NCERT Solutions for Class-XII Chemistry

CHAPTER -4

NCERT Chemistry Class 12

1. Write down the electronic configuration of:
(i) Cr^{3+} (iii) Cu^{+} (v) Co^{2+} (vii) Mn^{2+}
(ii) Pm^{3+} (iv) Ce^{4+} (vi) Lu^{2+} (viii) Th^{4+}

1. (i) The atomic number of Cr is 24 and the electronic configuration is [Ar] $3d^5 4s^1$
When 3 electrons are removed, it becomes Cr^{3+}. The electronic configuration of Cr^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^3$ Or [Ar] $3d^3$

(ii) The atomic number of Pm is 61 and the electronic configuration is $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 4f^5\ 5s^2\ 5p^6\ 6s^2$ or [Xe] $4f^5 6s^2$. When 3 electrons are removed, it becomes Pm^{+3}, having the electronic configuration, Pm^{3+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 4f^4$ Or, $[Xe]^{54} 4f^4$

(iii) The atomic number of Cu is 29 and has the electronic configuration of [Ar] $3d^{10} 4s^1$. On removing one electron, the $Cu^{+}$is obtained with the electronic configuration, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$ Or [Ar] $3d^{10}$

(iv) The atomic number of Ce is 58 and has the electronic configuration of [Xe] $4f^1 5d^1 6s^2$. When the valence electrons are removed, the Ce^{4+} ion with configuration, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6$ Or [Xe] is obtained.

(v) The atomic number of Co is 27 and has the electronic configuration of [Ar] $3d^7 4s^2$. When 2 electrons are removed from s-orbital, it becomes $Co^{2+}$with electronic configuration, $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^7$ Or, [Ar] $3d^7$.

(vi) The atomic number of Lu is 71 and has the electronic configuration of [Xe] $4f^{14} 5d^1 6s^2$. When 2 electrons are removed, $Lu^{2+}$with the configuration $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 4f^{14}\ 5d^1$ Or, [Xe] $4f^{14} 5d^1$

(vii) The atomic number of Mn is 25 and has the electronic configuration of [Ar] $3d^5 4s^2$. When 2 electrons are removed, Mn^{2+} ion is obtained and has an electronic configuration of $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}$ Or, $[Ar]^{18}\ 3d^{10}$.

(viii) The atomic number of Th is 90 and has the electronic configuration of [Rn] $6d^2\ 7s^2$. When 4 electrons are removed, the electronic configuration becomesTh^{4+}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^{10}\ 4s^2\ 4p^6\ 4d^{10}\ 5s^2\ 5p^6\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$ Or, [Rn]

2. Why are Mn^{2+} compounds more stable than Fe^{2+} towards oxidation to their +3 state?

2. Electronic configuration of Mn^{2+} is $[Ar]^{18}\ 3d^5$.
Electronic configuration of Fe^{2+} is $[Ar]^{18}\ 3d^6$.
It is known that half-filled and fully-filled orbitals are more stable. Therefore, Mn in (+2) state has a stable d^5 configuration. This is the reason Mn^{2+} shows resistance to oxidation

to Mn^{3+}. Also, Fe^{2+} has $3d^6$ configuration and by losing one electron, its configuration changes to a more stable $3d^5$ configuration. Therefore, Fe^{2+} easily gets oxidized to Fe^{+3} oxidation state.

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

3. The oxidation states displayed by the first half of the first row of transition metals are given in the table below.

METALS	Sc([Ar] $3d^14s^2$)	Ti([Ar] $3d^24s^2$)	V([Ar] $3d^34s^2$)	Cr([Ar] $3d^54s^1$)	Mn([Ar] $3d^54s^2$)
OXIDATION STATES		+2	+2	+2	+2
	+3	+3	+3	+3	+3
		+4	+4	+4	+4
			+5	+5	+6
				+6	+7

Except for Sc, all others metals display +2 oxidation state. This is because as the atomic number increases, the number of electrons in the valence shell increases. +2 oxidation state is attained by the loss of the two 4s electrons by these metals. As the number of electron increases, the possibility of an ion with +2 oxidation state being stable (by attaining half-filled structure) also increases. Finally, Mn2+ ions have half-filled structure and are very stable.

4. To what extent do the electronic configurations decide the stability of oxidation states in the first series of the transition elements? Illustrate your answer with examples.

4. The elements in the first-half of the transition series exhibit many oxidation states with Mn exhibiting maximum number of oxidation states (+2 to +7). The stability of +2 oxidation state increases with the increase in atomic number. This happens as more electrons are getting filled in the d-orbital. However, Sc does not show +2 oxidation state. Its electronic configuration is $4s^2$ $3d^1$. It loses all the three electrons to form Sc^{3+}. +3 oxidation state of Sc is very stable as by losing all three electrons, it attains stable noble gas configuration, [Ar]. Ti (+ 4) and V(+5) are very stable for the same reason. For Mn, +2 oxidation state is very stable as after losing two electrons, its d-orbital is exactly half-filled, [Ar] $3d^5$.

5. What may be the stable oxidation state of the transition element with the following d electron configurations in the ground state of their atoms : 3d3, 3d5, 3d8and 3d4?

5. For answering this question, we can compare the electronic configuration of standard elements and then write their corresponding oxidation states.

S.No	Electronic configurations in ground state	Stable oxidation states
1	$3d^3$ Vanadium	+2,+3,+4,+5
2	$3d^5$ Chromium	+3,+4,+6
3	$3d^5$ Manganese	+2,+4,+6,+7
4	$3d^8$ Nickel	+1,+2,+3,+4

5	$3d^4$	$3d^4$ configuration is not stable at ground state

6. Name the oxometal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.

6. (i) vanadate, VO_3^-
Oxidation state of V is + 5

(ii) Chromate, CrO_4^{2-}
Oxidation state of Cr is + 6.

(iii) Permanganate, MnO_4^-
Oxidation state of Mn is + 7

7. What is lanthanoid contraction? What are the consequences of lanthanoid contraction?
On moving along the lanthanoid series, the atomic number increases. Also, with the increase in atomic number, the number of electrons in the 4*f* orbital also increases. The 4*f* electrons have a poor shielding effect. Therefore, the effective nuclear charge experienced by the outer electrons increases. Consequently, the force of attraction between the nucleus and valence electrons increases. This results in a decrease in the size of lanthanoids with the increase in the atomic number. This is termed as lanthanoid contraction.

CONSEQUENCES:

1. The properties of second and third transition series are similar in nature.
2. Separation of lanthanoids from its compounds is possible due to lanthanide contraction.
3. The variation in the basic strength of lanthanide hydroxides os due to this contraction. (Basic strength decreases from $La(OH)_3$ to $Lu(OH)_3$)

8. What are the characteristics of the transition elements and why are they called transition elements? Which of the d-block elements may not be regarded as the transition elements?

8. Transition elements are those elements in which the atoms or ions (in stable oxidation state) contain partially filled d-orbital. These elements lie in the d-block and show a transition of properties between s-block and p-block. Therefore, these are called transition elements. Elements such as Zn, Cd, and Hg cannot be classified as transition elements because these have completely filled d-subshell.

9. In what way is the electronic configuration of the transition elements different from that of the non-transition elements?

9. Transition metals have a partially filled d−orbital. Therefore, the electronic configuration of transition elements is $(n-1)\,d^{1\text{-}10}\,ns^{0\text{-}2}$ The non-transition elements either do not have a

partially filled d−orbital. Therefore, the electronic configuration of non-transition elements is $\underline{ns^{1-2} \text{ or } ns^2\ np^{1-6}}$.

10. What are the different oxidation states exhibited by the lanthanoids?

10. In the lanthanide series, +3 oxidation state is most common i.e., Ln(III) compounds are predominant. However, +2 and +4 oxidation states can also be found in the solution or in solid compounds.

11. Explain giving reasons:

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

(ii) The enthalpies of atomization of the transition metals are high.

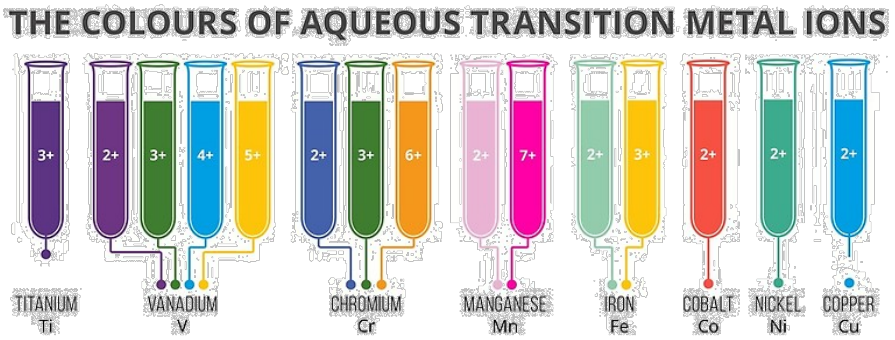
(iii) The transition metals generally form coloured compounds.

(iv) Transition metals and their many compounds act as good catalyst.

11. (1) Paramagnetic behaviour is shown by transition metals as paramagnetism is due to the presence of unpaired electrons which have a magnetic moment associated with its spin and angular momentum, as the orbital angular momentum is satisfied in the first transition series. So the paramagnetic is only due to the unpaired electrons.

(2) Enthalpies of atomization is the enthalpy change when 1 mol of gaseous atoms is formed from its element in its defined physical state under standard conditions (298.15K, 1 atm). In case of the transition metals enthalpies are high due to high effective nuclear charge and a large number of valence electrons which also leads to strong metallic bonding.
Eg: 515 KJ/mol for for Vanadium,473 KJ/mol for Titanium.

(3) Transition metals are generally coloured because of absorption of radiations which fall in the visible region as on obtaining energy electrons jump from one d-orbital to another.



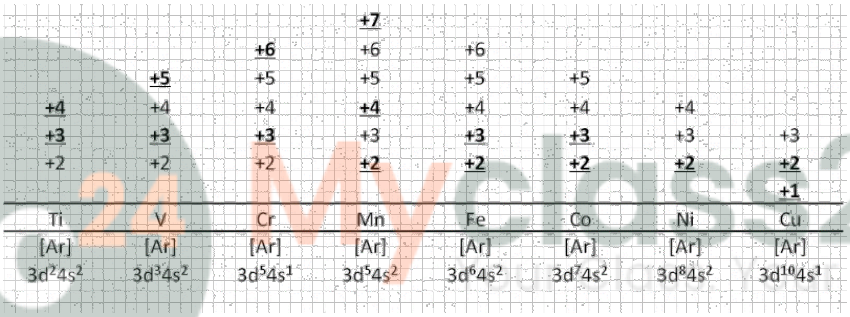
(4) Transition metals and their compounds act as good catalysts due to its ability to show variable oxidation state and form complexes, another reason is that they provide a suitable surface for reaction to take place.
Eg: Vanadium Oxide in contact process, Finely divided iron in Haber's Process.

12. What are interstitial compounds? Why are such compounds well known for transition metals?

12. Transition metals are large in size and contain lots of interstitial sites. Transition elements can trap atoms of other elements (that have small atomic size), such as H, C, N, in the interstitial sites of their crystal lattices. The resulting compounds are called interstitial compounds.

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

13. In transition metals, it can be observed that the oxidation state of the metal varies from +1 to +7 which is obtained by removing all its valence electrons. In transition elements the oxidation state differ by 1 unlike non transition elements whose oxidation state differs by 2, for example in transition metals (Cu^{2+},Cu^{3+} and Fe^{2+} ,Fe^{3+}) and In non-transition elements, this variation is selective, always differing by 2, e.g. S exhibits +2, +4, +6 oxidation states and N exhibits +3, + 5, etc.



	Ti	V	Cr	Mn	Fe	Co	Ni	Cu
	[Ar]	[Ar]	[Ar]	[Ar]	[Ar]	[Ar]	[Ar]	[Ar]
	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^2$	$3d^{10} 4s^1$
+7				+7				
+6			+6	+6	+6			
+5		+5	+5	+5	+5	+5		
+4	+4	+4	+4	+4	+4	+4	+4	
+3	+3	+3	+3	+3	+3	+3	+3	+3
+2	+2	+2	+2	+2	+2	+2	+2	+2
+1								+1

14. Describe the preparation of potassium dichromate from iron chromite ore. What is the effect of increasing pH on a solution of potassium dichromate?

14. Potassium dichromate is prepared from chromite ore($FeCr_2O_4$) by the following steps:

Step1: Preparation of sodium dichromate in the reaction of Chromite ore with sodium hydroxide and oxygen gas.

$4FeCr_2O_4 + 16NaOH + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8H_2O$

Step2: Conversion of Sodium Chromate on reaction with concentrated Sulfuric acid gives Sodium dichromate as a product.

$2Na_2CrO_4 + \text{conc. } H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

Step3: Sodium dichromate on reaction with potassium chloride converts to potassium dichromate as a product.

$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

As potassium dichromate is less soluble than sodium chloride so, potassium dichromate is obtained in form of orange crystals.

Dichromate ion exists in equilibrium with chromate ion at around pH. However, by changing the pH they can be interconverted.

15. Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with:
(i) iodide (ii) iron(II) solution and (iii) H_2S

15. $K_2Cr_2O_7$ acts as a very strong oxidizing agent in acidic medium.
$K_2Cr_2O_7$ gets reduced and acts as an oxidizing agent by oxidizing Iodide to iodine

(i) $K_2Cr_2O_7$ oxidizes iodide to iodine

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$2I^- \rightarrow I_2 + 2e^-$ } x3

Overall: $Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + 7H_2O + 3I_2$

(ii) $K_2Cr_2O_7$ oxidizes iron(II) to iron(III)

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$Fe^{2+} \rightarrow Fe^{3+} + e^-$} x6

Overall: $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 7H_2O + 6Fe^{3+}$

(iii) $K_2Cr_2O_7$ oxidized H_2S to sulphur

$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$

$H_2S \rightarrow S + 2H^+ + 2e^-$} x^3

Overall: $Cr_2O_7^{2-} + 8H^+ + 3H_2S \rightarrow 2Cr^{3+} + 7H_2O + 3S$

16. Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with (i) iron(II) ions (ii) SO_2 and (iii) oxalic acid?
Write the ionic equations for the reactions.

16. Potassium permanganate can be prepared from MnO_2. It can be done by fusing the ore with KOH in presence of an oxidizing agent like atmospheric oxygen/KNO_3 etc to give green coloured K_2MnO_4 as the product.

$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

The Product K_2MnO_4 is extracted with water and then oxidised by passing ozone/chlorine into the solution or electrolytically.

Electrolytic oxidation:

K_2MnO_4 à à Ü $2K^+ + MnO_4^{2-}$

At Anode, manganite ions are oxidized to permanganate ons.

MnO_4^{2-} à à Ü $MnO_4^- + e^-$

(i) Acidified $KMnO_4$ solution oxidizes Fe(II) ions to Fe(III) ions and water as product

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

$Fe^{2+} \rightarrow Fe^{3+} + e^-$ } x5

Overall: $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$

(ii) Acidified potassium permanganate oxidizes SO_2 to sulphuric acid as follows:

$MnO_4^- + 6H^+ + 5e^- \rightarrow Mn^{2+} + 3H_2O$}x2

$2H_2O + 2SO_2 + O_2 \rightarrow 4H^+ + 2SO_4^{2-} + 2e^-$} x5

Overall: $MnO_4^- + 4H_2O + 10SO_2 + 5O_2 \rightarrow 8H^+ + 10SO_4^{2-} + 2H^+$

(iii) Acidified potassium permanganate oxidizes oxalic acid to carbon dioxide

$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O\}$ x2

$C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-\}$ x5

Overall: $2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

17. For M^{2+}/M and M^{3+}/M^{2+} systems the EV values for some metals are as follows:

Cr^{2+}/Cr	–0.9V	Cr^{3}/Cr^{2+}	–0.4 V
Mn^{2+}/Mn	–1.2V	Mn^{3+}/Mn^{2+}	+1.5 V
Fe^{2+}/Fe	–0.4V	Fe^{3+}/Fe^{2+}	+0.8 V

Use this data to comment upon:

(i) the stability of Fe^{3+} in acid solution as compared to that of 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.

17. (1) Reduction potential tells us the ease with which the Metal can get reduced, As E° for Cr^{3+}/Cr^{2+} is negative (–0.4 V), this means that Cr^{3+} ions in solution cannot be reduced to Cr^{2+} ions i.e., Cr^{3+} ions are very stable. As a further comparison of E° values show that Mn^{3+} ions more readily than Fe^{3+} ions which means that Mn^{3+} is least stable. So Stability of metal ions is as follows:
$Mn^{3+}<Fe^{3+}<Cr^{3+}$.

(2) Reduction potential tells us the ease with which the Metal can get reduced or the difficulty with which they are oxidized, As the reduction potential increases in the following order $Mn^{2+}/Mn < Cr^{2+}/Cr < Fe^{2+}/Fe$ So oxidation of Fe is not as easy as Cr and Mn. So increasing order of the metals to get oxidised is as follows: Fe<Cr<Mn

18. Predict which of the following will be coloured in aqueous solution? Ti^{3+}, V^{3+}, Cu^{+}, Sc^{3+}, Mn^{2+}, Fe^{3+} and Co^{2+}. Give reasons for each.

18. Metal ions which have valence electrons in d-orbital and in which d-d transition can take place will be coloured and the metal ions which have completely filled orbital or have d-orbital will be colourless as no d-d transition is possible in those configurations.

Element	Atomic Number	Ionic State	Electronic configuration in ionic state
Ti	22	Ti^{3+}	[Ar] $3d^1$
V	23	V^{3+}	[Ar] $3d^2$
Cu	29	Cu^{+}	[Ar] $3d^{10}$
Sc	21	Sc^{3+}	[Ar]
Mn	25	Mn^{2+}	[Ar] $3d^5$
Fe	26	Fe^{3+}	[Ar] $3d^5$
Co	27	Co^{2+}	[Ar] $3d^7$

From the above table, it can be observed that only Sc^{3+} and Cu^{+} have either completely filled d-orbital or empty d-orbital. So, all other ions except Sc^{3+} and Cu^{+} will be coloured

in aqueous solution because of absorption of radiations which fall in the visible region as on obtaining energy electrons jump from one d-orbital to another.

19. Compare the stability of +2 oxidation state for the elements of the first transition series.

19.

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

From the above table, it is evident that the maximum number of oxidation states is shown by Mn, varying from +2 to +7. The number of oxidation states increases on moving from Sc to Mn. On moving from Mn to Zn, the number of oxidation states decreases due to a decrease in the number of available unpaired electrons. The relative stability of the +2 oxidation state increases on moving from top to bottom. This is because on moving from top to bottom, it becomes more and more difficult to remove the third electron from the d-orbital.

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

(i) electronic configuration (iii) oxidation state

(ii) atomic and ionic sizes and (iv) chemical reactivity.

20. **(i) Electronic configuration**

The general electronic configuration for lanthanoids is $[Xe]^{54}$ $4f^{0-14}$ $5d^{0-1}$ $6s^2$ and that for actinoids is $[Rn]^{86}$ $5f^{1-14}$ $6d^{0-1}$ $7s^2$. Unlike 4f orbitals, 5f orbitals are not deeply buried and participate in bonding to a greater extent.

(ii) Oxidation states

The principal oxidation state of lanthanoids is (+3). However, sometimes we also encounter oxidation states of + 2 and + 4. This is because of extra stability of fully-filled and half-filled orbitals. Actinoids exhibit a greater range of oxidation states. This is because the 5f, 6d, and 7s levels are of comparable energies. Again, (+3) is the principal oxidation state for actinoids. Actinoids such as lanthanoids have more compounds in +3 state than in +4 state.

(iii) Atomic and Ionic sizes

Similar to lanthanoids, actinoids also exhibit actinoid contraction (overall decrease in atomic and ionic radii). The contraction is greater due to the poor shielding effect of 5f orbitals.

(iv) Chemical reactivity

In the lanthanide series, the earlier members of the series are more reactive. They have reactivity that is comparable to Ca. With an increase in the atomic number, the lanthanides start behaving similar to Al. Actinoids, on the other hand, are highly reactive metals, especially when they are finely divided. When they are added to boiling water, they give a mixture of oxide and hydride. Actinoids combine with most of the non-metals at moderate temperatures. Alkalies have no action on these actinoids. In case of acids, they are slightly affected by nitric acid (because of the formation of a protective oxide layer).

21. How would you account for the following:

(i) Of the d4 species, Cr^{2+} is strongly reducing while manganese (III) is strongly oxidizing.

(ii) Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents, it is easily oxidized.

(iii) The d1 configuration is very unstable in ions.

21. (i) The +2 oxidation state becomes more stable on moving across a period i.e. the tendency of metals to give electrons becomes more. Therefore, vanadium(II) oxide and chromium(II) oxide are strong reducing agents.

As if the value of electrode potential is higher i.e. more energy required to withdraw an electron from an isolated atom, more readily it can be reduced and lesser the electrode potential more readily it can be oxidized.

The electrode potential of $Cr^{3+} \mid Cr^{2+}$is negative so it acts reducing agent or can undergo oxidation which makes it a more stable ion while that of $Mn^{3+} \mid Mn^{2+}$ is positive and it undergoes reduction acts as strong oxidizing agent. Also, Mn^{3+} has an exactly half-filled d- orbital which is highly stable.

(ii) Cobalt gets oxidized from +2 to +3 oxidation state in the presence of complexing reagents.

(iii) The d^1 electron can be easily lost after the loss of *ns* electrons. Therefore, the elements having d^1 configuration undergo disproportionation reactions.

22. What is meant by 'disproportionation'? Give two examples of disproportionation reaction in aqueous solution.

22. It is found that sometimes a relatively less stable oxidation state undergoes an oxidation−reduction reaction in which it is simultaneously oxidised and reduced. This is called disproportionation.

For example

(i) $3CrO_4^{3-} + 8H^+ \longrightarrow 2CrO_4^{2-} + Cr^{3+} + 4H2_2O$

Cr(V) Cr(VI) Cr(III)

Cr(V) is oxidized to Cr(VI) and reduced to Cr(III).

(ii) $3MnO_4^{2-} + 4H^+ \longrightarrow 2MnO_4^- + Mn_2O + 2H_2O$

Mn(VI) Mn(VII) Mn(IV)

Mn (VI) is oxidized to Mn (VII) and reduced to Mn (IV).

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

23. In the first transition series, Cu exhibits +1 oxidation state very frequently. It is because Cu (+1) has an electronic configuration of [Ar] $3d^{10}$. The completely filled d-orbital makes it highly stable.

24. Calculate the number of unpaired electrons in the following gaseous ions: Mn3+, Cr^{3+}, V^{3+} and Ti^{3+}. Which one of these is the most stable in aqueous solution?

24.

Mn^{3+} : $3d^4$	unpaired electrons = 4
V^{3+} : $3d^2$	unpaired electrons =2
Cr^{3+} : $3d^3$	unpaired electrons= 3
Ti^{3+} : $3d^1$	unpaired electrons =1

Cr^{3+} is the most stable in aqueous solutions owing to a t_{2g}^3 configuration.

25. 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) The highest oxidation state is exhibited in oxoanions of a metal.

25. (i) In the case of a lower oxide of a transition metal, the metal atom has a low oxidation state. This means that some of the valence electrons of the metal atom are not involved in bonding. As a result, it can donate electrons and behave as a base. On the other hand, in the case of a higher oxide of a transition metal, the metal atom has a high oxidation state. This means that the valence electrons are involved in bonding and so, they are unavailable. There is also a high effective nuclear charge. As a result, it can accept electrons and behave as an acid.

For example, $Mn^{II}O$ is basic and $Mn_2^{VII}O_7$ is acidic.

(ii) Oxygen and fluorine act as strong oxidising agents because of their high electronegativities and small sizes. Hence, they bring out the highest oxidation states from the transition metals. In other words, a transition metal exhibits higher oxidation states in oxides and fluorides. For example, in OsF_6 and V_2O_5, the oxidation states of Os and V are +6 and +5 respectively.

(iii) Oxygen is a strong oxidising agent due to its high electronegativity and small size. So, oxo-anions of a metal have the highest oxidation state. For example, in MnO_4^-, the oxidation state of Mn is +7.

26. Indicate the steps in the preparation of:
(i) $K_2Cr_2O_7$ from chromite ore. (ii) $KMnO_4$ from pyrolusite ore.

26. (i) the chromite ore ($FeCr_2O_4$) is fused with sodium hydroxide (NaOH)

$4FeCr_2O_4 + 16\ NaOH + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8H_2O$

The yellow solution of sodium chromate is then filtered and acidified with sulphuric acid giving its dichromate.

$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

On cooling, sodium sulphate crystallizes out as $Na_2SO_4.10H_2O$ and is removed.

$Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$

(ii) the pyrolusite ore(MnO_2) is oxidised in the presence of potassium hydroxide by heating.

$2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$

The green potassium manganate (K_2MnO_4) is then treated with a current of chlorine or ozone to oxidise potassium manganate to potassium permanganate.

$2K_2MnO_4 + Cl_2 \rightarrow 2KCl + 2KMnO_4$

$K_2MnO_4 + O_3 + H_2O \rightarrow 2KMnO_4 + 2KOH + O_2$

27. What are alloys? Name an important alloy which contains some of the lanthanoid metals. Mention its uses.

27. An alloy is a solid solution of two or more elements in a metallic matrix. It can either be a partial solid solution or a complete solid solution. Alloys are usually found to possess different physical properties than those of the component elements. An important alloy of lanthanoids is Mischmetal. It contains lanthanoids (94−95%), iron (5%), and traces of S, C, Si, Ca, and Al.

Uses

(i) Mischmetal is used in cigarettes and gas lighters.
(ii) It is used in flame throwing tanks.
(iii) It is used in tracer bullets and shells.

28. What are inner transition elements? Decide which of the following atomic numbers are the atomic numbers of the inner transition elements: 29, 59, 74, 95, 102, 104.

28. Inner transition metals are those elements in which the last electron enters the f-orbital. The elements in which the 4f and the 5f orbitals are progressively filled are called f-block elements. Among the given atomic numbers, the atomic numbers of the inner transition elements are 59, 95, and 102.

29. The chemistry of the actinoid elements is not so smooth as that of the lanthanoids. Justify this statement by giving some examples from the oxidation state of these elements.

29. lanthanoids show oxidation states of +2, +3, +4 because of the large energy gap between 5d and 4f sub-shells while actinoids show oxidation states of +3 to +7 because of the small energy difference between 5f, 6d, and 7s orbitals.

30. Which is the last element in the series of the actinoids? Write the electronic configuration of this element. Comment on the possible oxidation state of this element.

30. last actinoid is lawrencium-103 Electronic configuration: $[Rn]^{86}\ 5f^{14}\ 6d^{1}\ 7s^{2}$ Possible oxidation state: +3

31. Use Hund's rule to derive the electronic configuration of Ce3+ ion and calculate its magnetic moment on the basis of 'spin-only' formula.

31. The atomic number of Cerium (Ce) is Z = 58.

The electronic configuration of $_{58}Ce = [Xe]^{54}\ 4f^{1}\ 5d^{1}\ 6s^{2}$ And, the electronic configuration of $Ce^{3+} = [Xe]^{54}\ 4f^{1}$, i.e., there is only one unpaired electron, i.e., n = 1.

Now, the magnetic moment on the basis of spin only formula is given as:

$$\mu = \sqrt{n(n+2)}BM \Rightarrow \mu = \sqrt{1(1+2)}$$

$$\Rightarrow \mu = \sqrt{3}MB \Rightarrow \mu = 1.73BM$$

Note: Bohr magneton or BM is a unit for expressing the magnetic moment of an electron caused by its orbital or spin angular momentum.

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

32. The lanthanides that exhibit +2 and +4 states are shown in the given table. The atomic numbers of the elements are given in the parenthesis.

+2	+4
Nd (60)	Ce (58)
Sm (62)	Pr (59)
Eu (63)	Nd (60)
Tm (69)	Tb (65)
Yb (70)	Dy (66)

Ce after forming Ce^{4+} attains a stable electronic configuration of [Xe].

Tb after forming Tb^{4+} attains a stable electronic configuration of [Xe] 4*f*7.

Eu after forming Eu^{2+} attains a stable electronic configuration of [Xe] 4*f*7.

Yb after forming Yb^{2+} attains a stable electronic configuration of [Xe] 4*f*14.

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

(i) electronic configuration

(ii) oxidation states and

(iii) chemical reactivity.

33.

Lanthanoids	Actinoids
1.The electronic configuration of lanthanoids is $[Xe]^{54}\ 4f^{1-14}$	1.The electronic configuration of actinoids is $[Rn]^{86}\ 5f^{1-14}\ 6d^{0-1}\ 7s^2$
2. They show limited oxidation states (+2, +3, +4) out of which +3 is most common. This is because of the large energy gap between 4f and 5d subshells.	2. Actinoids show a large number of oxidation states (+3,+4,+5,+6,+7) because of the small energy gap between 5f, 6d, and 7s subshells.
3. The first few members of the series are quite reactive, almost like calcium with increasing atomic no. their behaviour becomes similar to that of aluminium	3.They are highly reactive metals especially in the finely divided state. When they are added to boiling water they give a mixture of oxide and hydride.

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

34.

Atomic number	Electronic configuration
61	$[Xe]^{54}\ 4f^5\ 5d^0\ 6s^2$
91	$[Rn]^{86}\ 5f^2\ 6d^1\ 7s^2$
101	$[Rn]^{86}\ 5f^{13}\ 5d^0\ 7s^2$
109	$[Rn]^{86}\ 5f^{14}\ 6d^7\ 7s^2$

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 configuration
(ii) Oxidation states
(iii) Ionisation enthalpies
(iv) Atomic sizes

35. (i) <u>Electronic configuration:</u>

In the first transition series, 3d orbitals are progressively filled while in the second and third transition series, 4d and 5d orbitals are filled. However the first series shows only two exceptions Cr and Cu, both have a single electron in the 4s orbital ($3d^5\ 4s^1$, $3d^{10}\ 4s^1$) but the second series shows more exceptions. Similarly, third series elements show exceptions. Thus in the same vertical column, in a number of series, the electronic configuration of the three series are not similar at all.

(ii) <u>Oxidation states:</u>

The number of oxidation states shown by the elements in the middle of each series is maximum and minimum at the extreme ends. However, the first row elements differ from the second and third-row elements in the fact that for all the first row

elements, +2 and +3 states are important. For second and third row elements, higher oxidation states are more important than those of the first row elements.

(iii) Ionisation enthalpies:

The first ionization enthalpies in each series generally increase gradually as we move from left to right through 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 a 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 those of corresponding elements of the 5d series are nearly the same as those of4d series because of Lanthanoid contraction

Note: Lanthanoid contraction is the regular decrease (contraction) in the atomic and ionic radii of lanthanoids with increasing atomic number

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).

36.

Metal ion	Number of d-electrons	Filling of d-orbitals
Ti^{2+}	**2**	t_{2g}^2
V^{2+}	**3**	t_{2g}^3
Cr^{3+}	**3**	t_{2g}^3
Mn^{2+}	**5**	$t_2^3 e_g^2$
Fe^{2+}	**6**	$t_{2g}^4 e_g^2$
Fe^{3+}	**5**	$t_2^3 e_g^2$
CO^{2+}	**7**	$t_{2g}^5 e_g^2$
Ni^{2+}	**8**	$t_{2g}^6 e_g^2$

Cu^{2+}	**9**	$t_{2g}^6 e_g^3$

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

37. The properties of the elements of the first transition series differ from those of the heavier transition elements in many ways.

(i) The atomic sizes of the elements of the first transition series are smaller than those of the heavier elements (elements of 2nd and 3rd transition series).
However, the atomic sizes of the elements in the third transition series are virtually the same as those of the corresponding members in the second transition series. This is due to lanthanoid contraction.

(ii) +2 and +3 oxidation states are more common for elements in the first transition series, while higher oxidation states are more common for the heavier elements.

(iii) The enthalpies of atomisation of the elements in the first transition series are lower than those of the corresponding elements in the second and third transition series.

(iv) The melting and boiling points of the first transition series are lower than those of the heavier transition elements. This is because of the occurrence of stronger metallic bonding (M−M bonding).

(v) The elements of the first transition series form low-spin or high-spin complexes depending upon the strength of the ligand field. However, the heavier transition elements form only low-spin complexes, irrespective of the strength of the ligand field.

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

38. Answer is given as magnetic moment $\mu = \sqrt{n(n+2)}$

For value n = 1, $\mu = \sqrt{1(1+2)} = \sqrt{3} = 1.732.$

For value n = 2, $\mu = \sqrt{2(2+2)} = \sqrt{8} = 2.83$

For value n = 3, $\mu = \sqrt{3(3+2)} = \sqrt{15} = 3.87$

For value n = 4 $\mu = \sqrt{4(4+2)} = \sqrt{24} = 4.899$

For value n = 5 $\mu = \sqrt{5(5+2)} = \sqrt{35} = 5.92$

(i) $K_4[Mn(CN)_6]$

For in transition metals, the magnetic moment is calculated from the spin-only formula.

Therefore,

$\sqrt{n(n+2)} = 2.2$

We can see from the above calculation that the given value is closest to n = 1. Also, in this complex, Mn is in the +2 oxidation state. This means that Mn has 5 electrons in the dorbital.

Hence, we can say that CN^- is a strong field ligand that causes the pairing of electrons.

(ii) $[Fe(H_2O)_6]^{2+}$

$\sqrt{n(n+2)} = 5.3$

We can see from the above calculation that the given value is closest to n = A. Also, in this complex, Fe is in the +2 oxidation state. This means that Fe has 6 electrons in the dorbital. Hence, we can say that H_2O is a weak field ligand and does not cause the pairing of electrons.

(iii) $K_2[MnCl_4]$

$\sqrt{n(n+2)} = 5.9$

We can see from the above calculation that the given value is closest to n = 5. Also, in this complex, Mn is in the +2 oxidation state. This means that Mn has 5 electrons in the dorbital. Hence, we can say that Cl^- is a weak field ligand and does not cause the pairing of electrons.