

The *d*- and *f*-Block Elements

ANSWERS

Topic 1

1. Mn^{2+} has an electronic configuration of $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^0$. In Mn^{3+} state the electron has to be taken out from stable d^5 orbital which is half-filled and requires very high ionisation energy. In case of Fe^{2+} ion, the third electron is taken out from $3d^6$ configuration which results in more stable $3d^5$ configuration.

2. With increasing atomic number the effective nuclear charge increases after losing two electrons from *s*-orbital. The ionic size decreases which results in more stability. The stability is less in the beginning due to few electrons to lose or share.

3. Sc^{3+} has stable electronic configuration (vacant *d*-orbital), therefore Sc^{3+} is more stable than Sc^+ .

Fe^{3+} is more stable than Fe^{2+} due to half-filled *d*-orbitals.

Mn^{2+} is more stable than Mn^{3+} due to half-filled *d*-orbitals.

V^{5+} is more stable (due to vacant *d*-orbital) than V^{3+} .

4. (i) $3d^3$: Stable oxidation state will be +5 due to outer electronic configuration $3d^3 4s^2$ (+2, +3, +4, +5).

(ii) $3d^5$: Stable oxidation state will be +2 and +7 due to outer electronic configuration $3d^5 4s^2$ (+2, +3, +4, +6, +7).

(iii) $3d^8$: Stable oxidation state will be +2 due to outer electronic configuration $3d^8 4s^2$ (+2, +3, +4).

(iv) $3d^4$: Stable oxidation state will be +3 and +6 due to outer electronic configuration $3d^4 4s^2$. There is no d^4 configuration in ground state, as it becomes $3d^5 4s^1$.

5. Manganese shows oxidation state of +7 in its oxometal anion MnO_4^- which is equivalent to its group number 7. Cr in $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} shows +6 oxidation state which is equivalent to its group number 6.

6. General characteristics of transition elements.

(i) Electronic configuration - $(n-1)d^{1-10}ns^{0-2}$

(ii) Metallic character - With the exceptions of Zn, Cd and Hg, they have typical metallic structures.

(iii) Atomic and ionic size - Ions of same charge in a given series show progressive decrease in radius with increasing atomic number.

(iv) Oxidation state - Variable ; ranging from +2 to +7.

(v) Paramagnetism - The ions with unpaired electrons are paramagnetic.

(vi) Ionisation enthalpy - Increases due to increase in nuclear charge.

(vii) Formation of coloured ions - Due to unpaired electrons.

(viii) Formation of complex compounds - Due to small size and high charge density of metal ions.

(ix) They possess catalytic properties - Due to their ability to adopt multiple oxidation states.

(x) Formation of interstitial compounds.

(xi) Alloy formation.

They are called transition elements due to their incompletely filled *d*-orbitals in ground state or any stable oxidation state and they are placed between *s* and *p*-block elements. Zn, Cd and Hg have fully filled d^{10} configuration in their ground state hence may not be regarded as the transition elements.

7. The electronic configuration of the transition elements is $(n-1)d^{1-10}ns^{0-2}$. $(n-1)$ stands for penultimate shell and *d*-orbitals may have one to ten *d*-electrons and *n* denotes valence *s* or the outermost shell which can have one or two electrons. Hence the basic difference in electronic configuration of transition metals is that their penultimate shell is incomplete and progressively filled and not the valence shell.

8. (i) Paramagnetism arises from the presence of unpaired electrons, each such electron has magnetic moment associated with its spin angular momentum and orbital angular momentum. For the compounds of the first series of transition metals, the contribution of the orbital angular momentum is effectively quenched and hence is of no significance. For these, the magnetic moment is determined by the number of unpaired electrons and is calculated by using the 'spin-only' formula, i.e., $\mu = \sqrt{n(n+2)} \text{ B.M.}$

Where *n* is the number of unpaired electrons and μ is the magnetic moment in units of Bohr magneton (B.M.). A single unpaired electron has a magnetic moment of 1.73 Bohr magneton (B.M.).

(ii) Because of large number of unpaired electrons in their atoms they have stronger interatomic interactions and hence stronger metallic bonding between atoms resulting in higher enthalpies of atomisation.

(iii) Due to presence of unpaired electrons and *d-d* transitions, the transition metals are generally coloured. When an electron from a lower energy *d*-orbital is excited to a higher energy *d*-orbital, the energy of excitation corresponds to the frequency of light absorbed. This frequency generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand.

(iv) The transition metals and their compounds are known for their catalytic activity. This activity is ascribed to their ability

to adopt multiple oxidation states and to form complexes. Vanadium(V) oxide (in contact process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysts at a solid surface involve the formation of bonds between reactant molecules and atoms of the surface of the catalyst.

9. Interstitial compounds are those which are formed when small atoms like H, C or N are trapped inside the interstitial site crystal lattice of metals. They are usually non-stoichiometric and are neither typically ionic nor covalent, for example, TiC, Mn₄N, Fe₃H, VH_{0.56} and TiH_{1.7}, etc.

These do not correspond to any normal oxidation state of the metal. Because of the nature of their composition, these compounds are referred to as interstitial compounds. The principal physical and chemical characteristics of these compounds are as follows :

- They have high melting points, higher than those of pure metals.
- They are very hard, some borides approach diamond in hardness.
- They retain metallic conductivity
- They are chemically inert.

10. The variability of oxidation states, a characteristic of transition elements, arises out of incomplete filling of *d*-orbitals in such a way that their oxidation states differ from each other by unity, e.g., V^{II}, V^{III}, V^{IV}, V^V. This is in contrast with the variability of oxidation states of non-transition elements where oxidation states normally differ by a unit of two.

In the *p*-block the lower oxidation states are favoured by the heavier members (due to inert pair effect), the opposite is true in the groups of *d*-block. For example, in group 6, Mo(VI) and W(VI) are found to be more stable than Cr(VI). Thus, Cr(VI) in the form of dichromate in acidic medium is a strong oxidising agent, whereas MoO₃ and WO₃ are not.

11. Potassium dichromate is prepared from chromite, which in turn is obtained by the fusion of chromite ore (FeCr₂O₄) with sodium or potassium carbonate in free access of air. The reaction with sodium carbonate occurs as follows:

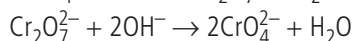
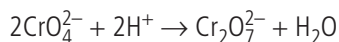
$4\text{FeCr}_2\text{O}_4 + 8\text{Na}_2\text{CO}_3 + 7\text{O}_2 \rightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{CO}_2$
The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, Na₂Cr₂O₇·2H₂O can be crystallised.

$2\text{Na}_2\text{CrO}_4 + 2\text{H}^+ \rightarrow \text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{Na}^+ + \text{H}_2\text{O}$

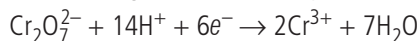
Sodium dichromate is more soluble than potassium dichromate. The latter is therefore, prepared by treating the solution of sodium dichromate with potassium chloride.

$\text{Na}_2\text{Cr}_2\text{O}_7 + 2\text{KCl} \rightarrow \text{K}_2\text{Cr}_2\text{O}_7 + 2\text{NaCl}$

Orange crystals of potassium dichromate crystallise out. The chromate and dichromate ions are interconvertible in aqueous solution depending upon pH of the solution. If pH of potassium dichromate is increased it is converted to yellow potassium chromate.

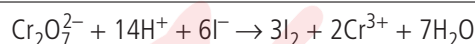
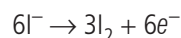
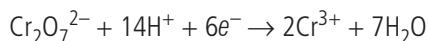


12. K₂Cr₂O₇ is a powerful oxidising agent. In dilute sulphuric acid medium the oxidation state of Cr changes from +6 to +3. The oxidising action can be represented as follows:



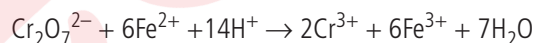
(i) Iodide : Iodide ion (I⁻) is oxidised to I₂ by the acidified solution of K₂Cr₂O₇.

Reaction :

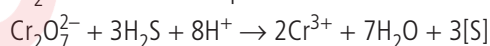


(ii) Iron(II) solution : Ferrous salts (Fe²⁺) are oxidised to ferric (Fe³⁺) salts when they are treated with acidified K₂Cr₂O₇.

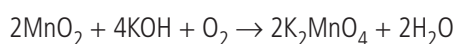
Reaction :



(iii) H₂S : H₂S is oxidised to sulphur.



13. Potassium permanganate (KMnO₄) is prepared by the fusion of a mixture of pyrolusite (MnO₂), potassium hydroxide and oxygen, first green coloured potassium manganate is formed.

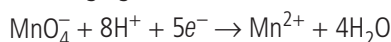


The potassium manganate is extracted by water, which then undergoes disproportionation in neutral or acidic solution to give potassium permanganate.

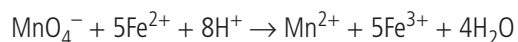
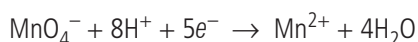
Electrolytically :



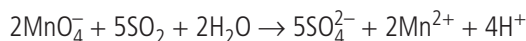
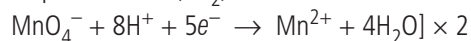
In acidic medium of dilute sulphuric acid, KMnO₄ acts as strong oxidising agent and it reacts as:



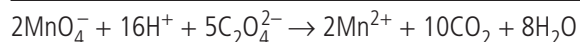
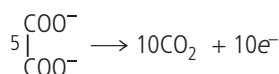
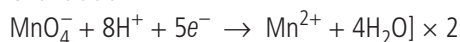
(i) Iron(II) solution :



(ii) Sulphur dioxide (SO₂) :



(iii) Oxalic acid



14. (i) From the E° values for M^{3+}/M^{2+} for Cr, Mn and Fe, it is very clear that Fe^{3+} is more stable than Mn^{3+} in an acidic medium, whereas less stable than Cr^{3+} because of the higher reduction potential in comparison to $\text{Cr}^{3+}/\text{Cr}^{2+}$ and lower reduction potential than $\text{Mn}^{3+}/\text{Mn}^{2+}$.

(ii) Reduction potential for Mn^{2+}/Mn is most negative and therefore, it will be most easily oxidised and ease of getting oxidised will be $\text{Mn} > \text{Cr} > \text{Fe}$.

15. The configuration of the given metal ions can be given as

| | |
|------------------------------|----------------------|
| $\text{Ti}^{3+} - 3d^1 4s^0$ | 1 unpaired electron |
| $\text{V}^{3+} - 3d^2 4s^0$ | 2 unpaired electrons |
| $\text{Cu}^+ - 3d^{10} 4s^0$ | No unpaired electron |
| $\text{Sc}^{3+} - 3d^0 4s^0$ | No unpaired electron |
| $\text{Mn}^{2+} - 3d^5 4s^0$ | 5 unpaired electrons |
| $\text{Fe}^{3+} - 3d^5 4s^0$ | 5 unpaired electrons |
| $\text{Co}^{2+} - 3d^7 4s^0$ | 3 unpaired electrons |

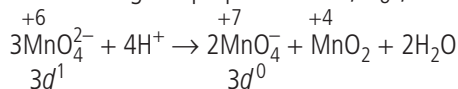
Out of these only Cu^+ and Sc^{3+} are colourless. All other ions are coloured due to presence of unpaired electrons.

16. The common oxidation state of 3d series elements is + 2 which arises due to participation of only 4s electrons. The tendency to show highest oxidation state increases from Sc to Mn, then decreases due to pairing of electrons in 3d-subshell. Thus in the series Sc(II) does not exist, Ti(II) is less stable than Ti(IV). At the other end of the series oxidation state of Zn is +2 only. +2 oxidation state stability increase on moving top to bottom, because more and more difficult to remove the 3rd electron from the d-orbital.

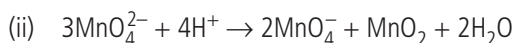
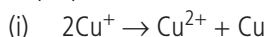
17. (i) Both Cr^{2+} and Mn^{3+} have d^4 configuration, Cr^{2+} is reducing since its configuration is converted to d^3 from d^4 . d^3 has half filled t_{2g} configuration with higher stability. Mn^{3+} is oxidising since in changing from d^4 to d^5 the configuration becomes half filled which has extra stability.

(ii) Co(II) gets oxidised to Co(III) in presence of complexing agent because Co(III) is more stable than Co(II). Most of the strong field ligands cause pairing of electrons forming diamagnetic octahedral complexes which are very stable due to very large crystal field stabilization energy.

(iii) d^1 configuration is very unstable in ions because after losing one more electron it will become more stable due to vacant d-orbital. All elements with d^1 configuration are either reduced or undergo disproportionation, e.g.,



18. Disproportionation reaction involves the oxidation and reduction of the same substance. The two examples of disproportionation reaction are



19. Copper exhibits +1 oxidation state in the first series of transition metals because when one electron is lost, the configuration becomes stable due to fully filled d^{10} configuration.

| | |
|------------------------------|----------------------|
| $\text{Mn}^{3+} - 3d^4 4s^0$ | 4 unpaired electrons |
| $\text{Cr}^{3+} - 3d^3 4s^0$ | 3 unpaired electrons |
| $\text{V}^{3+} - 3d^2 4s^0$ | 2 unpaired electrons |
| $\text{Ti}^{3+} - 3d^1 4s^0$ | 1 unpaired electron |

Cr^{3+} is most stable in aqueous solution due to half filled t_{2g} level.

21. (i) Lowest oxidation compounds of transition metals are basic due to their ability to get oxidised to higher oxidation states. Whereas the higher oxidation state compounds of metal gets reduced to lower ones and hence are acidic in nature.

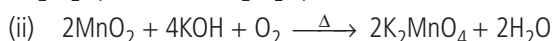
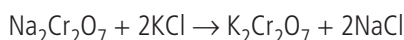
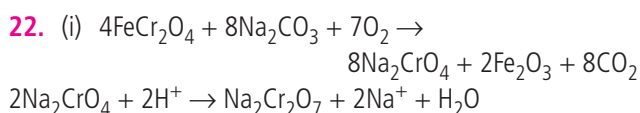
e.g., MnO is basic whereas Mn_2O_7 is acidic.

(ii) Due to high electronegativities of oxygen and fluorine, the oxides and fluorides of transition metals exhibit highest oxidation state.

e.g. $\begin{array}{c} +6 \\ \text{OsF}_6 \end{array}, \begin{array}{c} +5 \\ \text{V}_2\text{O}_5 \end{array}$

(iii) In oxoanions of metals, the metals form bonds with oxygen and hence are present in their highest oxidation states. For example : Cr forms CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$, both contain chromium in +6 oxidation state.

Permanganate ion, MnO_4^- contains Mn in its highest oxidation state of +7.

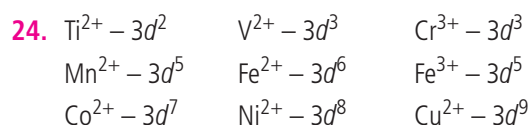


23. (i) Electronic configurations : In 1st transition series, 3d-orbitals are progressively filled whereas in 2nd transition series, 4d-orbitals are progressively filled and in 3rd transition series, 5d-orbitals are progressively filled.

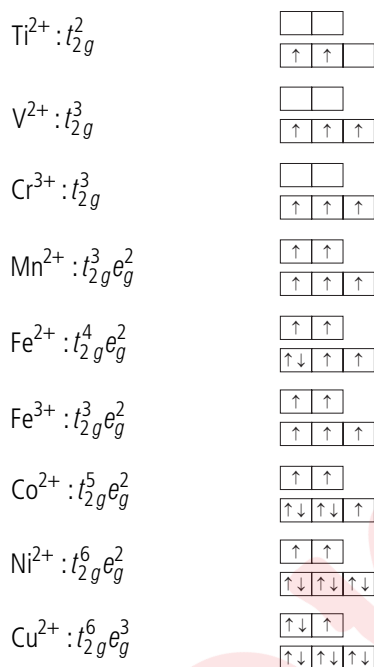
(ii) Oxidations states : Elements show variable oxidation states in both the series. The highest oxidation state is equal to total number of electrons in 's' as well as 'd' orbitals. The number of oxidation states shown are less in 5d transition series than 4d series. In 3d series +2 and +3 oxidation states are common and they form stable complexes in these oxidation states. In other series OsO_4 and PtF_6 are formed which are quite stable in higher oxidation state.

(iii) Ionisation enthalpies : The ionisation enthalpies in each series generally increases gradually from left to right. The ionisation enthalpy of 5d series do not differ appreciably due to lanthanoid contraction.

(iv) Atomic sizes : The atomic sizes of 4d and 5d-series do not differ appreciably due to lanthanoid contraction. The atomic radii of second and third series are larger than first series (3d series).



Filling of orbitals in octahedral hydrated ions



25. $\text{K}_4[\text{Mn}(\text{CN})_6]$: Oxidation state of Mn is +2, Mn^{2+} has an electronic configuration of $[\text{Ar}]3d^5$.

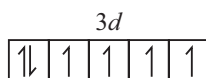
As $\mu = 2.2$ BM which corresponds to one unpaired electron. The orbital diagram for Mn^{2+} is



$[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$: $\mu = 5.3$ BM corresponds to 4 unpaired electrons.

The configuration of Fe^{2+} is $[\text{Ar}] 3d^6$

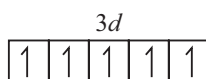
The orbital diagram for Fe^{2+} is



$\text{K}_2[\text{MnCl}_4]$: $\mu = 5.9$ BM corresponds to 5 unpaired electrons.

The configuration of Mn^{2+} is $[\text{Ar}]3d^5$.

The orbital diagram for Mn^{2+} is



26. (i) In first transition series lower oxidation state is more stable whereas in heavier transition elements higher oxidation states are more stable.

(ii) The ionisation enthalpy of 5d transition series is higher than 3d and 4d transition series.

(iii) M–M bonding is most common in heavier transition metals but less in first series.

(iv) The elements of first transition series do not form complexes with higher coordination number of 7 and 8.

(v) The elements of first series can form high spin or low spin complexes depending upon strength of ligands but elements of other series form low spin complexes irrespective of strength of ligands.

Topic 2

- | | |
|-------------------------|-----------------------------------------------------------------------------------------------|
| 1. (i) Cr^{3+} | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3$ |
| (ii) Pm^{3+} | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$ $4p^6 5s^2 4d^{10} 5p^6 4f^4$ |
| (iii) Cu^+ | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ |
| (iv) Ce^{4+} | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$ $4p^6 5s^2 4d^{10} 5p^6$ |
| (v) Co^{2+} | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7$ |
| (vi) Lu^{2+} | $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10}$ $4p^6 5s^2 4d^{10} 5p^6 4f^{14} 5d^1$ |
| (vii) Mn^{2+} | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$ |
| (viii) Th^{4+} | $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$ $4d^{10} 5s^2 5p^6 4f^{14} 5d^{10} 6s^2 6p^6$ |

2. Lanthanoid contraction : The steady decrease in the size of lanthanoid ions with the increase in atomic number is called lanthanoid contraction. It is due to poor shielding effect and increased nuclear charge.

The cumulative effect of the contraction of the lanthanoid series, known as lanthanoid contraction, causes the radii of the members of the third transition series to be very similar to those of the corresponding members of the second series. The almost identical radii of Zr (160 pm) and Hf (159 pm), a consequence of the lanthanoid contraction, account for their occurrence together in nature and for the difficulty faced in their separation.

3. In lanthanoids, +3 oxidation state is predominant. However, occasionally +2 and +4 ions in the solution or in solid compounds are also obtained. e.g. Ce^{4+} , Tb^{4+} , Eu^{2+} , Yb^{2+} , etc. +2 and +4 oxidation states are exhibited due to extra stability of empty, half-filled or fully filled f-subshells.

4. (i) Electronic configuration : Lanthanoids have general electronic configuration of $[\text{Xe}] 4f^{1-14} 5d^{0-1} 6s^2$ and actinoids have general electronic configuration of $[\text{Rn}] 5f^{1-14} 6d^{0-1} 7s^2$. Thus, lanthanoids belong to 4f-series whereas actinoids belong to 5f-series.

(ii) Atomic and ionic sizes : The atomic size of lanthanoids decreases from lanthanum to lutetium. Though the decrease is not regular in case of atomic radii, the decrease in the ionic size (M^{3+}) is regular. Decrease in size between two successive elements is higher in actinoids due to poor screening by 5f electrons.

(iii) Oxidation state : The most common oxidation state of lanthanoids is +3 while actinoids show more variable oxidation states than lanthanoids ranging from +3 to +7. The tendency of showing greater range of oxidation states can be attributed to the fact that the 5f, 6d and 7s levels are of comparable energies and larger distance of 5f as compared to 4f from the nucleus.

(iv) Chemical reactivity : Actinoids are far more reactive than lanthanoids. They react with non-metals at moderate temperatures whereas lanthanoids react at high temperatures. Most actinoids are attacked by HCl but are slightly affected by HNO_3 due to formation of a protective layer of oxide and alkalies give no reaction.

Lanthanoids liberate hydrogen from dilute acids and burn in halogens to form halides.

5. Lanthanoids and actinoids are called inner transition elements because inner f-orbitals are progressively filled and the last electron goes to antepenultimate f-orbital.

Elements with atomic number 59, 95, 102 are inner transition metals because they belong to lanthanoids and actinoids.

Pr (59) : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^3$

Am (95) : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^7$

No (102) : $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 5p^6 4d^{10} 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14}$

6. 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.

There is a greater range of oxidation states, which is attributed to the fact that the 5f, 6d and 7s levels are of comparable energies. 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. 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 earlier and latter elements. It is unsatisfactory to review their chemistry in terms of oxidation states.

7. Lawrencium (Lr) is the last element of actinoids. Its outer electronic configuration is $5f^{14} 6d^1 7s^2$ and its possible oxidation state is +3.

8. The electronic configuration of Ce^{3+} is $[\text{Xe}]4f^1$

$$\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.732 \text{ B.M.}$$

9. All lanthanoids show Ln^{3+} oxidation state. But some of them show +2 and +4 states also in solution and solid form like Ce^{4+} , Eu^{2+} , Yb^{2+} , Tb^{4+} , etc. The variable oxidation state is related to electronic configuration due to extra stability of half filled, fully filled or empty orbitals. e.g., Ce^{4+} has $4f^0$, Eu^{2+} has $4f^7$, Tb^{4+} has $4f^7$ and Yb^{2+} has $4f^{14}$ configuration.

10. $Z = 61 : [\text{Xe}] 4f^5 6s^2$ $Z = 91 : [\text{Rh}] 5f^2 6d^1 7s^2$
 $Z = 101 : [\text{Rh}] 5f^{13} 7s^2$ $Z = 109 : [\text{Rh}] 5f^{14} 6d^7 7s^2$

11. An alloy is a blend of metals prepared by mixing the components. Alloys are homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of other. Mischmetal is an alloy which contains some of the lanthanoid metals. It contains 95% lanthanoid metals, 5% iron and traces of S, C, Ca and Al. Mischmetal is used in Mg-based alloy to produce bullets, shell and lighter flint.

12. (i) Electronic configuration : Lanthanoids have general electronic configuration of $[\text{Xe}] 4f^{1-14} 5d^{0-1} 6s^2$ and actinoids have general electronic configuration of $[\text{Rn}]5f^{1-14} 6d^{0-1} 7s^2$. Thus, lanthanoids belong to 4f-series whereas actinoids belong to 5f-series.

(ii) Oxidation state : The most common oxidation state of lanthanoids is +3 while actinoids show more variable oxidation states than lanthanoids ranging from +3 to +7. The tendency of showing greater range of oxidation states can be attributed to the fact that the 5f, 6d and 7s levels are of comparable energies and larger distance of 5f as compared to 4f from the nucleus.

(iii) Chemical reactivity : Actinoids are far more reactive than lanthanoids. They react with non-metals at moderate temperatures whereas lanthanoids react at high temperatures. Most actinoids are attacked by HCl but are slightly affected by HNO_3 due to formation of a protective layer of oxide and alkalies give no reaction.

Lanthanoids liberate hydrogen from dilute acids and burn in halogens to form halides.

