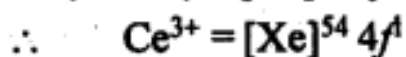
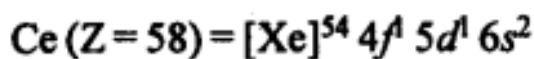




8.31. Use Hund's rule to derive the electronic configuration of Ce^{3+} ion, and calculate its magnetic moment on the basis of 'spin-only' formula.

Sol:



$$\therefore \mu = \sqrt{n(n+2)}$$

Here $n = 1$ i.e., only one unpaired electron.

$$\therefore \mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM.}$$

8.32. Name the members of the lanthanoid series which exhibit +4 oxidation states and those which exhibit +2 oxidation states. Try to correlate this type of behaviour with the electronic configurations of these elements.

Sol:

+4 oxidation state in Ce ($Z = 58$), Pr ($Z = 59$), Tb ($Z = 65$).

+2 oxidation state in Nd ($Z = 60$), Sm ($Z = 62$), Eu ($Z = 63$), Tm ($Z = 69$), Yb ($Z = 70$).

+2 oxidation state is exhibited when the lanthanoid has the configuration $5f^0 6s^2$ so that two electrons are easily lost.

+4 oxidation state is exhibited by the elements which after losing four electrons acquire configuration $4f^0$ or $4f^1$.

8.33. Compare the chemistry of actinoids with that of lanthanoids with reference to:

(i) Electronic configuration

(ii) Oxidation states

(iii) Chemical reactivity

Sol:

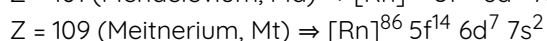
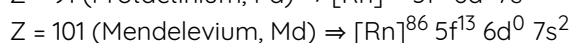
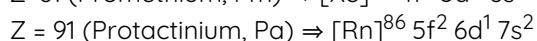
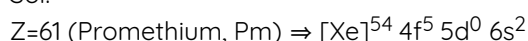
(i) Electronic configuration : In lanthanoids $4f$ - orbitals are progressively filled whereas in actinoids $5f$ -orbitals are progressively filled.

(ii) Oxidation states : Lanthanoids shows +3 oxidation state. Some elements shows +2 and +4 oxidation state also. Actinoids shows +3, +4, +5, +6, +7 oxidation states. Although +3 and +4 are most common.

(iii) Chemical reactivity : Actinoids are more reactive than lanthanoids due to bigger atomic size and lower ionisation energy.

8.34. Write the electronic configurations of the elements with the atomic numbers 61, 91, 101 and 109.

Sol:



8.35. Compare the general characteristics of the first series of the

transition metals with those of the second and third series metals in the respective vertical columns. Give special emphasis on the following points:

- (i) electronic configurations
- (ii) oxidation states
- (iii) ionisation enthalpies and
- (iv) atomic sizes

Sol:

(i) Electronic configuration: The elements in the same vertical column generally have similar electronic configuration. First transition series shows only two exceptions, i.e., $\text{Cr} = 3d^5 4s^1$ and $\text{Cu} = 3d^{10} 4s^1$. But second transition series shows more exceptions, i.e., $\text{Y} = 4d^1 5s^2$, $\text{Nb} = 4d^1 5s^1$, $\text{Mo} = 4d^5 5s^1$, $\text{Ru} = 4d^1 5s^1$, $\text{Rh} = 4d^8 5s^1$, $\text{Pd} = 4d^{10} 5s^0$, $\text{Ag} = 4d^{10} 5s^1$. In third transition, there are two exceptions, i.e., $\text{Pt} = 5d^9 6s^1$ and $\text{Au} = 5d^{10} 6s^1$.

Thus in the same vertical column, in a number of cases, the electronic configuration of the elements of three series are not similar.

(ii) Oxidation states: The elements in the same vertical column generally show similar oxidation states. The number of oxidation states shown by the elements in the middle of each series is maximum and minimum at the extreme ends.

(iii) Ionization enthalpies: The first ionization enthalpies in each series generally increases gradually as we move from left to right though some exceptions are observed in each series. The first ionization enthalpies of some elements in the second (4d) series are higher while some of them have lower value than the elements of 3d series in the same vertical column. However, the first ionization enthalpies of third (5d) series are higher than those of 3d and 4d series. This is because of weak shielding of nucleus by 4f-electrons in the 5d series.

(iv) Atomic sizes: In general, ions of the same charge or atoms in a given series show progressively decrease in radius with increasing atomic number though the decrease is quite small. But the size of the atoms of the 4d series is larger than the corresponding elements of the 3d series whereas size of elements of the 5d-series nearly the same as those of 4d series because of lanthanoid contraction.

8.36. Write down the number of 3d electrons in each of the following ions: Ti^{2+} , V^{2+} , Cr^{3+} , Mn^{2+} , Fe^{2+} , Fe^{3+} , Co^{2+} , Ni^{2+} and Cu^{2+} . Indicate how would you expect the five 3d orbitals to be occupied for these hydrated ions (octahedral).

Sol:

Sol.	Ion	Configuration	No. of 3d electrons	No. of unpaired electrons	Occupancy of 3d orbitals
(i)	Ti ²⁺	3d ²	2	2	$t_{2g}^2 e_g^0$
(ii)	V ²⁺	3d ³	3	3	$t_{2g}^3 e_g^0$
(iii)	Cr ³⁺	3d ³	3	3	$t_{2g}^3 e_g^0$
(iv)	Mn ²⁺	3d ⁵	5	5	$t_{2g}^3 e_g^2$
(v)	Fe ²⁺	3d ⁶	6	4	$t_{2g}^4 e_g^2$
(vi)	Fe ³⁺	3d ⁵	5	5	$t_{2g}^3 e_g^2$
(vii)	Co ²⁺	3d ⁷	7	3	$t_{2g}^5 e_g^2$
(viii)	Ni ²⁺	3d ⁸	8	2	$t_{2g}^6 e_g^2$
(ix)	Cu ²⁺	3d ⁹	9	1	$t_{2g}^6 e_g^3$

8.37. Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition elements.

Sol:

The above mentioned statement is true, because

- Atomic radii of the heavier transition elements (4d and 5d series) are larger than those of the corresponding elements of the first transition series though those of 4d and 5d series are very close to each other.
- Melting and boiling points of heavier transition elements are greater than those of the first transition series due to stronger intermetallic bonding.
- Enthalpies of atomisation of 4d and 5d series are higher than the corresponding elements of the first series.
- Ionization enthalpies of 5d series are higher than the corresponding elements of 3d and 4d series.

8.38. What can be inferred from the magnetic moment values of the following complex species?

Example	Magnetic moment (BM)
$K_4[Mn(CN)_6]$	2.2
$[Fe(H_2O)_6]^{2+}$	5.3
$K_2[MnCl_4]$	5.9

Sol:

Magnetic moment, $\mu = \sqrt{n(n+2)} \text{ BM}$

For $n=1$, $\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ B.M.}$

$n=2$, $\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \text{ B.M.}$

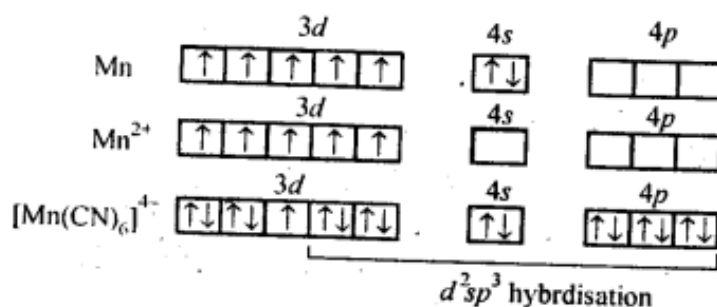
$n=3$, $\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87 \text{ B.M.}$

$n=4$, $\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.89 \text{ B.M.}$

$n=5$, $\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.92 \text{ B.M.}$

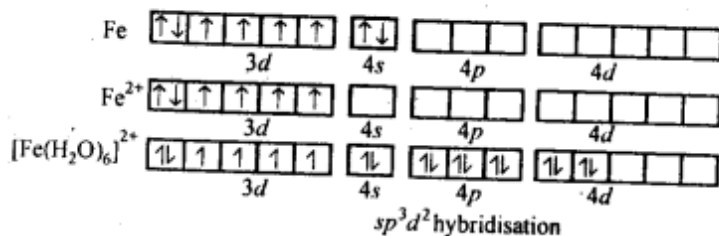
(i) $\text{K}_4[\text{Mn}(\text{CN})_6]$: In this complex, Mn is in +2 oxidation state and $\mu = 2.2 \text{ BM}$.

It means that it has only one unpaired electron. When CN^- ligands approach Mn^{2+} ion, the electrons in 3d-orbital pair up.



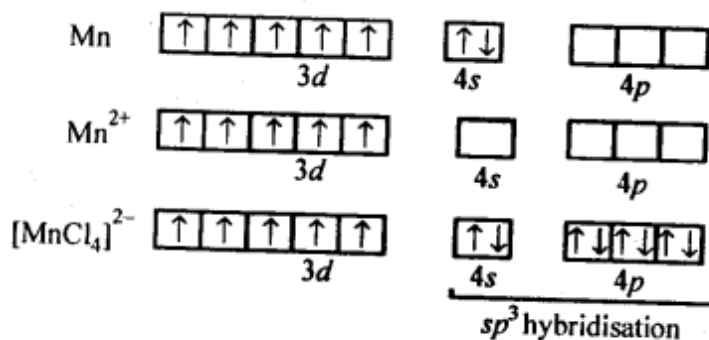
Thus CN^- is a strong ligand. The hybridisation is d^2sp^3 forming inner-orbital octahedral complex.

- (ii) $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$: In this complex, Fe is in +2 oxidation state and $\mu = 5.3$. It means that there are four unpaired electrons in 3d. Also, the 3d electrons do not pair up when the H_2O molecules approach. Thus, H_2O is a weak ligand.



The hybridisation involved is sp^3d^2 , forming an outer-orbital octahedral complex.

- (iii) $\text{K}_2[\text{MnCl}_4]$: In this complex, Mn is in +2 oxidation state and $\mu = 5.92$. It means that there are five unpaired electrons. The hybridisation involved is sp^3 , forming a tetrahedral complex. Cl is a weak ligand.



***** END *****