down the group stability of higher oxidation state increases while that of lower oxidation state decreases.

(vi) The relative stability strength can be estimated by sum of different ionisation energies. Least the sum more will be stability.

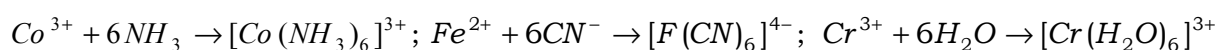
(7) **Coloured ions** : Transition metal exhibit colour due to d-d transition accordance to crystal field splitting. The electron of  $d_{xy}$ ,  $d_{yz}$  or  $d_{zx}$  orbital absorbs some energy and reflected back rest colour which is the cause of crystal or aq. solution. The ion which has unpaired electron can show its characteristics colour e.g.  $Cu^{++} \rightarrow$  Blue colour due to absorption of red colour  $Te^{++} \rightarrow$  is purple it absorbs yellow wavelength.

(8) **Magnetic property** : Due to presence of unpaired electron in  $(n - 1)$  d-orbital the most of transition metals are paramagnetic in nature. The magnetic moment of transition metal is expressed in B.M. i.e. Bohr magnetons

$$\mu_{eff} = \sqrt{n(n + 2)} \text{ B.M. where } n = \text{number of unpaired electron } \mu = \text{effective is called as spin only moment.}$$

On the basis of this formula  $Sc^{++}, Ti^{4+}$  are diamagnetic while  $Mn^{++}$  having highest  $\mu$  effective = 5.92 B.M.

(9) **Complex formation** : Transition metal ion form a large number of complexes in which central metal ion is linked to a number of ligands. A ligand may be a neutral molecule such as  $NH_3$ , or an ion such as  $Cl^-$  or  $CN^-$ .



This is because of the following characteristics properties of transition metals :

(i) They have high nuclear charge and small size i.e. charge / size ratio is large.

(ii) They have empty d-orbitals to accept the lonepairs of electron donated by ligands. The stability of complexes is increases with increase in atomic number of the element in a series and with decrease size of its atom.

(10) **Interstitials compound** : Transition metals have capability to form alloy in which it forms bond with non metal atom like  $K, H, C, B, N$ , situated in its interstitial space in their crystal lattice. These alloys are hard, rigid, less ductile & malleable. Steel and cast iron are the example.

(11) **Alloy formation** : Due to similar size they are able to form alloy with each other. They are easily miscible and forms alloy. Alloy with  $Hg$  are termed as amalgams,  $Fe$  and  $Pt$  do not form amalgams.

(12) **Non stoichiometric compounds** : Non stoichiometric compounds are those in which the chemical composition does not correspond to their ideal chemical formulae. The compounds of transition metals with  $O, S, Se, Te$ , are generally non stoichiometric and have indefinite composition. The non stoichiometry is due to :

(i) Variable valency of transition metal

(ii) Presence of defects in their solid state (structure).  $F_{0.84}O$  and  $F_{0.94}O$  and it is written as  $FeO$ .

(13) **Catalytic property** : Many transition metals and their compounds show catalytic properties. The most common being  $Fe, Pt, Ni, V_2O_5$  etc. This property is either due to their variable valency (incompleted orbitals) which enables them to form unstable intermediate compounds or due to the fact that they can provide a suitable reaction surface.

**Transition metals and their compounds as catalyst**

<b>Catalyst</b>	<b>Function</b>
$TiCl_4$	Used as <b>Natta</b> catalyst in the production of polythene
$FeSO_4 + H_2O_2$	Used as <b>Fenton's reagent</b> in the oxidation of alcohols to aldehydes.
$Ni$	<b>Raney nickel</b> in reduction processes : manufacture of hexamethylenediamine, production of $H_2$ from $NH_3$ , reducing anthraquinone to anthraquinol in the production of $H_2O_2$
$Ni$ complexes	<b>Reppé</b> synthesis (polymerisation of alkynes to give benzene, cyclooctatetraene).
$Cu$	Used in manufacturing of $(CH_3)_2SiCl_2$ used to make silicones.
$Cu/V$	Used in the oxidation of cyclohexanol/cyclohexanone mixture to acidic acid which is used to prepare Nylon-66.
$CuCl_2$	<b>Decon</b> process of making $Cl_2$ from $HCl$
$MnO_2$	Used in the decomposition of $KClO_3$ to $KCl$ and $O_2$ .
$V_2O_5$	Used in contact process of $H_2SO_4$ .
$Fe$	Promoted Fe used in the <b>Haber-Bosch</b> process of $NH_3$
$FeCl_3$	Used in the production of $CCl_4$ from $CS_2$ and $Cl_2$ .
$PdCl_2$	<b>Wacker</b> process for converting $C_2H_4$ into $CH_3CHO$ .
$Pt/PtO$	<b>Adams</b> catalyst in reduction.
$Pt$	In three stage convertors for cleaning car exhaust fumes.
$Pt/Rh$	In <b>Ostwald</b> process for $HNO_3$ from $NH_3$ .
$ZnO/CuO$	In synthesis of $CH_3OH$ from $CO$ and $H_2$ .
$Co/Fe$	In synthesis of hydrocarbons by $CO$ and $H_2$ in <b>Fischer-Tropsch</b>
Nickel Boride (P-2 catalyst)	<b>Browns</b> catalyst
$TiCl_4 + (C_2H_5)_3Al$	<b>Zeigler Natta</b> catalyst
$Pd / BaSO_4$	<b>Lindlar's</b> catalyst
$[Ph_3P]_3 RhCl$	<b>Wilkinson's</b> catalyst

(14) **Reactivity** : The d-block elements are unreactive due to the following facts :

- (i) On account of small size of their atoms, ionisation energies of d-block elements are fairly high.
- (ii) The transition metal ions are not hydrated easily.
- (iii) Due to presence of covalent bonding. These have high heats of sublimation.

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(iv) The tendency to remain unreactive is more pronounced in platinum and gold in the third transition series.

(15) **Standard electrode potential** : The standard reduction potential of all the transition elements (except *Cu* and *Hg* in *3d* series etc) is lower (negative) than that of hydrogen (taken as zero). Thus all the transition elements with negative reduction potential liberate hydrogen from dilute acids,  
 $M + 2H^+ \rightarrow M^{2+} + H_2 \uparrow$

(16) **Reducing properties** : Transition metals having negative standard reduction potential should be good reducing agents *i.e.* they should be oxidised easily to their ions.

### Some important reagents of transition elements

<b>Baeyer's reagent</b> : Dilute alkaline $KMnO_4$	<b>Schueitger reagent</b> : $[Cu(NH_3)_4]SO_4$
<b>Barfoed's reagent</b> : $Cu(CH_3COO)_2 + CH_3COOH$	<b>Nessler's reagent</b> : Alkaline solution of $K_2HgI_4$
<b>Benedict's solution</b> : Sodium citrate + $Na_2CO_3$	<b>Fehling solution A</b> : $CuSO_4$ solution
<b>Lucas reagent</b> : $HCl$ (conc.) + anhydrous $ZnCl_2$	<b>Fenton's reagent</b> : $FeSO_4 + H_2O_2$
<b>Etard's reagent</b> : $CrO_2Cl_2$	<b>Milon's reagent</b> : Solution of mercuric and mercurous nitrate
<b>Tollen's reagent</b> : Ammonical solution of $AgNO_3; [Ag(NH_3)_2]OH$	

## Lanthanides and actinides

Lanthanides and actinides are collectively called *f*-block elements because last electron in them enters into *f*- orbitals of the antepenultimate (*i.e.*, inner to penultimate) shell partly but incompletely filled in their elementary or ionic states. The name inner transition, elements is also given to them because they constitute transition series with in transition series (*d*-block elements) and the last electron enters into antepenultimate shell (*n-2*) *f*. In addition to incomplete *d*-subshell, their *f*-subshell is also incomplete. Thus, these elements have three incomplete outer shells *i.e.*, (*n-2*), (*n-1*) and *n* shells and the general electronic configuration of *f*-block elements is

$$(n-2) f^{1-14} (n-1) d^{0-10} ns^2$$

(1) **Lanthanides** : The elements with atomic numbers 58 to 71 *i.e.* cerium to lutetium (which come immediately after lanthanum  $Z = 57$ ) are called lanthanides or **lanthanones or rare earths**. These elements involve the filling of 4 *f*-orbitals. Their general electronic configuration is,  $[Xe]4f^{1-14} 5d^{0-10} 6s^2$ . Promethium (*Pm*), atomic number 61 is the only synthetic (man made) radioactive lanthanide.

### Properties of lanthanides

(i) These are highly dense metals and possess high melting points.

(ii) They form alloys easily with other metals especially iron. *e.g.* **misch metal** consists of a rare earth element (94–95%), iron (upto 5%) and traces of *S*, *C*, *Ca* and *Al*, pyrophoric alloys contain *Ce* (40–5%), *La* + neodymium (44%), *Fe* (4–5%), *Al* (0–5%) and the rest is *Ca*, *Si* and *C*. It is used in the preparation of ignition devices *e.g.*, trace bullets and shells and flints for lighters.

(iii) **Oxidation state** : Most stable oxidation state of lanthanides is + 3. Oxidation states + 2 and + 4 also exist but they revert to + 3 *e.g.*  $Sm^{2+}$ ,  $Eu^{2+}$ ,  $Yb^{2+}$  lose electron to become + 3 and hence are good reducing

agents, where as  $Ce^{4+}$ ,  $Pr^{4+}$ ,  $Tb^{4+}$  in aqueous solution gain electron to become + 3 and hence are good oxidizing agents. There is a large gap in energy of 4  $f$  and 5  $d$  subshells and thus the number of oxidation states is limited.

(iv) **Colour** : Most of the trivalent lanthanide ions are coloured both in the solid state and in aqueous solution. This is due to the partly filled  $f$ -orbitals which permit  $f-f$  transition. The elements with  $xf$  electrons have a similar colour to those of  $(14 - x)$  electrons.

(v) **Magnetic properties** : All lanthanide ions with the exception of  $Lu^{3+}$ ,  $Yb^{3+}$  and  $Ce^{4+}$  are paramagnetic because they contain unpaired electrons in the 4  $f$  orbitals. These elements differ from the transition elements in that their magnetic moments do not obey the simple “spin only” formula  $\mu_{eff} = \sqrt{n(n+2)}$  B.M. where  $n$  is equal to the number of unpaired electrons. In transition elements, the orbital contribution of the electron towards magnetic moment is usually quenched by interaction with electric fields of the environment but in case of lanthanides the 4  $f$ -orbitals lie too deep in the atom for such quenching to occur. Therefore, magnetic moments of lanthanides are calculated by taking into consideration spin as well as orbital contributions and a more complex formula

$$\mu_{eff} = \sqrt{4S(S+1) + L(L+1)} \text{ B.M.}$$

which involves the orbital quantum number  $L$  and spin quantum number  $S$ .

(vi) **Complex formation** : Although the lanthanide ions have a high charge (+3) yet the size of their ions is very large yielding small charge to size ratio i.e., low charge density. As a consequence, they have poor tendency to form complexes. They form complexes mainly with strong chelating agents such as EDTA,  $\beta$ -diketones, oxine etc. No complexes with  $\pi$ -bonding ligands are known.

(vii) **Lanthanide contraction** : The regular decrease in the size of lanthanide ions from  $La^{3+}$  to  $Lu^{3+}$  is known as lanthanide contraction. It is due to greater effect of the increased nuclear charge than that of the screening effect.

### Consequences of lanthanide contraction

(a) It results in slight variation in their chemical properties which helps in their separation by ion exchange

(b) Each element beyond lanthanum has same atomic radius as that of the element lying above it in the group (e.g.  $Zr$  145 pm,  $Hf$  144 pm);  $Nb$  134 pm,  $Ta$  134 pm ;  $Mo$  129 pm,  $W$  130 pm).

(c) The covalent character of hydroxides of lanthanides increases as the size decreases from  $La^{3+}$  to  $Lu^{3+}$ . However basic strength decreases. Thus  $La(OH)_3$  is most basic whereas  $Lu(OH)_3$  is least basic. Similarly, the basicity of oxides also decreases in the order from  $La^{3+}$  to  $Lu^{3+}$ .

(d) Tendency to form stable complexes from  $La^{3+}$  to  $Lu^{3+}$  increases as the size decreases in that order.

(e) There is a slight increase in electronegativity of the trivalent ions from  $La$  to  $Lu$ .

(f) Since the radius of  $Yb^{3+}$  ion (86 pm) is comparable to the heavier lanthanides  $Tb$ ,  $Dy$ ,  $Ho$  and  $Er$ , therefore they occur together in natural minerals.

(2) **Actinides** : The elements with atomic numbers 90 to 103 i.e. thorium to lawrencium (which come immediately after actinium,  $Z = 89$ ) are called actinides or actinones. These elements involve the filling of 5  $f$ -orbitals. Their general electronic configuration is,  $[Rn]5f^{1-14} 6d^{0-1} 7s^2$

They include three naturally occurring elements thorium, protactinium and uranium and eleven transuranium elements or transuranics which are produced artificially by nuclear reactions. They are synthetic or man made elements. All actinides are radioactive.

### Properties of actinides

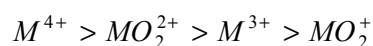
(i) **Oxidation state** : The dominant oxidation state of actinides is +3 which shows increasing stability for the heavier elements. *Np* shows +7 oxidation state but this is oxidising and is reduced to the most stable state +5. *Pu* also shows states upto +7 and *Am* upto +6 but the most stable state drops to *Pu* (+4) and *Am* (+3). *Bk* in +4 state is strongly oxidising but is more stable than *Cm* and *Am* in 4 state due to  $f^7$  configuration. Similarly, *No* is markedly stable in +2 state due to its  $f^{14}$  configuration. When the oxidation number increases to + 6, the actinide ions are no longer simple. The high charge density causes the formation of oxygenated ions e.g.,  $UO_2^{2+}$ ,  $NpO_2^{2+}$  etc. The exhibition of large number of oxidation states of actinides is due to the fact that there is a very small energy gap between 5 $f$ , 6 $d$  and 7 $s$  subshells and thus all their electrons can take part in bond formation.

(ii) **Actinide contraction** : There is a regular decrease in ionic radii with increase in atomic number from *Th* to *Lr*. This is called actinide contraction analogous to the lanthanide contraction. It is caused due to imperfect shielding of one 5  $f$  electron by another in the same shell. This results in increase in the effective nuclear charge which causes contraction in size of the electron cloud.

(iii) **Colour of the ions** : Ions of actinides are generally coloured which is due to  $f - f$  transitions. It depends upon the number of electrons in 5 $f$  orbitals.

(iv) **Magnetic properties** : Like lanthanides, actinide elements are strongly paramagnetic. The magnetic moments are lesser than the theoretically predicted values. This is due to the fact that 5  $f$  electrons of actinides are less effectively shielded which results in quenching of orbital contribution.

(v) **Complex formation** : Actinides have a greater tendency to form complexes because of higher nuclear charge and smaller size of their atoms. They form complexes even with  $\pi$ -bonding ligands such as alkyl phosphines, thioethers etc, besides EDTA,  $\beta$ -diketones, oxine etc. The degree of complex formation decreases in the order.



where  $M$  is element of actinide series. There is a high concentration of charge on the metal atom in  $MO_2^{2+}$  which imparts to it relatively high tendency towards complex formation.

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