

Chapter 8: The d and f block elements

Intext Question

8.1. Silver atom has completely filled *d* orbitals $(4d^{10})$ in its ground state. How can you say that it

is a transition element? **Solution:**

In its ground state, Ag has a completely filled 4d orbital $(4d^{10}5s^1)$. Silver now has two oxidation states (+1 and +2). An electron is removed from the s-orboital in the +1 oxidation state. In the +2

oxidation state, however, an electron is removed from the d-orbital. As a result, the d-orbital is now

incomplete $(4d^9)$. As a result, it is a transitional element.

8.2. In the series Sc (Z = 21) to Zn (Z = 30), the enthalpy of atomization of zinc is the lowest, i.e., 126 kJmol⁻¹. Why?

Solution: The amount of metallic bonding that an element has determines the enthalpy of atomization. The greater an element's metallic bonding, the greater its enthalpy of atomization. There are some unpaired electrons in all transition metals (except Zn, electronic configuration:

 $3d^{10}$ $4s^2$), which accounts for their stronger metallic bonding. Because of the absence of these unpaired electrons, Zn has the weakest inter-atomic electronic bonding and, as a result, the lowest enthalpy of atomization.

8.3. Which of the 3*d* series of the transition metals exhibits the largest number of oxidation states and why?

Solution: The electronic configuration of Mn (Z = 25) is $3d^5 4s^2$.

Mn has the greatest number of unpaired electrons in the d-subshell (5 electrons). As a result, Mn has the most oxidation states, ranging from +2 to +7.

8.4. The $E^{\theta}(M^{2+}/M)$ value for copper is positive (+0.34V). What is possibly the reason for this?

(Hint: consider its high $\Delta_{a}H^{\theta}$ and $\mathrm{low}\Delta_{\mathrm{hvd}}H^{\theta}$)

Solution: A metal's $E^{\theta}(M^{2^+}/M)$ value is determined by the energy changes involved in the following:

1. Sublimation: The amount of energy required to convert one mole of an atom from its solid to gaseous state.

 $M_{(s)} \rightarrow M_{(g)} \qquad \Delta_s H$ (Sublimation energy)

2. Ionization: The amount of energy required to extract electrons from one mole of gaseous atoms.

$$M_{(g)} \rightarrow M^{2+}_{(g)} \qquad \Delta_i H$$
 (Ionisation energy)

3. Hydration energy: The amount of energy released when one mole of ions is hydrated.

 $M^{2+}(g) \rightarrow M^{2+}(aq) = \Delta_{hyd} H (Hydration energy)$

Copper now has a high atomization energy but a low hydration energy. As a result, the copper



$$E^{ heta}\left(\mathrm{M}^{2+}/\mathrm{M}
ight)$$
 value is positive.

8.5. How would you account for the irregular variation of ionization enthalpies (first and second) in the first series of the transition elements?

Solution: Because of the continuous filling of the inner d-orbitals, ionization enthalpies are found to

increase in the given series. The extra stability of configurations such as d^0 , d^5 , and d^{10} can be attributed to the irregular variations in ionization enthalpies. Because these states are extremely stable, their ionization enthalpies are extremely high.

Cr has a low ionization energy in the first ionization state. This is due to the fact that after losing one electron, it achieves the stable configuration $(3d^5)$. Zn, on the other hand, has a very high first ionization energy because an electron must be removed from stable and fully-filled orbitals $(3d^{10} \ 4s^2)$.

Second ionization energies are higher than first ionization energies because it is more difficult to remove an electron after an electron has already been removed. Furthermore, elements such as Cr and Cu have extremely high second ionization energies because they have attained the stable configuration $(Cr^+: 3d^5 \text{ and } Cu^+: 3d^{10})$ after losing the first electron. As a result, extracting one more electron from this stable configuration will require a significant amount of energy.

8.6. Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?Solution: Oxide and fluoride ions are both highly electronegative and have very small sizes. They are able to oxidize the metal to its highest oxidation state due to these properties.

8.7. Which is a stronger reducing agent Cr^{2+} or Fe^{2+} and why? **Solution:** When Cr^{2+} and Fe^{2+} act as reducing agents, the following reactions occur. $Cr^{2+} \rightarrow Cr^{3+}$

 $Fe^{2+} \rightarrow Fe^{3+}$ The value for $E^{\circ}_{Cr^{3+}/Cr^{2+}}$ is -0.41 V and the value of $E^{\circ}_{Fe^{3+}/Fe^{2+}}$ is +0.77 V. This means that Cr^{2+} is easily oxidized to Cr^{3+} , whereas Fe^{2+} is not easily oxidized to Fe^{3+} . As a result, Cr^{2+} is a more effective reducing agent than Fe^{3+} .

8.8. Calculate the 'spin only' magnetic moment of $M^{2+}(aq)$ ion (Z = 27).

Solution: The atomic number is 27 and its electronic configuration is $[Ar]3d^7$.

Therefore, it has 3 unpaired electrons.

For value, n = 3,

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

$$= \sqrt{3(3+2)}$$

$$= 3.87$$

$$\simeq 4 \text{ BM}$$



8.9. Explain why Cu^+ ion is not stable in aqueous solutions?

Solution: Cu^{2+} is more stable in an aqueous medium than Cu^+ . This is because, while removing one electron from Cu^+ to Cu^{2+} requires energy, the high hydration energy of Cu^{2+} compensates for it. As a result, the Cu+ ion in an aqueous solution is unstable. It is disproportionate to provide Cu^{2+} and Cu.

 $2\mathrm{Cu}^{+}_{(aq)} \rightarrow \mathrm{Cu}^{2+}_{(aq)} + \mathrm{Cu}_{(s)}$

8.10. Actinoid contraction is greater from element to element than lanthanoid contraction. Why? **Solution:** 5f orbitals are filled in actinoids. These 5f orbitals provide less shielding than 4f orbitals (in lanthanoids). Thus, in the case of actinoids, the effective nuclear charge experienced by electrons in valence shells is much greater than that experienced by lanthanoids.

As a result, the size contraction in actinoids is greater than that in lanthanoids.

Exercise

8.1. Write down the electronic configuration of:

(i) Cr^{3+} (ii)Pm³⁺ (iii)Cu⁺ (iv)Ce⁴⁺ $(v)Co^{2+}$ (vi)Lu²⁺ (vii)Mn²⁺ (viii)Th⁴⁺ Solution: (i) $Cr^{3+}:[Ar]3d^3$ (ii) Pm^{3+} : [Xe] $3d^3$ $(iii)Cu^+:[Ar]3d^{10}$ $(iv)Ce^{4+}:[Xe]$ $(v)Co^{2+}:[Ar]3d^7$ $(vi)Lu^{2+}:[Xe]4f^{14}5d^{1}$ $(vii) Mn^{2+} : [Ar] 3d^5$ (viii)Th⁴⁺:[Rn]



Solution: The electronic configuration of Mn^{2+} is $[Ar]3d^5$ and the electronic configuration of Fe^{2+} is $[Ar]3d^6$. Half-filled and fully-filled orbitals are known to be more stable. As a result, Mn in the (+2) state has a stable d^5 configuration. This is why Mn^{2+} is resistant to oxidation to Mn^{3+} . Furthermore, Fe^{2+} has a $3d^6$ configuration that can be changed to a more stable $3d^5$ configuration by losing one electron. As a result, Fe^{2+} is easily oxidized to Fe^{3+} oxidation state.

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

Solution: The table below shows the oxidation states of the first half of the first row of transition metals.

Oxidation state Sc Ti V Cr Mn +2 +2 +2 +2 +2 +3 +3 +3 +3 +3 +4 +4 +4 +4 +5 +5 +6 +6 +7

With the exception of Sc, all other metals exhibit +2 oxidation state. In addition, as one moves from Sc to Mn, the atomic number rises from 21 to 25. As a result, the number of electrons in the 3d - orbital increases from one to five.

$$Sc(+2) = d^{1}$$
$$Ti(+2) = d^{2}$$
$$V(+2) = d^{3}$$
$$Cr(+2) = d^{4}$$
$$Mn(+2) = d^{5}$$

The loss of two 4s electrons by these metals results in a +2 oxidation state. Because the number of d electrons in the (+2) state increases from Ti(+2) to Mn(+ 2), so does the stability of the +2 state (as

d-orbital is becoming more and more half-filled). Mn (+2) contains d^5 electrons (that is half-filled d shell, which is highly stable).

8.4. 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. **Solution:**

The elements in the first half of the transition series have a large number of oxidation states, with Mn having the most (+2 to +7). The stability of the +2 oxidation state increases as the atomic number increases. This occurs as more electrons are filled in the d-orbital. Sc, on the other hand, does not

have a +2 oxidation state. It has the electronic configuration 4s2 3d1. To form Sc^{3+} , it loses all three electrons. +3 oxidation state of scandium is very stable because it achieves a stable noble gas configuration, [Ar], by losing all three electrons. For the same reason, Ti (+4) and V (+5) are extremely



stable. +2 oxidation state of manganese is very stable because its d-orbital is exactly half-filled after losing two electrons, $[Ar]3d^5$.

8.5. What may be the stable oxidation state of the transition element with the following *d* electron configurations in the ground state of their atoms: $3d^3$, $3d^5$, $3d^8$ and $3d^4$? **Solution:**

Electronic configuration in ground state stable oxidation state

(i) $3d^3$ (vanadium) +2, +3, +4, +5	
(ii) $3d^5$ (chromium) +3, +4, +6	
(iii) $3d^5$ (Manganese) +2, +4, +6, +7	
(iv) $3d^8$ (cobalt) +2, +3	
(v) $3d^4$ There is no $3d^4$ configuration in group	und state

8.6. 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. **Solution:**

- (i) Vanadate VO_3^{2-} , Oxidation state of V: +5.
- (ii) Chromate, CrO_4^{2-} , Oxidation state of Cr: +6.
- (iii) Permanganate, MnO_4^- , Oxidation state of Mn: +7.

8.7. What is lanthanoid contraction? What are the consequences of lanthanoid contraction?

Solution: The atomic number gradually increases by one as we progress through the lanthanoid series. This means that the number of electrons and protons in an atom grows by one. The effective nuclear charge grows as electrons are added to the same shell. This occurs because the increase in nuclear attraction caused by the addition of a proton is greater than the increase in interelectronic repulsions caused by the addition of an electron. In addition, as the atomic number increases, so does the number of electrons in the 4f orbital. The shielding effect of 4f electrons is poor. As a result, the effective nuclear charge felt by the outer electrons rises. As a result, the nucleus's attraction to the outermost electrons increases. As a result, the size of lanthanoids decreases steadily as the atomic number increases. The process is known as lanthanoid contraction.

Consequences of lanthanoid contraction

(i) The properties of the second and third transition series are similar.

(ii) Lanthanide contraction allows for the separation of lanthanoids.

(iii) Lanthanide contraction causes variation in the basic strength of lanthanide hydroxides. (From $La(OH)_3$ to $Lu(OH)_3$, the basic strength decreases.)

8.8. 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? **Solution:** Transition elements are those in which the atoms or ions have partially filled d-orbitals (in a stable oxidation state). These elements are in the d-block and show a property transition between the s-block and the p-block. As a result, these are referred to as transition elements.



Elements with completely filled d-subshells, such as Zn, Cd, and Hg, cannot be classified as transition elements.

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

Solution: Transition metals have a dorbital that is partially filled. As a result, the transition elements' electronic configuration is $(n-1)d^{1-10}ns^{0-2}$. Non-transition elements either lack a dorbital or have a completely filled dorbital. As a result, non-transition elements have an electronic configuration of ns^{1-2} or ns^2np^{1-6} .

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

Solution: In the lanthanide series, the +3 oxidation state is most common, resulting in the dominance of Ln(III) compounds. However, +2 and +4 oxidation states can be found in solution and solid compounds.

8.11. 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.

Solution: (i) Transition metals have paramagnetic properties. The presence of unpaired electrons causes paramagnetism, with each electron having a magnetic moment associated with its spin angular momentum and orbital angular momentum. The orbital angular momentum, on the other hand, is quenched in the first transition series. As a result, the resulting paramagnetism is solely due to the unpaired electron.

(ii) Transition elements have a large number of valence electrons and a high effective nuclear charge. As a result, they form extremely strong metallic bonds. As a result, transition metals have a high enthalpy of atomization.

(iii) The majority of transition metal complexes are colored. This is due to the absorption of radiation from the visible light region in order to promote an electron from one dorbital to another. When ligands are present, the d-orbitals split into two sets of orbitals with different energies. As a result, electrons can be transferred from one set to another. The energy required for these transitions is quite low and lies within the visible range of radiation. Transition metal ions absorb a specific wavelength of radiation and reflect the rest, imparting color to the solution.

(iv) Two fundamental facts explain the catalytic activity of transition elements.

(a) Transition metals form unstable intermediate compounds due to their ability to exhibit variable oxidation states and form complexes. As a result, they open up a new path for the reaction with a lower activation energy, E_a .

(b) Transition metals also provide an appropriate surface for the reactions to take place.

8.12. What are interstitial compounds? Why are such compounds well known for transition metals? **Solution:** Transition metals are large in size and have a large number of interstitial sites. In the interstitial sites of their crystal lattices, transition elements can trap atoms of other elements (with small atomic sizes), such as H, C, and N. Interstitial compounds are the resulting compounds.

8.13. How is the variability in oxidation states of transition metals different from that of the non-



transition metals? Illustrate with examples.

Solution: By removing all of the valence electrons from transition elements, the oxidation state can be changed from +1 to the highest oxidation state. In addition, the oxidation states of transition elements differ by one (Fe^{2+} and Fe^{3+} ; Cu^+ and Cu^{2+}). The oxidation states of non-transition elements differ by two, for example, +2 and +4, or +3 and +5, and so on.

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

Solution: The preparation of potassium dichromate from chromite ore $(FeCr_2O_4)$ in the following

steps.

Step 1: Preparation of sodium chromate

Step 2: Conversion of sodium chromate into sodium dichromate.

 $\begin{aligned} & 4\text{FeCr}_2\text{O}_4 + 16\text{NaOH} + 7\text{O}_2 \rightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{H}_2\text{O} \\ & 4\text{FeCr}_2\text{O}_4 + 2\text{Na}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \rightarrow \text{Na}_2\text{CrO}_4 + \text{Na}_2\text{SO}_4 + \text{H}_2\text{O} \end{aligned}$

Step 3: Conversion of sodium dichromate to potassium dichromate.

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

Potassium chloride, which is less soluble than sodium chloride, forms orange-colored crystals and can be removed through filtration.

At pH 4, the dichromate ion $(Cr_2O_7^{2-})$ is exist in equilibrium state with chromate ion

 (CrO_4^{2-}) . They can, however, be interconverted by varying the pH.

8.15. Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with:

(i) iodide (ii) iron(II) solution and (iii) $\,H_2S\,$

Potassium dichromate $(K_2Cr_2O_7)$ acts as a very strong oxidising agent in the acidic medium.

$$K_2Cr_2O_7 + 4H_2SO_4 \rightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

 $K_2 C r_2 O_7\,$ accepts electrons in order to be reduced and acts as an oxidizing agent. The following reactions of $K_2 C r_2 O_7\,$ with other iodides, iron (II) solution, and H2S are given.

(i) Potassium dichromate oxidizes iodide to iodine.

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

 $\left[2I^- \rightarrow I_2 + 2e^-\right] \times 3$
 $Cr_2O_7^{2-} + 14H^+ + 6I^- \rightarrow 2Cr^{3+} + I_2 + 7H_2O$

(ii) Potassium dichormate oxidizes iron (II) solution to iron (III) solution i.e., ferrous ions to ferric ions.



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

 $\left[Fe^{2+} \rightarrow Fe^{3+} + e^-\right] \times 6$
 $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

(iii) Potassium dichormate oxidizes hydrogen sulfide to sulfur.

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

 $\left[H_2S \rightarrow S + 2H^+ + 2e^-\right] \times 3$
 $Cr_2O_7^{2-} + 14H^+ + 3H_2S \rightarrow 2Cr^{3+} + 3S + 7H_2O$

8.16. 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.

Solution: Pyrolusite can be used to make potassium permanganate (MnO_2) . To produce K_2MnO_4 , the ore is fused with KOH in the presence of either atmospheric oxygen or an oxidizing agent such as KNO_3 or $KClO_4$.

$$2MnO_2 + 4KOH + O_2 \xrightarrow{Heat} 2K_2MnO_4 + 2H_2O$$

(Green)

The green mass can be extracted with water and oxidized electrolytically or by introducing chlorine/ozone into the solution.

$$K_2MnO_4 \leftrightarrow 2K^+ + MnO_4^2$$

 $H_2O \leftrightarrow H^+ + OH^-$

At anode, manganate ions are oxidized to form permanganate ions.

 $MnO_4^{2-} \leftrightarrow MnO_4^{-} + e^{-}$ Green Purple

Oxidation by chlorine

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

$$2MnO_4^{2^-} + Cl_2 \rightarrow 2MnO_4^- + 2Cl^-$$

Green Purple

Oxidation by ozone

 $2K_2MnO_4 + O_3 + H_2O \rightarrow 2KMnO_4 + 2KOH + O_2$ $2MnO_4^{2-} + O_3 + H_2O \rightarrow 2MnO_4^{2-} + 2OH^- + O_2$

(i) Acidified $KMnO_4$ solution oxidizes Fe (II) ions to Fe (III) ions i.e., ferrous ions to ferric ions.



$$MnO_{4}^{-} + 8H^{+} + 5e^{-} \rightarrow Mn^{2+} + 4H_{2}O$$

$$\left[Fe^{2+} \rightarrow Fe^{3+} + e^{-}\right] \times 5$$

$$MnO_{4}^{-} + 8H^{+} + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_{2}O$$

(ii) Acidified potassium permanganate oxidizes $\,\mathrm{SO}_2\,$ to sulphuric acid.

$$MnO_{4}^{-} + 6H^{+} + 5e^{-} \rightarrow Mn^{2+} + 3H_{2}O] \times 2$$

$$\left[2H_{2}O + 2SO_{2} + O_{2} \rightarrow 4H^{+} + 2SO_{4}^{2-} + 2e^{-}\right] \times 5$$

$$2MnO_{4}^{-} + 10SO_{2} + 5O_{2} + 4H_{2}O \rightarrow 2Mn^{2+} + 8H^{+} + 10SO_{4}^{2-}$$

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

$$MnO_{4}^{-} + 8H^{+} + 5e^{-} \rightarrow Mn^{2+} + 4H_{2}O] \times 2$$

$$\begin{bmatrix} C_{2}O_{4}^{2-} \rightarrow 2CO_{2} + 2e^{-} \end{bmatrix} \times 5$$

$$2MnO_{4}^{-} + 16H^{+} + C_{2}O_{4}^{2-} \rightarrow 2Mn^{2+} + 2CO_{2} + 8H_{2}O$$

8.17. For M^{2+}/M and M^{3+}/M^{2+} systems, the E^- values for some metals are as follows: Cr^{3+}/Cr^{2+} = 0.4 V Mn^{2+}/Mn = 1.2V

 $Mn^{3+}/Mn^{2+} = +1.5 V$ $Fe^{2+}/Fe = -0.4 V$ $Fe^{3+}/Fe^{2+} = +0.8 V$

 $Cr^{2+}/Cr = 0.9V$ 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 oxidised as compared to a similar process for either chromium or manganese metal.

Solution:

(i) Fe^{3+}/Fe^{2+} has a higher E^- value than Cr^{3+}/Cr^{2+} but a lower value than Mn^{3+}/Mn^{2+} . So, reducing Fe^{3+} to Fe^{2+} is easier than reducing Mn^{3+} to Mn^{2+} , but not as easy as reducing Cr^{3+} to Cr^{2+} . As a result, Fe^{3+} has a higher stability than Mn^{3+} but a lower stability than Cr^{3+} . These metal ions can be arranged in increasing order of stability as follows: $Mn^{3+} < Fe^{3+} < Cr^{3+}$. (ii) The reduction potentials for the given pairs increase in the order listed below.

 $Mn^{2+}/Mn < Cr^{2+}/Cr < Fe^{2+}/Fe$

As a result, oxidizing Fe to Fe^{2+} is more difficult than oxidizing Cr to Cr^{2+} or Mn to Mn^{2+} . Thus, these metals can be arranged in increasing order of oxidation ability as:



Fe < Cr < Mn

8.18. Predict which of the following will be coloured in aqueous solution? Give reasons for each. **Solution:** Only ions with electrons in the d-orbital plane will be colored. Ions with an empty d-orbital will be colorless.

Ті	22	Ti ³⁺	$[Ar]3d^1$
v	23	V ³⁺	$[Ar]3d^2$
Cu	29	Cu ³⁺	$[Ar]3d^{10}$
Sc	21	Sc ³⁺	[Ar]
Mn	25	Mn ²⁺	$[Ar]3d^5$
Fe	26	Fe ³⁺	$[Ar]3d^5$
Со	27	Co ²⁺	$[Ar]3d^7$

It is clear from the table above that only Sc^{3+} has an empty d-orbital. All other ions, with the exception of Sc^{3+} , will be colored in aqueous solution due to d-d transitions.

8.19. Compare the stability of +2 oxidation state for the elements of the first transition series. **Solution:**

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	



Со	+1	+2	+3	+4	+5	
Ni	+1	+2	+3	+4		
Cu	+1	+2	+3			
Zn		+2				

According to the above table, Mn has the greatest number of oxidation states, ranging from +2 to +7. As one moves from Sc to Mn, the number of oxidation states increases. The number of oxidation states decreases as one moves from Mn to Zn due to a decrease in the number of available unpaired electrons. Moving from top to bottom, the relative stability of the +2 oxidation state increases. This is because removing the third electron from the d-orbital becomes increasingly difficult as one moves from top to bottom.

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

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

(i) Electronic configuration

The general electronic configuration for lanthanoids and actinoids are $[Xe]^{54} 4f^{0-14}5d^{0-1}6s^2$

and $[\text{Rn}]^{86} 6f^{0-14} 6d^{0-1} 7s^2$ respectively. 5f orbitals, unlike 4f orbitals, are not deeply buried and thus participate in bonding to a greater extent.

(ii) Oxidation states

Lanthanoids have a primary oxidation state of (+3). However, we occasionally come across oxidation states of + 2 and + 4. This is due to the extra stability of fully and half-filled orbitals. Actinoids have a wider range of oxidation states. This is due to the fact that the energies of the 5f, 6d, and 7s levels are comparable. Actinoids' primary oxidation state is (+3) once again. Lanthanoids, for example, have more compounds in the +3 state than in the +4 state.

(iii) Atomic and lonic dimensions

Actinoids, like lanthanoids, exhibit actinoid contraction (overall decrease in atomic and ionic radii). Because of the poor shielding effect of 5f orbitals, the contraction is greater.

(iv) Chemical reactivity

The earlier members of the lanthanide series are more reactive. They have a reactivity similar to Ca. Lanthanides begin to behave similarly to Al as their atomic number increases. Actinoids, on the other hand, are extremely reactive metals, particularly when finely divided. When they are combined with boiling water, they produce an oxide/hydride mixture. At low temperatures, actinoids combine with the majority of nonmetals. Alkalies have no effect on actinoids. In the case of acids, nitric acid has a minor effect on them (because of the formation of a protective oxide layer).

8.21. How would you account for the following:



(i) Of the d^4 species, Cr^{2+} is strongly reducing while manganese (III) is strongly oxidising. (ii) Cobalt (II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.

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

Solution: (i) Cr^{2+} is a strongly reducing element in nature. It is set up in a d4 configuration. It is

oxidized to ${\rm Cr}^{3+}$ while acting as a reducing agent (electronic configuration, d^3). This d^3 arrangement

can be written as configuration, resulting in a more stable configuration Mn3+ (d4), for example, acts as an oxidizing agent and is reduced to Mn2+ (d5). This has a highly stable d-orbital that is exactly half-filled.

(ii) In aqueous solutions, Co(II) is stable. In the presence of strong field complexing reagents, however, it is oxidized to Co. (III). Despite the fact that Co has a high third ionization energy, the increased amount of crystal field stabilization energy (CFSE) released in the presence of strong field ligands overcomes this ionization energy.

(iii) lons in the d1 configuration tend to lose one more electron in order to achieve the stable d0 configuration. Furthermore, the hydration or lattice energy is more than enough to remove the lone electron present in these ions' d-orbitals. As a result, they act as reducing agents.

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

Solution: It has been discovered that a relatively less stable oxidation state can or sometimes undergo an oxidation-reduction reaction in which it is oxidised and reduced at the same time. This is referred to as disproportionation.

For example,

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

$$\begin{array}{c} 3\mathrm{CrO}_4^{3-} + 8\mathrm{H}^+ \rightarrow 2\mathrm{CrO}_4^{2-} + \mathrm{Cr}^{3+} + 4\mathrm{H}_2\mathrm{O}\\ \mathrm{Cr}(\mathrm{V}) & \mathrm{Cr}(\mathrm{VI}) & \mathrm{Cr}(\mathrm{III}) \end{array}$$

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

 $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$ Mn(VI) Mn(VIII) Mn(IV)

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

Solution: Cu frequently exhibits +1 oxidation state in the first transition series. This is due to the fact that Cu (+1) has an electronic configuration of $[Ar]3d^{10}$. It is extremely stable due to the completely filled d-orbital.

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



Gaseous ions Number of unpaired electrons

- (i) $Mn^{3+}, [Ar]3d^4 = 4$
- (ii) $Cr^{3+}, [Ar] 3d^3 = 3$
- (iii) V^{3+} , [Ar] $3d^2$ 2
- (iv) $Ti^{3+}, [Ar]3d^1$

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

8.25. 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.

Solution:

(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.

(i) In the case of a transition metal's lower oxide, the metal atom has a low oxidation state. This means that some of the metal atom's valence electrons are not involved in bonding. As a result, it has the ability to donate electrons and act as a base.

In the case of a higher oxide of a transition metal, on the other hand, the metal atom has a high oxidation state. Because the valence electrons are involved in bonding, they are unavailable. There is also a powerful 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) Because of their high electronegativities and small sizes, oxygen and fluorine are powerful oxidizing agents. As a result, they extract the transition metals' highest oxidation states. A transition metal, in other words, has higher oxidation states in oxides and fluorides. For example, the oxidation states of Os and V in OsF_6 and V_2O_5 are +6 and +5, respectively.

(ii) Because of its high electronegativity and small size, oxygen is a powerful oxidizing agent. As a result, a metal's oxo-anions have the highest oxidation state. For example, the oxidation state of

Mn is +7 in MnO_4^- .

8.26. Indicate the steps in the preparation of:

(i) $K_2Cr_2O_7$ from chromite ore.

(ii) $KMnO_4$ from pyrolusite ore.

Solution:

(i) Potassium dichromate is prepared from chromite ore in the following steps. **Step (1):** Preparation of sodium chromate

 $4\text{FeCr}_2\text{O}_4 + 16\text{NaOH} + 7\text{O}_2 \rightarrow 8\text{Na}_2\text{CrO}_4 + 2\text{Fe}_2\text{O}_3 + 8\text{H}_2\text{O}$

Step (2): Conversion of sodium chromate into sodium dichromate Step 3: Conversion of sodium dichromate to potassium dichromate. $2Na_2Cr_2O_7 + conc. H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$



Step(3): Conversion of sodium dichromate to potassium dichromate

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

Potassium chloride, which is less soluble than sodium chloride, forms orange-colored crystals and can be removed through filtration.

At pH 4, the dichromate ion $(Cr_2O_7^{2-})$ is exist in equilibrium state with chromate ion.

However, by changing the pH, they can be interconverted.

$$2\mathrm{CrO}_{4}^{2-} \xleftarrow{\mathrm{Acid}}{\mathrm{Alkali}} \rightarrow 2\mathrm{HCrO}_{4}^{-} \xleftarrow{\mathrm{Acid}}{\mathrm{Alkali}} \rightarrow \mathrm{Cr}_{2}\mathrm{O}_{7}^{2-}$$

(ii)

Pyrolusite can be used to make potassium permanganate (MnO_2) . To produce K_2MnO_4 , the ore is fused with KOH in the presence of either atmospheric oxygen or an oxidizing agent such as KNO_3 or $KClO_4$.

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\text{Heat}} 2K_2MnO_4 + 2H_2O$$

(Green)

The green mass can be extracted with water and oxidized electrolytically or by introducing chlorine/ozone into the solution.

$$K_2MnO_4 \leftrightarrow 2K^+ + MnO_4^2$$

$$H_2O \leftrightarrow H^+ + OH^-$$

At anode, manganate ions are oxidized to form permanganate ions.

$$MnO_4^{2-} \leftrightarrow MnO_4^{-} + e^{-}$$

Green Purple

Oxidation by chlorine

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

$$2MnO_4^{2-} + Cl_2 \rightarrow 2MnO_4^{-} + 2Cl^{-}$$

Green Purple

Oxidation by ozone

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

$$2MnO_4^{2-} + O_3 + H_2O \rightarrow 2MnO_4^{2-} + 2OH^- + O_2$$

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

Solution: A solid solution of two or more elements in a metallic matrix is known as an alloy. It can be either a partial solid solution or a full solid solution. Alloys typically have physical properties that differ from those of their constituent elements.

Mischmetal is a significant lanthanide alloy. Lanthanoids (94.5%), iron (5%), and traces of S, C, Si, Ca, and Al are all present.

(1) Mischmetal is used in cigarette lighters and gas lighters.

(2) It's used in flamethrower tanks.

(3) It is used in the manufacture of tracer bullets and shells.



8.28. 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.

Solution: Inner transition metals are those in which the final electron enters the f-orbital. The elements in which the 4f and 5f orbitals are gradually filled are referred to as f-block elements. Among the given atomic numbers, the inner transition elements have atomic numbers 59, 95, and 102.

8.29. 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.

Solution: Lanthanoids have three oxidation states (+2, +3, +4). The +3 state is the most common of these oxidation states. Lanthanoids have a limited number of oxidation states due to the large energy difference between the 4f, 5d, and 6s orbitals. The energy difference between the 5f, 6d, and 7s orbitals, on the other hand, is very small. As a result, actinoids have a large number of oxidation states. For example, uranium and plutonium have oxidation states of +3, +4, +5, and +6, whereas neptunium has oxidation states of +3, +4, +5, and +7. In the case of actinoids, the most common oxidation state is also +3.

8.30. 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.

Solution: Lawrencium, Lr, is the last element in the actinoid series. It has an atomic number of 103 and its electronic configuration is $[Rn]5f^{14}6d^{1}7s^{2}$. Its most common oxidation state is +3, because after losing three electrons, it achieves a stable f¹⁴ configuration.

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.

Solution: The electronic configuration of cerium is

 $Ce = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6 4f^1 5d^1 6s^2$

The magnetic moment can be calculated by the formula

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

Here, *n* is the number of unpaired electrons.

In Ce, *n* = 2

Therefore,

$$\mu = \sqrt{2(2+2)}$$
$$= \sqrt{2 \times 4}$$
$$= 2\sqrt{2}$$
$$= 2.828 \text{ BM}$$

8.32. 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.

Solution:

The lanthanides with +2 and +4 states are listed in the table below. The elements' atomic numbers are given in parenthesis.





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

Ce achieves a stable electronic configuration of [Xe] after forming Ce⁴⁺. Tb achieves a stable electronic configuration of $[Xe]4f^7$ after forming Tb⁴⁺. Following the formation of Eu²⁺, Eu achieves a stable electronic configuration of $[Xe]4f^7$.

After forming Yb²⁺, Yb achieves the stable electronic configuration $[Xe]4f^{14}$.

8.33. Compare the chemistry of the actinoids with that of lanthanoids with reference to:(i) electronic configuration(ii) oxidation states and(iii) chemical reactivity.

Solution: Electronic configuration

The general electronic configuration for lanthanoids and actinoids are $\left[\mathrm{Xe}\right]^{54} 4 f^{0-14} 5 d^{0-1} 6 s^2$

and $[\text{Rn}]^{86} 6f^{0-14} 6d^{0-1} 7s^2$ respectively. 5f orbitals, unlike 4f orbitals, are not deeply buried and thus participate in bonding to a greater extent.

Oxidation states

Lanthanoids have a primary oxidation state of (+3). However, we occasionally come across oxidation states of + 2 and + 4. This is due to the extra stability of fully and half-filled orbitals. Actinoids have a wider range of oxidation states. This is due to the fact that the energies of the 5f, 6d, and 7s levels are comparable. Actinoids' primary oxidation state is (+3) once again. Lanthanoids, for example, have more compounds in the +3 state than in the +4 state.

Chemical reactivity

The earlier members of the lanthanide series are more reactive. They have a reactivity similar to Ca. Lanthanides begin to behave similarly to Al as their atomic number increases. Actinoids, on the other hand, are extremely reactive metals, particularly when finely divided. When they are combined with boiling water, they produce an oxide/hydride mixture. At low temperatures, actinoids combine with the majority of nonmetals. Alkalies have no effect on actinoids. In the case of acids, nitric acid has a minor effect on them (because of the formation of a protective oxide layer).

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

Solution:



Atomic number	Electronic configuration
61	$[Xe]4f^55d^06s^2$
91	$[\mathrm{Rn}]5f^26d^17s^2$
101	$[\text{Rn}]5f^{13}5d^{0}7s^{2}$
109	$[\text{Rn}]5f^{14}6d^77s^2$

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.

Solution: (i) The 3d, 4d, and 5d orbitals are filled in the first, second, and third transition series, respectively.

We know that elements in the same vertical column have similar electronic configurations in general. Two elements in the first transition series have unusual electronic configurations:

$$Cr(24) = 3d^5 4s^1$$

$$Cu(29) = 3d^{10}4s^1$$

In the second transition series, there are also exceptions. They are as follows:

$$\mathrm{Mo}(42) = 4d^55s$$

$$Tc(43) = 4d^65s^1$$

 $\operatorname{Ru}(44) = 4d^7 5s^1$

 $\mathrm{Rh}(45) = 4d^85s^1$

 $Pd(46) = 4d^{10}5s^0$

$$Ag(47) = 4d^{10}5s^1$$

In the third transition series, there are some exceptions as well. These are:

 $W(74) = 5d^4 6s^2$

$$Pt(78) = 5d^9 6s^1$$

 $Au(79) = 5d^{10}6s^1$

As a result of these exceptions, it is common for the electronic configurations of elements in the same group to differ.

(i) The number of oxidation states shown by the elements in each of the three transition series is greatest in the middle and lowest at the extreme ends. For all elements in the first transition series, however, the +2 and +3 oxidation states are quite stable. In the +2 and +3 oxidation states, all metals in the first transition series form stable compounds. In the second and third transition series, where higher oxidation states are more important, the stability of the +2 and +3 oxidation states decreases.



For example
$$\begin{bmatrix} II \\ Fe(CN)_6 \end{bmatrix}^{4-}$$
, $\begin{bmatrix} III \\ Co(NH_3)_6 \end{bmatrix}^{3+}$, $\begin{bmatrix} II \\ Ti(H_2O)_6 \end{bmatrix}^{3+}$ are stable co

are stable complexes, However,

no such complexes are known for the second and third transition series, which include Mo, W, Rh, and In. They combine to form complexes with high oxidation states. For instance, WCl_6 , ReF_7 , RuO_4 , and so on.

(ii) The first ionisation enthalpy increases from left to right in each of the three transition series. There are, however, some exceptions. The third transition series has higher first ionisation enthalpies than the first and second transition series. This happens because 4f electrons have a poor shielding effect in the third transition series.

Certain elements in the second transition series have higher first ionisation enthalpies than elements in the first transition series corresponding to the same vertical column.

There are also elements in the 2nd transition series whose first ionisation enthalpies are lower than those of the elements in the 1st transition series corresponding to the same vertical column. (iv) Across a period, atomic size decreases from left to right. Now, among the three transition series, the atomic sizes of the elements in the second transition series are greater than those of the elements in the first transition series corresponding to the same vertical column. The atomic sizes of the elements in the third transition series, on the other hand, are nearly identical to those of the corresponding members in the second transition series. This is due to the contraction of the lanthanoid.

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).

Solution:

Metal ion	Number of d electrons	Filling of <i>d</i> orbitals
Ti ²⁺	2	t_{2g}^2
V^{2+}	3	t_{2g}^{3}
Cr ³⁺	3	t_{2g}^{3}
Mn^{2+}	5	$t_{2g}^3 e_g^2$
Fe ²⁺	6	$t_{2g}^4 e_g^2$
Fe ³⁺	5	$t_{2g}^3 e_g^2$
Co ²⁺	7	$t_{2g}^5 e_g^2$
Ni ²⁺	8	$t_{2g}^6 e_g^2$
Cu ²⁺	9	$t_{2g}^6 e_g^3$

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

Solution: In many ways, the properties of the elements of the first transition series differ from those of the heavier transition elements.

(i) The atomic sizes of the first transition series elements are smaller than those of the heavier elements (elements of 2nd and 3rd transition series).



The atomic sizes of the elements in the third transition series, on the other hand, are nearly identical to those of the corresponding members in the second transition series. This is due to the contraction of the lanthanoid.

(ii) Elements in the first transition series have more +2 and +3 oxidation states, whereas heavier elements have more higher oxidation states.

(iii) The first transition series elements have lower enthalpies of atomisation than the second and third transition series elements.

(iv) The melting and boiling points of the transition elements in the first transition series are lower than those of the heavier transition elements. Because of the occurrence of stronger metallic bonding (M-M bonding), this is the case.

(v) Depending on the strength of the ligand field, the elements of the first transition series form lowspin or high-spin complexes. However, regardless of the strength of the ligand field, the heavier transition elements form only low-spin complexes.

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

K₂[MnCl₄]: 5.9

Solution:

The magnetic moment can be calculated by

 $\mu = \sqrt{n(n+2)}$ For value n = 1, $\mu = \sqrt{1(1+2)}$ =1.732For value n = 2, $\mu = \sqrt{2(2+2)}$ = 2.83For value n = 3, $\mu = \sqrt{3(3+2)}$ = 3.87For value n = 4, $\mu = \sqrt{4(4+2)}$ =4.899For value n = 5, $\mu = \sqrt{5(5+2)}$ = 5.92

(i) For $K_4[Mn\big(CN\big)_6\,]$ in transition metals, the magnetic moment can be calculated from the spin-only formula. Therefore,

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

The above calculation shows that the given value is closest to n = 1. Mn is also in the +2 oxidation



state in this complex. This means Mn has 5 electrons in its d- orbital. As a result, we can say that cyanide ion is a strong field ligand that causes electron pairing.

Solved Examples

8.1. On what ground can you say that scandium (Z = 21) is a transition element but zinc (Z = 30) is not?

Solution: It is classified as a transition element based on the incompletely filled 3d orbitals of a

scandium atom in its ground state $\binom{3d^1}{2}$. Zinc, on the other hand, has completely filled d orbitals $\binom{3d^{10}}{2}$.

^{1*} in both its ground and oxidized states, so it is not considered a transition element.

8.2. Why do the transition elements exhibit higher enthalpies of atomisation? **Solution:** Since their atoms contain a large number of unpaired electrons, they have stronger interatomic interaction and thus stronger bonding between atoms, resulting in higher enthalpies of atomisation.

8.3. Name a transition element which does not exhibit variable oxidation states. **Solution:** Scandium (Z = 21) lacks variable oxidation states.

8.4. Why is Cr^{2+} reducing and Mn^{3+} oxidising when both have d^4 configuration? **Solution:** Cr^{2+} decreases in concentration as its configuration shifts from d^4 to d^3 , the latter having a half-filled ${}^{t_{2g}}$ level. The transition from Mn^{3+} to Mn^{2+} , on the other hand, results in the half-filled (d^5) configuration, which has increased stability.

8.5. How would you account for the increasing oxidising power in the series $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$?

Solution: This is because the lower species to which they are reduced are becoming more stable.

8.6. For the first row transition metals the E o values are:

$$E^{0}$$
 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.

Solution: The $E^{\circ}(M^{2^+}/M)$ values are irregular, which can be explained by the irregular variation of ionisation enthalpies $(\Delta_i H_1 + \Delta_i H_2)$ and sublimation enthalpies, which are much lower for manganese and vanadium.

8.7. Why is the E^- value for the Mn^{3+}/Mn^{2+} couple much more positive than that for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+} ? Explain.

Solution: This is primarily due to the much larger third ionisation energy of Mn (where the required change is d^5 to d^4). This also explains why +3 oxidation state of Mn is unimportant.



8.8. Calculate the magnetic moment of a divalent ion in aqueous solution if its atomic number is 25.

Solution: The divalent ion in aqueous solution with atomic number 25 will have the d^5 configuration (five unpaired electrons).

The magnetic moment can be calculated as

$$\mu = \sqrt{n(n+2)}$$
$$= \sqrt{5(5+2)}$$
$$= 5.92 \text{ BM}$$

8.9. What is meant by 'disproportionation' of an oxidation state? Give an example. **Solution:** Disproportionation occurs when an oxidation state becomes less stable in comparison to other oxidation states, one lower and one higher. In acidic solution, manganese (VI), for example, becomes unstable in comparison to manganese (VII) and manganese (IV). The reaction is shown below.

 $3Mn^{VI}O_4^{2-} + 4H^+ \rightarrow 2Mn^{VII}O_4^- + Mn^{IV}O_2 + 2H_2O$

8.10. Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state. **Solution:** Cerium (Z = 58)