

TRANSITION AND INNER TRANSITION ELEMENTS**1. What are transition metals? Give four examples.**

Transition elements that have incompletely filled d sub shell in the neutral or cationic state are called transition metals

Four examples.

First (3d) : Ti , V , Cr , Fe

Second : (4d) Mo , Ru , Rh, pd

Third (5d) : W, Os ,Ir, Pt,

Fourth : (6d) Db , Sg, Bh, Ds

2. Explain the oxidation states of 4d series elements.

a) At the beginning of the series, +3 oxidation state is stable but towards the end +2 oxidation state becomes stable

b) The oxidation states of **4d series elements** vary from

+3 for Y and + 2 to +8 for Ru , Cd for +2.

c) The highest oxidation state of **4d elements** are found in their compounds with the higher electronegative elements like O, F and Cl. for example: RuO_4 .

d) Generally in going down a group, a stability of the higher oxidation state increases while that of lower oxidation state decreases.

3. What are inner transition elements?

The last electron enters into $(n - 2) f$ - orbital which is inner to the penultimate shell, they are also called inner transition elements.

In the inner transition elements there are two series of elements.

1) Lanthanoids (previously called lanthanides (57-71))

2) Actinoids (previously called actinides (89-103))

4. Justify the position of lanthanides and actinides in the periodic table.

The actual position of Lanthanoids in the periodic table is at group number 3 and period number 6. However, in the sixth period after lanthanum,

The electrons are preferentially filled in inner 4f sub shell and these fourteen elements following lanthanum show similar chemical properties.

Therefore these elements are grouped together and placed at the bottom of the periodic table. This position can be justified as follows.

1. Lanthanoids have general electronic configuration $[\text{Xe}] 4f^{1-14} 5d^{0-1} 6s^2$

2. The common oxidation state of lanthanoids is +3

3. All these elements have similar physical and chemical properties.

5. What are actinides? Give three examples.

The fourteen elements following actinium ,i.e., from thorium (Th) to lawrentium (Lr) are called actinoids

Actinide - These are elements with atomic numbers from 90 to 103

Examples.

The 15 elements include: Actinium (Ac), Thorium (Th), Protactinium (Pa), Uranium (U),

6 Why Gd³⁺ is colourless?

The At.No of Gd is 64. EC is (Xe) 4f⁷ 5d¹ 6s². In Gd³⁺, they have exactly half filled f-orbitals
Hence (Xe) 4f⁷ 5d⁰ 6s⁰. Due to this it is colourless.

7. Explain why compounds of Cu²⁺ are coloured but those of Zn²⁺ are colourless.

1) Zn²⁺ ion has all paired electrons (configuration [Ar] 3d¹⁰)

Cu²⁺ ion has an **unpaired electron** (its configuration is [Ar] 3d⁹)

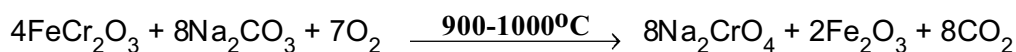
2) i) In case of Zn²⁺ ion **fully filled** d orbital is present therefore no d-d transition can be possible in this case and it is colorless.

ii) In case of Cu²⁺ ion because of d-d transition electrons emits light in the visible range and hence they are colored compounds

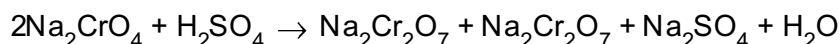
8. Describe the preparation of potassium dichromate.

Potassium dichromate is prepared from chromate ore. The ore is concentrated by gravity separation

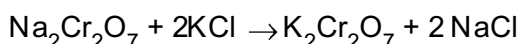
i) Conversion of Chromate ore into Sodium chromate



ii) Conversion of Sodium chromate into Sodium di chromate



iii) Conversion of Sodium di chromate into Potassium dichromate



9. What is lanthanide contraction and what are the effects of lanthanide contraction?

As we move across 4f series, the atomic and ionic radii of lanthanoids show gradual decrease with increase in atomic number. This decrease in ionic size is called lanthanoid contraction.

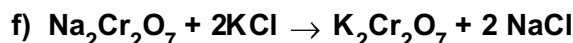
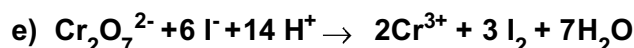
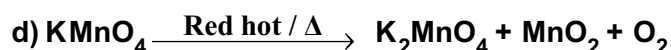
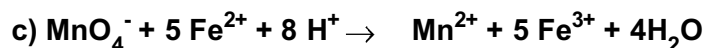
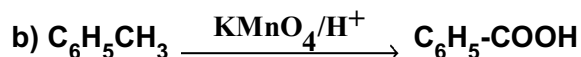
A. Basicity differences

As we from Ce³⁺ to Lu³⁺, the basic character of Ln³⁺ ions decrease. Due to the decrease in the size of Ln³⁺ ions, the ionic character of Ln - OH bond decreases (covalent character increases) which results in the decrease in the basicity.

B. Similarities among lanthanoids:

In the complete f - series only 10 pm decrease in atomic radii and 20 pm decrease in ionic radii is observed. because of this very small change in radii of lanthanoids, their chemical properties are quite similar.

10. complete the following



11. What are interstitial compounds?

An interstitial compound or alloy is a compound that is formed when small atoms like hydrogen carbon or nitrogen are trapped in the interstitial holes in a metal lattice .

Example :TiC, ZrH_{1.92}, Mn₄N etc

12. Calculate the number of unpaired electrons in Ti³⁺, Mn²⁺ and calculate the spin only magnetic moment.

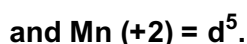
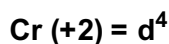
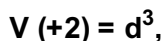
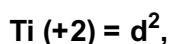
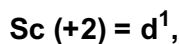
ion	configuration	n	$\mu_s = \sqrt{n(n+2)} \mu_B$	μ_s (observed)
Ti ³⁺	d ¹	1	$\mu_s = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \mu_B$	paramagnetic
Mn ²⁺	d ⁵	5	$\mu_s = \sqrt{5(5+2)} = \sqrt{35} = 5.91 \mu_B$	paramagnetic

13. Write the electronic configuration of Ce⁴⁺ and Co²⁺.

- i) configuration of Ce⁴⁺ [Xe₅₄] 4f⁰ 5d⁰ 6s⁰
 ii) configuration of Co²⁺ [Ar₁₈] 3d⁷ 4s⁰

14. Explain briefly how +2 states becomes more and more stable in the first half of the first row transition elements with increasing atomic number.

- i) All the metals display +2 oxidation states except Sc.
 ii) On moving from the Sc to the Mn, the atomic numbers increase from 21 to the 25.
 iii) It means the number of electrons in the 3d-orbital also increases from 1 to 5.



iv) The +2 oxidation state is achieved by loss of the two 4s electrons by the metals. Since the number of d electrons in (+2) state also increases from Ti(+2) to Mn(+2), the stability of +2 state increases (as d-orbital is becoming more and more half-filled). Mn (+2) has d⁵ electrons

15. Which is more stable? Fe³⁺ or Fe²⁺ - explain.

Fe³⁺ ion is more stable due to its half-filled 3d⁵ electron configuration.

As half filled and completely filled shells are more stable Fe³⁺ ion is more stable.

While Fe²⁺ ion is partially filled d sub shell (3d⁶) is not stable. Hence, Fe³⁺ is more stable than Fe²⁺.

16. Explain the variation in E°_{M3+/M2+} /3d series.

ii) In 3d series as we move from Ti to Zn, the standard reduction potential (E°_{M3+/M2+}) value is approaching towards less negative value and copper has a positive reduction potential. ie elemental copper is more stable than Cu²⁺.

ii) In the general trend, ($E^\circ_{M^{3+}/M^{2+}}$)

The value for manganese and zinc are more negative than the regular trend. It is due to extra stability which arises due to the half filled d^5 configuration in Mn^{2+} and completely filled d^{10} configuration in Zn^{2+} .

iii) Transition metals in their high oxidation states tend to be oxidizing. For example, Fe^{3+} is moderately a strong oxidant, and it oxidises copper to Cu^{2+} ions.

The feasibility of the reaction is predicted from the following standard electrode potential values.

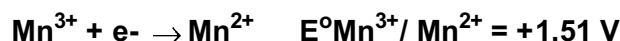


iv) The standard electrode potential for the ($E^\circ_{M^{3+}/M^{2+}}$) half-cell gives the relative stability between M^{3+} and M^{2+} .



v) The negative values for titanium, vanadium and chromium indicate that the higher oxidation state is preferred. If we want to reduce such a stable Cr^{3+} ion, strong reducing agent which has high negative value for reduction potential like metallic zinc ($E^0 = -0.76 \text{ V}$) is required.

eg) The high reduction potential of M^{3+}/M^{2+} indicates Mn^{2+} is more stable than Mn^{3+} .



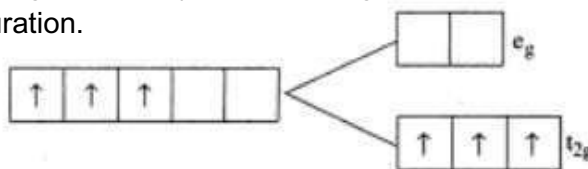
Mn^{3+} has a $3d^4$ configuration while that of Mn^{2+} is $3d^5$. The extra stability associated with a half filled d sub shell makes the reduction of Mn^{3+} very feasible ($E^0 = +1.51 \text{ V}$).

17. Compare lanthanides and actinides.

1 Differentiating electron enters in 4f orbital	Differentiating electron enters in 5f orbital
2 Binding energy of 4f orbitals are higher	Binding energy of 5f orbitals are lower
3 They show less tendency to form complexes	They show greater tendency to form complexes
4 Most of the lanthanoids are colourless	Most of the actinoids are coloured. eg) U^{3+} (red), U^{4+} (green), UO_2^{2+} (yellow)
5 They do not form oxo cations	They do form oxo cations such as UO_2^{2+} , O_2^{2+} , etc

18. Explain why Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidizing.

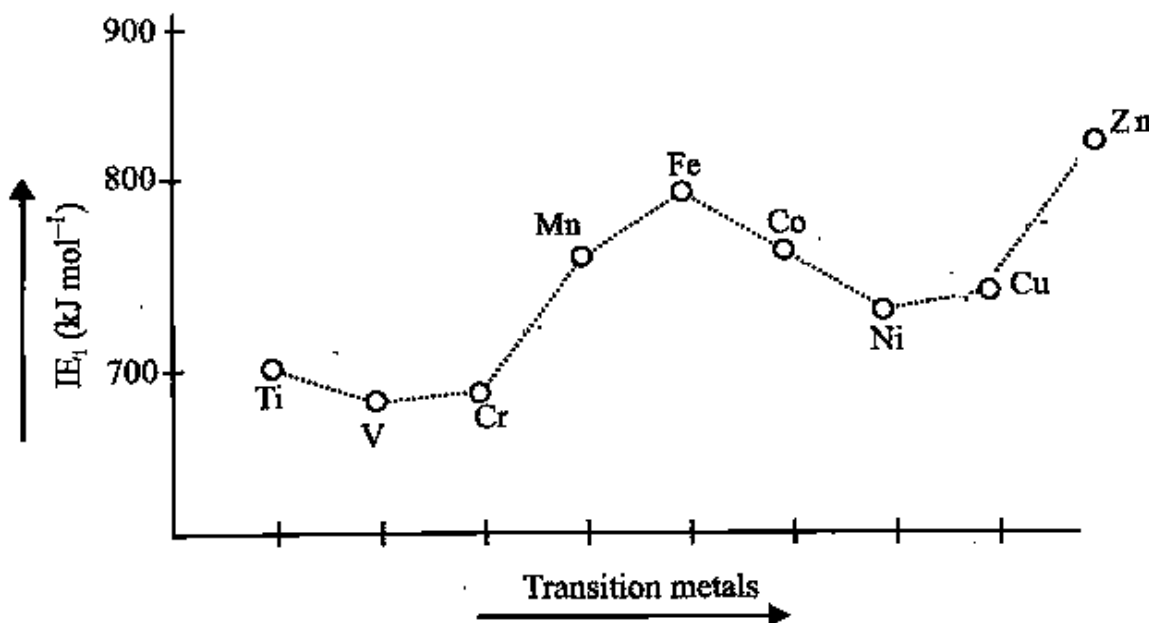
Cr^{2+} is strongly reducing in nature. It has a d^4 configuration. While acting as a reducing agent, it gets oxidized to Cr^{3+} (electronic configuration, d^3). This d^3 configuration can be written as t_{2g}^3 configuration, which is a more stable configuration.



In the case of Mn^{3+} (d^4), it acts as an oxidizing agent and gets reduced to Mn^{2+} (d^5). This has an exactly half-filled d-orbital and has an extra-stability.

19. Compare the ionization enthalpies of first series of the transition elements.

- 1) As we move from left to right in a transition metal series, the ionization enthalpy increases as expected. This is due to increase in nuclear charge corresponding to the filling of d electrons.
- 2) The increase in first ionisation enthalpy with increase in atomic number along a particular series is not regular.
- 3) The added electron enters (n-1)d orbital and the inner electrons act as a shield and decrease the effect of nuclear charge on valence ns electrons. Therefore, it leads to variation in the ionization energy values



- 4) Chromium has low first ionization enthalpy because lose one electron gives stable configuration ($3d^5$) While Zinc has very high ionization enthalpy because electron has to be removed from 4s orbitals.

20. Actinoid contraction is greater from element to element than the lanthanoid contraction, why?

- i) In actinoids, 5f orbitals are filled. These 5f orbitals have a poorer shielding effect than 4f orbitals (in lanthanoids).
- ii) Thus, the effective nuclear charge experienced by electrons in valence shells in case of actinoids is much more than that experienced by lanthanoids.
- iii) Hence, the size contraction in actinoids is greater as compared to that in lanthanoids.

21. Out of $\text{Lu}(\text{OH})_3$ and $\text{La}(\text{OH})_3$ which is more basic and why?

$\text{La}(\text{OH})_3$ is most basic and $\text{Lu}(\text{OH})_3$ is least basic. Due to lanthanide contraction. As the size of lanthanide ions decreases from La^{3+} to Lu^{3+} , the covalent character of the hydroxides increases and hence the basic strength decreases.

22. Why europium (II) is more stable than Cerium (II)?

- i) Europium (II) is more stable than Cerium (II) As we move from left to right, effective nuclear charge increases due to which lanthanide contraction takes place. The inert pair effect becomes more dominative.
- ii) In Eu^{2+} , 4f sub shell is half filled and Ce^{2+} , 4f and 5d sub shells are partially filled. so, $\text{Eu}(\text{II})$ more stable than $\text{Ce}(\text{II})$

23. Why do zirconium and Hafnium exhibit similar properties?

Zr and Hf exhibit similar properties due to lanthanoid contraction.

Electrons present in f subshell didn't do good shielding due to which with the increasing atomic number or increasing effective nuclear charge size gets constricted.

The size of Hafnium and Zirconium becomes almost equal.

4d series	Zr	145 pm
5d Series	Hf	144 pm

24. Which is stronger reducing agent Cr^{2+} or Fe^{2+} ?

Cr^{2+} is a stronger reducing agent than Fe^{2+} .

This can be explained on the basis of the standard electrode potential values

$$E^\circ(\text{Cr}^{3+}/\text{Cr}^{2+}) = -0.41 \text{ V} \quad \text{and} \quad E^\circ(\text{Fe}^{3+}/\text{Fe}^{2+}) = +0.77 \text{ V}.$$

Thus Cr^{2+} is easily oxidised to Cr^{3+} but Fe^{2+} cannot be as readily oxidised to Fe^{3+} .

25. The $E^\circ_{\text{M}^{2+}/\text{M}}$ value for copper is positive. Suggest a possible reason for this.**1. Sublimation energy:**

The energy needed to convert one mole of atoms from a solid state to gaseous state.

2. Ionization energy:

The energy supplied to remove electrons from one mole of atoms, which are in the gaseous state.

3. Hydration energy:

The energy emitted to hydrate one mole of ions.

Now, Copper has a high energy of atomization and low hydration energy. Hence, the $E^\circ(\text{M}^{2+}/\text{M})$ value for copper is positive.

26. predict which of the following will be coloured in aqueous solution Ti^{2+} , V^{3+} , Cu^+ , Sc^{3+} , Fe^{3+} , Ni^{2+} and Co^{3+}

A transition metal ion is coloured if it has one or more unpaired electron in (n-1)d orbitals i.e. 3d orbitals in case of first transition series. When such species are exposed to visible radiation, d-d transition can take place.

(It does not contain unpaired electron in 3d orbitals so it is colourless)

ion	configuration	colour
Ti^{2+}	$3d^1 4s^0$	Violet
V^{3+}	$3d^2 4s^0$	Green
Cu^+	$3d^{10} 4s^0$	colourless
Sc^{3+}	$3d^0 4s^0$	colourless
Fe^{3+}	$3d^5 4s^0$	brown to yellow
Ni^{2+}	$3d^8 4s^0$	green
Co^{3+}	$3d^6 4s^0$	blue

27. Describe the variable oxidation state of 3d series elements.

The first transition metal Scandium exhibits only +3 oxidation state, but all other transition elements exhibit variable oxidation states by losing electrons from (n-1)d orbital and ns orbital as the energy difference between them is very small.

At the beginning of the series, +3 oxidation state is stable but towards the end +2 oxidation state becomes stable.

For example, the first element Sc has only one oxidation state +3; the middle element Mn has six different oxidation states from +2 to +7. The last element Cu shows +1 and +2 oxidation states only.

Oxidation States of the first row Transition Metals
(the most common ones are in bold types)

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
	+2	+2	+2	+2	+2	+2	+2	+1	+2
+3	+3	+3	+3	+3	+3	+3	+3	+2	
	+4	+4	+4	+4	+4	+4	+4		
		+5	+5	+5					
			+6	+6	+6				
				+7					

The relative stability of different oxidation states of 3d metals is correlated with the extra stability of half filled and fully filled electronic configurations. Example: Mn^{2+} ($3d^5$) is more stable than Mn^{4+} ($3d^4$).

28. Which metal in the 3d series exhibits +1 oxidation state most frequently and why?

Cu is the only metal in the first transition series (3d series) which shows +1 oxidation state most frequently. This is because the electronic configuration of Cu is $3d^{10} 4s^1$ and after losing one electron it acquires a stable $3d^{10}$ configuration.

29. Why first ionization enthalpy of chromium is lower than that of zinc?

The electronic configuration of Zn and Cr is given below :



First ionisation enthalpy of Cr is lower than that of Zinc because in case of zinc first electron has to be removed from a fully filled orbital and a fully filled electronic configuration is most stable so it requires high energy to remove an electron from it. While in case of Chromium an electron is easily removed from a half-filled orbital with less amount of energy.

30. Transition metals show high melting points why?

- The melting-points of the transition metals are high due to the 3d electrons being available for metallic bonding.
- This strength of the bond is due to the presence of unpaired or delocalized electrons in the outermost shell of the atom.
- The enthalpies of atomization and the densities of transition elements are also high that leads to high boiling and melting points.

