

Chapter:-8 The d-and f-Block Elements

POINTS TO BE REMEMBERED: ---

1. The elements of periodic table belonging to group 3 to 12 are known as d-Block elements.
2. The general electronic configuration of these elements is $(n-1)d^{1-10} ns^{1-2}$
3. d-Block elements are collectively known as Transition Elements because properties of these elements vary in between s-Block and p-Block elements.
4. A transition element should have partially filled $(n-1) d$ orbital.
5. Group 12 elements i.e. Zn, Cd, Hg have completely filled $(n-1) d$ -orbital in atomic & ionic state & thus these elements are considered as Typical Transition Elements.
6. All these elements are metals. They are less electropositive than s-block elements & more electropositive than p-block elements.
7. The atomic radii decreases from group 3 to 6 (i.e. Sc to Cr) because of increase in effective nuclear charge gradually.
8. The atomic radii of group 7,8 9 &10 elements (i.e. Fe,Co,Ni) is almost same because pairing of electrons take place in $(n-1)d$ orbital causing repulsion i.e. shielding of $(n-1)d$ orbital.
9. Group 11 &12 elements i.e. Cu & Zn have bigger size due to strong shielding of completely filled $(n-1)d$ orbital.
10. The transition elements show variable oxidation state due to small energy difference between $(n-1)d$ & ns orbital as a result both $(n-1)d$ & ns electrons take part in bond formation.
11. The highest oxidation state of an element is equal to number of unpaired electrons present in $(n-1)d$ & ns orbital.
12. Transition elements have high enthalpy of atomization/ sublimation Because of large number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence strong metallic bonding is present between atoms.
13. Most of transition elements are paramagnetic due to presence of unpaired electrons in $(n-1) d$ orbital.
14. Most of transition elements are used as catalyst. It is due to (i) partially filled $(n-1) d$ orbital (ii) Variable oxidation state (iii) Ability to change oxidation state frequently.
15. Most of transition elements form coloured compounds due to presence of unpaired electrons in $(n-1) d$ orbital & thus they can undergo d-d transition.
16. Most of transition elements form complex compounds due to (i) small size (ii) high charge (iii) presence of vacant d-orbital of suitable energy.
17. Transition elements have lower value of Reduction Potential due to high ionization potential, high heat of sublimation & low enthalpy of hydration.
18. Transition elements form interstitial compounds because size of interstitial voids is similar to size of non- metals C, N, O, H.
19. Transition elements form alloys due to similar ionic radii.
20. The oxides of transition metals in lower oxidation state are BASIC, intermediate oxidation state are AMPHOTERIC, highest oxidation state are ACIDIC.

LANTHANOIDS: ---

1. The 14 elements after Lanthanum having atomic number 58 to 71 are collectively known as Lanthanoids.
2. The general electronic configuration of these elements is $[Xe] 4f^{1-14}, 5d^{0-1}, 6s^2$.
3. Most common oxidation state of these elements is +3, but Ce shows +4, Eu +2, because they acquire stable configuration.
4. The size of Lanthanoids and its trivalent ion decreases from La to Lu due to poor shielding of 4f electrons. It is known as lanthanoids contraction.

ACTINOIDS:--

1. The 14 elements after Actinium having atomic number 90 to 113 are collectively known as Actinoids.

- The general electronic configuration of these elements is $[Rn] 5f^{1-14}, 6d^{0-1}, 7s^2$.
- The size of actinoids and its trivalent ion decreases from Ac to Lw due to poor shielding of 5f electrons. It is known as actinoids contraction.
- The elements after U (92) are man made known as transuranic elements.

POTASSIUM DICHROMATE:--

Preparation: - It takes place in three steps-

- Conversion of chromite ore to sodium chromate.
- Conversion of sodium chromate to sodium dichromate.
- Conversion of sodium dichromate to potassium dichromate

Following reaction take place:--

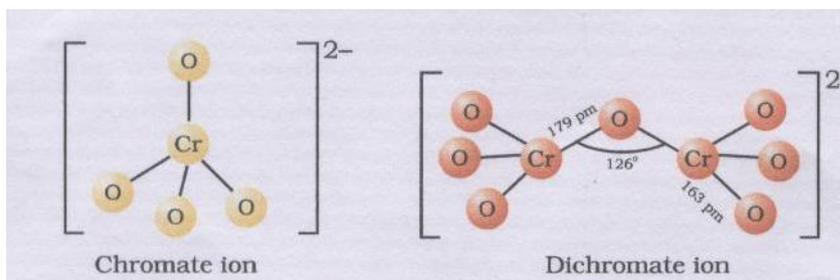


The chromates and dichromates are interconvertible in aqueous solution depending upon Ph of the solution.

A) In Acedic medium(PH<7)



B) In basic medium (PH >7)



POTASSIUM PERMANGNATE:--

Preparation: --

It takes place in two steps:-

- Conversion of pyrolusite ore into potassium magnate
- Conversion of potassium magnate to potassium permanganate

Following reactions take place:-



QUESTION ANSWERS

(TWO MARK QUESTIONS)

Q.1-Explain briefly how +2 oxidation state becomes more and more stable in the first half of the first row transition elements with increasing atomic number.

A.1-In M^{2+} ions, 3d-orbitals get occupied gradually as the atomic number increases. Since, the number of empty d-orbitals decreases, the stability of cations increases from Sc^{2+} to Mn^{2+} . Mn^{2+} is most stable as all d-orbitals are singly occupied.

Q.2- Explain why transition elements have many irregularities in their electronic configurations?

A.2-In the transition elements, there is a little difference in the energy of (n-1) d-orbitals and ns-orbitals. Thus, incoming electron can occupy either of shell. Hence, transition elements exhibit many irregularities in their electronic configurations.

Q.3-What are different oxidation states exhibited by Lanthanides?

A.3-The common stable oxidation state of lanthanides is +3. However some members also show oxidation states of +2 & +4.

Q.4-How is the variability in oxidation states of transition metals different from that of the non-transition metals? Illustrate with examples.

A.4-The transition elements use its (n-1)d, ns and np orbital and the successive oxidation states differ by unity. For example, Mn shows all the oxidation states from +2 to +7. On other hand non transition elements use its ns, np and nd orbitals and the successive oxidation states differ by two units e.g. Sn²⁺, Sn⁴⁺ etc.

Q.5- Why do transition elements show variable oxidation states?

A.5- The transition elements show variable oxidation state due to small energy difference between (n-1) d & ns orbital as a result both (n-1)d & ns electrons take part in bond formation.

Q.6-Why are Mn²⁺ compounds more stable than Fe²⁺ compounds towards oxidation to +3 state?

A.6-The electronic configuration of Mn²⁺ is [Ar] 3d⁵, i.e. all five d-orbitals are singly occupied. Thus this is stable electronic configuration and further loss of electron requires high energy. On other hand side the electronic configuration of Fe²⁺ is [Ar] 3d⁶, i.e. Loss of one electron requires low energy.

Q.7-To what extent do the electronic configuration decide the stability of oxidation state in the first series of the transition elements? Illustrate your answer with an example.

A.7-In a transition series, the oxidation state which lead to exactly half filled or completely filled orbitals are more stable. e.g. the electronic configuration of Fe is [Ar] 3d⁶ 4s². It shows various oxidation state but Fe(III) is more stable than Fe(II).

Q.8-What is meant by disproportionation? Give two examples.

A.8-Those reactions in which same substance undergoes oxidation as well as reduction are called disproportionation reactions. e.g.



Q.9- Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?

A.9- Copper with configuration [Ar] 3d¹⁰ 4s¹ exhibits +1 oxidation state. Copper loses 4s¹ electron easily and achieved a stable configuration 3d¹⁰ by forming Cu⁺.

Q.10- What are inner transition elements?

A.10- The f-block elements in which the last electron accommodated on (n-2) f-subshell are called inner transition elements. These include atomic numbers 58 to 71 and from 90 to 103.

Q.11- The paramagnetic character in 3d-transition series elements increases upto Mn and then decreases. Explain why?

A.11- In the 3d-transition series as we move from Sc (21) to Mn (25) the number of unpaired electrons increases and hence paramagnetic character increases. After Mn, the pairing of electrons in the d-orbital starts and the number of unpaired electrons decreases and hence, paramagnetic character decreases.

Q.12- Comment on the statement that elements of the first transition series possess many properties different from those of heavier transition metal

A.12-The following points justify that the given statement is true:-

(i) Ionization enthalpies of heavier transition elements are higher than the elements of 3d series. Consequently, heavier transition elements are less reactive in comparison to 3d-elements.

(ii) Melting points of heavier transition elements are higher than 3d-elements.

(iii) Higher oxidation states of heavier transition elements are stable whereas lower oxidation states are stable in 3d-elements.

Q.13-What are transition elements? Which d-block elements are not regarded as transition elements and why?

A.13- An element which has partially filled (n-1) d orbital is known as transition elements. Group 12 elements i.e. Zn, Cd, Hg have completely filled (n-1) d-orbital in atomic & ionic state & thus these elements are not considered as Transition Elements.

Q.14-What are interstitial compounds? Why are such compounds well known for transition metal?

A.14- Compounds of transition metal with relatively smaller non-metals are known as interstitial compounds. These compounds are well known for transition metals because size of C, N, O, and B is similar to size of interstitial voids of transition metal

Q.15-For the first row of transition metals the E^0 values are:-

E^0 values	V	Cr	Mn	Fe	Co	Ni	Cu
M^{2+}/M	-1.18	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34

Explain the irregularity in the above values.

A.15-The E^0 (M^{2+}/M) values are not regular which can be explained from the irregular variation of ionization energy and sublimation energy of Mn due to half-filled orbitals.

(THREE MARK QUESTIONS)

Q.1- Decide giving reason which one of the following pairs exhibits the property indicated:

- (i) Sc^{3+} or Cr^{3+} exhibits paramagnetism
- (ii) V or Mn exhibits more number of oxidation states
- (iii) V^{4+} or V^{5+} exhibits colour

A.1- (i) $Sc=[Ar] 3d^1 4s^2$; $Sc^{3+}=[Ar]$; it has no unpaired electron so diamagnetic
 $Cr=[Ar] 3d^5 4s^1$; $Cr^{3+}=[Ar] 3d^3$; it has three unpaired electrons paramagnetic
 (ii) $V=[Ar] 3d^3 4s^2$ $Mn=[Ar] 3d^5 4s^2$ Thus V exhibit oxidation states of +2, +3, +4, +5
 Whereas Mn exhibit oxidation states of +2 to +7.

(iii) $V^{4+}=[Ar] 3d^1 \rightarrow$ coloured $V^{5+}=[Ar] \rightarrow$ colourless

Q.2-(a) Describe the general trends in the following properties of the first series of the transition elements:-

- (i) Stability of +2-oxidation state
- (ii) Formation of oxometal ions

(b) Write steps involved in the preparation of $KMnO_4$ from K_2MnO_4

A.2- (a) i-The elements of first transition series show decreasing tendency to form divalent cation as we move left to right in the series. This trend is due to general increase in the first and second ionization energy. The greater stability of Mn^{2+} is due to half filled d^5 configuration and that of zinc is due to d^{10} configuration.

(ii) All metal except Sc from oxide of type MO which are basic. The highest oxidation number in all oxide, coincide with the group number and is attain in Sc_2O_3 to Mn_2O_7 . Formation of oxoanions is due to high electro negativity and small size of oxygen atom.

2-(b) It takes place in two steps:-

- (iii) Conversion of pyrolusite ore into potassium manganate.
- (iv) Conversion of potassium manganate to potassium permanganate.

Following reactions take place:-



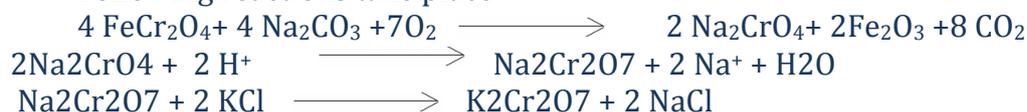
Q.3-(a) Write the steps involve in the preparation of $K_2Cr_2O_7$ from chromite ore.

(b) What is the effect of pH on dichromate ion solution?

A.3-(a):- It takes place in three steps-

- (iv) Conversion of chromite ore to sodium chromate.
- (v) Conversion of sodium chromate to sodium dichromate.
- (vi) Conversion of sodium dichromate to potassium dichromate

Following reactions take place:-



(b) Dichromate ion is orange in acidic solution (pH < 7) and turns yellow in basic solution. It is due to interconversion of dichromate ion to chromate ion. Following reactions take place:-



Q.4- (a) What is lanthanide contraction? What effect does it have on the chemistry of the elements, which follow lanthanoids?

(b) The chemistry of actinoid elements is not so much smooth as that of lanthanoids. Justify these statements by giving some examples from the oxidation state of these elements.

A.4- (a) The size of Lanthanoids and its trivalent ion decreases from La to Lu. It is known as lanthanoids contraction.

Cause: - It is due to poor shielding of 4f electrons.

Consequences of lanthanide contraction: - (i) Basic strength of hydroxide decreases from $\text{La}(\text{OH})_3$ to $\text{Lu}(\text{OH})_3$. (ii) Because of similar chemical properties lanthanides are difficult to separate.

(b) Lanthanoids show limited number of oxidation states i.e. +2, +3, +4 (out of which +3 is most common). This is because of a large energy gap between 4f, 5d and 6s subshell. The dominant oxidation state of actinides is also +3 but they show a number of other oxidation state also e.g. +4, +5, and +7. This is due to small energy difference between 5f, 6d and 7s orbitals.

Q.5- Give examples and suggest reasons for the following features of the transition metal chemistry:

(i) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.

(ii) A transition metal exhibits highest oxidation state in oxides and fluorides.

(iii) Of the d^4 species, Cr^{2+} is strongly reducing while manganese(III) is strongly oxidizing.

A.5-(i) The oxide of transition metals in lower oxidation states are generally basic while those in the higher oxidation states are acidic. Acidic character increases with increase in oxidation state is due to decrease in size of metal ion and increase in charge density. e.g. MnO (basic), Mn_3O_4 (amphoteric), Mn_2O_7 (acidic).

(ii) A transition metal exhibits higher oxidation states in oxides and fluorides because oxygen and fluorine are the most electronegative elements and thus easily can unpair electrons of metal atom.

(iii) Because oxidizing and reducing property depends on E^0 value. Since E^0 value of $\text{Cr}^{3+}/\text{Cr}^{2+}$ is negative while that of $\text{Mn}^{3+}/\text{Mn}^{2+}$ is positive, as a result $\text{Cr}(\text{II})$ act as reducing agent and $\text{Mn}(\text{III})$ is strong oxidizing.

Q.6- For M^{2+}/M and $\text{M}^{3+}/\text{M}^{2+}$ systems, the E^0 values for some metals are as follows:

Cr^{2+}/Cr	-0.9V	$\text{Cr}^{3+}/\text{Cr}^{2+}$	-0.4V
Mn^{2+}/Mn	-1.2V	$\text{Mn}^{3+}/\text{Mn}^{2+}$	+1.5V
Fe^{2+}/Fe	-0.4V	$\text{Fe}^{3+}/\text{Fe}^{2+}$	+0.8V

Use this data to comment upon :-

(i) the stability of Fe^{3+} in acid solution as compared to Cr^{3+} or Mn^{3+} and

(ii) the ease with which iron can be oxidized as compared to a similar process for either chromium or manganese metal.

A.6- (i) E^0 for $\text{Cr}^{3+}/\text{Cr}^{2+}$ is -0.4V i.e. negative, this means Cr^{3+} ions in the solution cannot be reduced to Cr^{2+} easily i.e. Cr^{3+} is stable. As $\text{Mn}^{3+}/\text{Mn}^{2+}$ is +1.5V i.e. positive means Mn^{3+} can easily be reduced to Mn^{2+} ions in comparison to Fe^{3+} ions. Thus relatively stability of these ions is:-



(ii) The oxidation potentials for the given pairs will be +0.9V, +1.2V and 0.4V. Thus, the order of their getting oxidized will be in the order $\text{Mn} > \text{Cr} > \text{Fe}$.

Q.7- Account for the following statements:

(i) Cobalt (II) is stable in aqueous solution but in the presence of strong ligands and air, it can be oxidized to Co (III).

(ii) The d^1 configuration is very unstable in ions.

(iii) One among the lanthanides, Ce (III) can be easily oxidized to Ce (IV).

A.7- (i) Strong ligands force cobalt (II) to lose one more electron from 3d-subshell and thereby induced d^2sp^3 hybridisation.

(ii) The ion with d^1 configuration try to lose the only electron in order to acquire inert gas configuration.

(iii) The configuration of Ce is $[Xe] 4f^1, 5d^1, 6s^2$. There is no much difference between the energy of 4f, 5d and 6s orbitals and thus, Ce can utilize electrons present in these orbitals and hence oxidation state of +4.

Q.8- Compare the chemistry of actinides with that of the lanthanoids with special reference to:

- | | |
|---------------------------------|--------------------------|
| (i) electronic configuration | (iii) oxidation state |
| (ii) atomic and ionic sizes and | (iv) chemical reactivity |

A.8-

Comparison of Lanthanoids and Actinides

Properties	Lanthanoids	Actinides
Electronic configuration	$[Xe] 4f^{1-14}, 5d^{0-1}, 6s^2$	$[Rn] 5f^{1-14}, 6d^{0-1}, 7s^2$
Atomic/ionic sizes	Size decreases from La to Lu, and size is more than actinides.	Size decreases from Ac to Lw, and size is smaller than lanthanoids due to poorer shielding of 5f electrons
Oxidation states	Common oxidation is +3 where other oxidation states are +2, +4. It is due to a large energy gap between 4f, 5d and 6s subshell	Common oxidation is +3 where other oxidation states are +2, +4, +5 and +7 due to small energy difference between 5f, 6d and 7s orbitals
Chemical reactivity	The earlier member quite reactive but with increasing atomic number they behave like aluminum.	The actinides highly reactive, especially in finely divided.
Complex formation	Less tendency to form complex due to less charge density.	More tendency to form complex due to high charge density.

Q.9-(a) What is actinides contraction? What effect does it have on the chemistry of the elements, which follow actinides?

(b) Name an important alloy, which contains some of the lanthanide metals. Mention its uses.

A.9- (a) The size of actinoid and its trivalent ion decreases from Ac to Lw. It is known as actinides contraction.

Cause: - It is due to poor shielding of 5f electrons.

Consequences of actinides contraction: - (i) Basic strength of hydroxide decreases from $Ac(OH)_3$ To $Lw(OH)_3$. (ii) Because of similar chemical properties actinides are difficult to separate.

(b) An important alloy containing lanthanoid metals is mischmetal, which contains 95% lanthanide metal and 5% Fe along with traces of S, C, Ca and Al. It is used in Mg-based alloy to produce bullets, shells and lighter flint.

Q.10- Complete following reactions:-



(FIVE MARK QUESTIONS)

Q.1-Explain giving reasons:

- (i) Transition metals and many of their compounds show paramagnetic behaviour.

- (ii) The enthalpies of atomisation of the transition metals are high.
- (iii) The transition metals generally form coloured compounds.
- (iv) Transition metals and their many compounds act as good catalyst.
- (v) Transition metals have a strong tendency to form complexes.

A.1- (i) Transition metals and many of their compounds show paramagnetic behaviour due to presence of unpaired electrons in (n-1) d orbital.

- (ii) The enthalpies of atomisation of the transition metals are high Because of large number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence strong metallic bonding is present between atoms.
- (iii) The transition metals generally form coloured compounds due to presence of unpaired electrons in (n-1) d orbital & thus they can undergo d-d transition.
- (iv) Transition metals and their many compounds act as good catalyst It is due to (i) partially filled (n-1) d orbital (ii) Variable oxidation state (iii) Ability to change oxidation state frequently.
- (v) Transition metals have a strong tendency to form complexes Most of transition elements form complex compounds due to (i) small size (ii) high charge (iii) presence of vacant d-orbital of suitable energy.

Q.2- Give reasons for the following:-

- (i) Fe has higher melting point than Cu.
- (ii) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is coloured while $[\text{Sc}(\text{H}_2\text{O})_6]$ is colourless.
- (iii) The 4d and 5d series of transition metals have more frequent metal-metal bonding in their compound than do the 3d metals.
- (iv) Transition metals some time exhibit very low oxidation state such as +1 and 0.
- (v) Hg is not considered a transition metal.

A.2-(i) This is because Fe ($3d^6, 4s^1$) has four unpaired electrons in 3d-subshell. While Cu ($3d^{10}, 4s^1$) only one unpaired electron in 4s shell. Hence metallic bonding is stronger in Fe than those in Cu.

(ii) The oxidation state of Ti in $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is +3 and its configuration is $[\text{Ar}] 3d^1$ i.e one unpaired electron and hence it is coloured. Whereas the oxidation state of Sc in $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ is +3 and its configuration is $[\text{Ar}] 3d^0$ i.e no unpaired electron and hence it is colourless.

(iii) In the same group of d-block elements, the 4d and 5d transition elements are larger size than that of 3d elements. Hence, the valence electrons are less tightly held and form metal-metal bond more frequently.

(iv) +1 oxidation state is shown by elements like Cu because after loss of one electron, it acquire stable configuration. Zero oxidation state is shown in metal carbonyl, because π -electrons donated by CO are accepted into the empty orbital.

(v) The characteristic properties of transition metal are due to partially filled d-orbitals. Hg has completely filled d-orbital, as a result it doesn't show properties of transition metals and hence is not considered as transition metal.

Q.3-(a) write electronic configuration of element having atomic number 101.

- (b) Which element show maximum oxidation state in 3d transition series?
- (c) What is mischmetal?
- (d) Explain why Cu^+ ion is not stable in aqueous solution?
- (e) Name the transition metal which is well known to exhibit +4 oxidation state?

A.3-(a) $[\text{Rn}] 5f^{13}, 6d^0, 7s^2$.

(b) Mn, Which shows +7 oxidation state in KMnO_4 .

(c) It is an important alloy, which contains 95% lanthanide metal and 5% Fe along with traces of S, C, Ca and Al. It is used in Mg-based alloy to produce bullets, shells and lighter flint.

(d) Water is a good complexing agent and thus Cu forms complex by losing one more electron from 3d orbital.

(e) Cerium (Z=58)

Q.4-(a) Write the preparation of potassium dichromate from iron chromite. What happens when potassium dichromate reacts with (i) Hydrogen sulphide (ii) FeSO_4 ?

- (b) Why do Zr and Hf exhibit almost similar properties?
- (c) Why is $\text{La}(\text{OH})_3$ stronger base than $\text{Lu}(\text{OH})_3$.

A.4- (a) Preparation:- It takes place in three steps-

- (i) Conversion of chromite ore to sodium chromate.
- (ii) Conversion of sodium chromate to sodium dichromate.
- (iii) Conversion of sodium dichromate to potassium dichromate

Following reaction takes place:-



Reactions: - (i) $\text{Cr}_2\text{O}_7^{2-} + 8 \text{H}^+ + 3 \text{H}_2\text{S} \rightarrow 2\text{Cr}^{3+} + 7 \text{H}_2\text{O} + 3\text{S}$

(ii) $\text{Cr}_2\text{O}_7^{2-} + 14 \text{H}^+ + 6 \text{Fe}^{2+} \rightarrow 2\text{Cr}^{3+} + 7 \text{H}_2\text{O} + 6 \text{Fe}^{3+}$.

(b) Because both have similar ionic size

(c) Due to lanthanoid contraction size of La^{3+} is smaller than Lu^{3+} as a result Lu-O bond will be stronger than La-O bond.

Q.5- Give reasons for the following:-

(i) Transition metals have high enthalpy of hydration.

(ii) Zn, Cd and Hg are not regarded as transition metal.

(iii) d block elements exhibit a large number of oxidation states than f block elements.

(iv) The second and third members in each group of transition elements have similar atomic radii.

(v) $\text{K}_2[\text{PtCl}_6]$ is a well known compound whereas the corresponding Ni compound is not known.

A.5-(i) Transition metal ions are smaller and have higher charge, therefore they have high enthalpy of hydration.

(ii) Group 12 elements i.e. Zn, Cd, Hg have completely filled (n-1) d-orbitals in atomic & ionic state & thus these elements are not considered as transition elements.

(iii) The difference in the energy of (n-1) d orbital and ns orbital is very small and thus both subshells are used for bond formation. Whereas in f block elements (n-2)f orbitals lie underneath and hence are not available for bond formation.

(iv) The second and third members in each group of transition elements have similar atomic radii due to lanthanoid contraction. It arises due to poor shielding of d and f electrons.

(v) The oxidation state of Pt is +4 which is stable for Pt. The +4 oxidation state for Ni is very difficult to achieve because the sum of the first four ionization energies is very high. Hence, the corresponding Ni(II) compound is known.