

CHAPTER 4

THE d & f BLOCK ELEMENTS

QUESTION AND ANSWERS

2MARKS

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

Sol: (i) $\text{Cr}^{3+} = [\text{Ar}]^{18} 3d^3$
(ii) $\text{Pm}^{3+} = [\text{Xe}]^{54} 4f^4$
(iii) $\text{Cu}^+ = [\text{Ar}]^{18} 3d^{10}$
(iv) $\text{Ce}^{4+} = [\text{Xe}]^{54}$
(v) $\text{Co}^{2+} = [\text{Ar}]^{18} 3d^7$
(vi) $\text{Lu}^{2+} = [\text{Xe}]^{54} 4f^{14} 5d^1$
(vii) $\text{Mn}^{2+} = [\text{Ar}]^{18} 3d^5$ (viii) $\text{Th}^{4+} = [\text{Rn}]^{86}$

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

Sol: Electronic configuration of Mn^{2+} is $3d^5$. This is a half-filled configuration and hence stable. Therefore, third ionization enthalpy is very high, i. e., third electron cannot be lost easily. Electronic configuration of Fe^{2+} is $3d^6$. It can lose one electron easily to achieve a stable configuration $3d^5$.

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?

Sol: Here after losing 2 electrons from p-orbitals, the 3d-orbital gets gradually occupied with increase in atomic number. Since the number of unpaired electrons in 3d orbital increases, the stability of the cations (M^{2+}) increases from Sc^{2+} to Mn^{2+} .

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.

Sol: In the first series of transition elements, the oxidation states which lead to exactly half-filled or completely filled d-orbitals are more stable. For example, Mn ($Z = 25$) has electronic configuration $[\text{Ar}] 3d^5 4s^2$. It shows oxidation states + 2 to + 7 but Mn (II) is most stable because of half-filled configuration $[\text{Ar}] 3d^5$. Similarly Sc^{3+} is more stable than Sc^+ and Fe^{3+} is more stable than Fe^{2+} due to half filled d-orbitals.

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

Sol: (a) $3d^3 4s^1 = + 5$.
(b) $3d^5 4s^2 = + 2, + 7, 3d^5 4s^1 = + 6$.
(c) $3d^8 4s^2 = + 2$.
(d) $3d^4 4s^2 = 3d^5 4s^1 = + 6$ (and + 3).

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.

Sol: $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-} (Group number = Oxidation state of Cr = 6).
 MnO_4^- (Group number = Oxidation state of Mn = 7).

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

Sol: Lanthanides exhibit + 2, + 3 and + 4 oxidation states. The most common oxidation state of lanthanoids is +3.

5MARKS

1. In what way are the electronic configuration of the transition elements different from non-transition elements?

Sol: Electronic configuration of transition elements : $(n - 1)d^{1-10} ns^{1-2}$. Electronic configuration of non-transition elements : ns^{1-2} or $ns^2 np^{1-6}$. From comparison, it is quite evident that the transition elements have incomplete d-orbitals (s- orbitals in some cases) while the non-transition elements have no d-orbitals present in the valence shells of their atoms. This is responsible for the difference in the characteristics of the elements belonging to these classess of elements.

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

Sol: Transition metals form large number of interstitial compounds. They are able to entrap small atoms of elements like H, G, N, B, etc., in their crystal lattice and even can make weak bonds with them.

Due to formation of interstitial compounds, their malleability and ductility decreases and tensile . strength increases. Steel and cast iron are hard in comparison to wrought iron due to the presence of trapped carbon atoms in interstitial spaces.

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

Sol: The transition metals show a number of variable oxidation states due to the participation of $(n - 1) d$ electrons in addition to ns electrons in the bond formation. They therefore, exhibit a large number of variable oxidation states. On the other hand, the non-transition metals generally belonging to s-block do not show variable oxidation states because by the loss of valence s-

electrons, they acquire the configuration of the nearest noble gas elements.

In the p-block the lower oxidation states are favoured by the heavier members (due to inert pair effect), the opposite is true in the groups of d-block. For example, in group 6, Mo(VI) and W(VI) are found to be more stable than Cr(VI). Thus Cr(VI) in the form of dichromate in acidic medium is a strong oxidising agent, whereas MoO_3 and WO_3 are not.

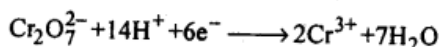
4. Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with:

(i) iodide

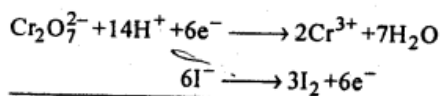
(ii) iron (II) solution and

(iii) H_2S

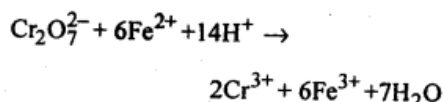
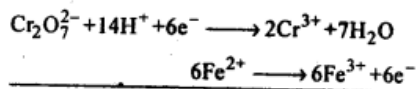
Sol: $\text{K}_2\text{Cr}_2\text{O}_7$ is a powerful oxidising agent. In dilute sulphuric acid medium the oxidation state of Cr changes from +6 to +3. The oxidising action can be represented as follows:



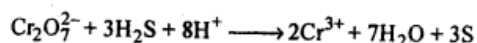
- (i) **Iodide:** Iodide ion (I^-) is oxidised to I_2 by the acidified solution of $\text{K}_2\text{Cr}_2\text{O}_7$.
Reaction:



- (ii) **Iron (II) solution:** Ferrous salts (Fe^{2+}) are oxidised to ferric (Fe^{3+}) salts when they are treated with acidified $\text{K}_2\text{Cr}_2\text{O}_7$.
Reaction:



- (iii) **H_2S :** H_2S is oxidised to sulphur.



5. How would you account for the following:

(i) Of the d^4 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 oxidised.

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

Sol: (i) E° value for $\text{Cr}^{3+}/\text{Cr}^{2+}$ is negative (-0.41 V) whereas E° values for $\text{Mn}^{3+}/\text{Mn}^{2+}$ is positive (+1.57 V). Hence, Cr^{2+} ion can easily undergo oxidation to give Cr^{3+} ion and, therefore, act as strong reducing agent whereas Mn^{3+} can easily undergo reduction to give Mn^{2+} and hence act as an oxidizing agent.

(ii) Co (III) has greater tendency to form coordination complexes than Co (II). Hence, in the presence of ligands, Co (II) changes to Co (III), i.e., is easily oxidized.

(iii) The ions with dx configuration have the tendency to lose the only electron present in d-subshell to acquire stable d^0 configuration. Hence, they are unstable and undergo oxidation or disproportionation.

6. 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.

Sol: (i) The lower oxide of transition metal is basic because the metal atom has low oxidation state whereas higher ones are acidic due to high oxidation state. For example, MnO is basic whereas Mn_2O_7 is acidic. Oxides in lower oxidation state are ionic hence basic. Oxides in higher oxidation state are covalent hence

acidic

(ii) A transition metal exhibits higher oxidation states in oxides and fluorides because oxygen and fluorine are highly electronegative elements, small in size and strongest oxidising agents. For example, osmium shows an oxidation states of + 6 in OsF_6 and vanadium shows an oxidation states of + 5 in V_2O_5 .

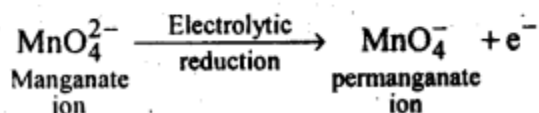
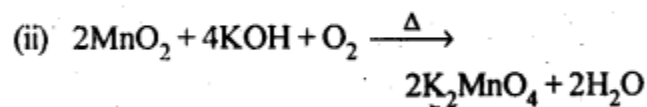
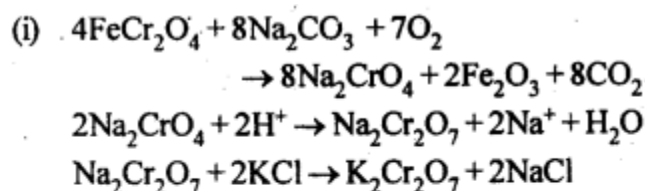
(iii) Oxo metal anions have highest oxidation state, e.g., Cr in $\text{Cr}_2\text{O}_7^{2-}$ has an. oxidation state of + 6 whereas Mn in MnO_4^- has an oxidation state of + 7. This is again due to the combination of the metal with oxygen, which is highly electronegative and oxidizing agent.

7. Indicate the steps in the preparation of:

(i) $\text{K}_2\text{Cr}_2\text{O}_7$ from chromite ore

(ii) KMnO_4 from pyrolusite ore.

Sol:



7MARKS

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

(i) electronic configurations

(ii) oxidation states

(iii) ionisation enthalpies and

(iv) atomic sizes

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

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

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

(iii) Ionization enthalpies: The first ionization enthalpies in each series generally increases gradually as we move from left to right though some exceptions are observed in each series. The first ionization enthalpies of some elements in the second (4d) series are higher while some of them have lower value than the elements of 3d series in the same vertical column. However, the

first ionization enthalpies of third (5d) series are higher than those of 3d and 4d series. This is because of weak shielding of nucleus by 4f-electrons in the 5d series.

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

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

(i)electronic configuration,

(ii)atomic and ionic sizes and

(iii)oxidation state

(iv)chemical reactivity.

Sol: (i) Electronic configuration: The general electronic configuration of lanthanoids is $[\text{Xe}]^{54} 4f^{1-14} 5d^{0-1} 6s^2$ and that of actinoids is $[\text{Rn}]^{86} 5f^{0-14} 6d^{0-1} 7s^2$, lanthanoids belong to 4f series whereas actinoids belong to 5f-series.

(ii) Atomic and ionic sizes: Both lanthanoids and actinoids show decrease in size of their atoms or ions in + 3 oxidation state as we go from left to right. In lanthanoids, the decrease is called lanthanoid contraction whereas in actinoids, it is called actinoid contraction. The contraction is greater from element to element in actinoids due to poorer shielding by 5f electrons.

(iii)Oxidation state: Lanthanoids show limited oxidation states (+ 2, + 3, + 4) out of which + 3 is most common whereas actinoids show +3, +4, +5, +6, +7 oxidation states. This is because of large energy gap between 4f 5d and 6s orbitals. However, actinoids

show a large number of oxidation states because of small energy gap- between 5f 6d and 1s orbitals.

(iv) Chemical reactivity: The earlier members of the lanthanoids series are quite reactive similar to calcium but, with increase in atomic number, they behave more like aluminium. The metals combine with hydrogen when gently heated in the gas. Carbides, Ln_3C , Ln_2C_3 and LnC_2 are formed when the metals are heated with carbon. They liberate hydrogen from dilute acid and burn in halogens to form halides. They form oxides M_2O_3 and hydroxides $\text{M}(\text{OH})_3$.

Actinoids are highly reactive metals, especially when finely divided. The action of boiling water on them gives a mixture of oxide and hydride and combination with most non-metals take place at moderate temperatures. HCl attacks all metals but most are slightly affected by nitric acid owing to the formation of protective oxide layers, alkalis have no action. Actinoids are more reactive than lanthanoids due to bigger atomic size and lower ionisation energy.

3. 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

Sol: (i) Magnetic properties: Transition elements and many of their compounds are paramagnetic, i.e., they are weakly attracted by a magnetic field. This is due to the presence of unpaired

electrons in atoms, ions or molecules. The paramagnetic character increases as the number of . unpaired electrons increases. The paramagnetic character is measured in terms of magnetic moment and is given by

$\mu = n(n+2) \text{ } \sqrt{\text{BM}}$ where n – number of unpaired electrons.

(ii) Because of large number of unpaired electrons in d-orbitals of their atoms they have stronger interatomic interactions and hence stronger metallic bonding between atoms resulting in higher enthalpies of atomisation.

(iii) Formation of coloured compounds (both in solid state as well as in aqueous solution) is another very common characteristics of transition metals. This is due to absorption of some radiation from visible light to cause d-d transition of electrons in transition metal atom. The d-orbitals do not have same energy and under the influence of ligands, the d-orbitals split into two sets of orbitals having different energies; transition of electrons can take place from one set of d-orbitals to another set within the same sub-shell. Such transitions are called d-d transitions. The energy difference for these d-d transitions fall in the visible region. When white light is incident on compounds of transition metals, they absorb a particular frequency and remaining colours are emitted imparting a characteristic colour to the complex. Zn^{2+} and Ti^{4+} salts are white because they do not absorb any radiation in visible region.

(iv)Catalytic properties: Many of transition metals and their compounds act as catalyst in variety of reactions, e.g., finely divided iron in manufacture of NH_3 by Haber's process, V_2O_5 or Pt in manufacture of H_2SO_4 by Contact process, etc.). The catalytic activity is due to following two reasons.

(a)The ability of transition metal ion to pass " easily from one oxidation state to another

and thus providing a new path to reaction with lower activation energy.

(b) The surface of transition metal acts as very good adsorbent and thus provides increased concentration of reactants on their surface causing the reaction to occur.

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

Sol: Lanthanoid Contraction : In the lanthanoids, the electrons are getting filled in the 4f-subshell. On moving from left to right, the nuclear charge increases and this increase is expected to be compensated by the increase in the magnitude of shielding effect by the 4f-electrons. However, the f-electrons have very poor shielding effect. Consequently, the atomic and ionic radii decrease from left to right and this is known as lanthanoid contraction.

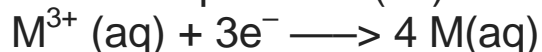
Consequences of lanthanoid Contraction

(a) Separation Lanthanoids: All the lanthanoids have quite similar properties and due to this reason they are difficult to separate.

(b) Variation in basic strength of hydroxides: Due to lanthanoid contraction, size of M^{3+} ions decreases and thus there is a corresponding increase in the covalent character in M—OH bond. Thus basic character of oxides and hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$.

(c) Similarity in the atomic sizes of the elements of second and third transition series present in the same group. The difference in the value of atomic radii of Y and La is quite large as compared to the difference in the value of Zr and Hf. This is because of the lanthanoid contraction.

(d) Variation in standard reduction potential: Due to lanthanoid contraction there is a small but steady increase in the standard reduction potential (E°) for the reduction process.



(e) Variation in physical properties like melting point, boiling point, hardness etc.

5. 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?

Sol: General characteristics of transition elements.

- (i) Electronic configuration – $(n-1) d^{1-10} ns^{1-2}$
- (ii) Metallic character – With the exceptions of Zn, Cd and Hg, they have typical metallic structures.
- (iii) Atomic and ionic size-ions of same charge in a given series show progressive decrease in radius with increasing atomic number.
- (iv) Oxidation state-Variable; ranging from +2 to +7.
- (v) Paramagnetism – The ions with unpaired electrons are paramagnetic.
- (vi) Ionisation enthalpy – Increases with increase in charge.
- Formation of coloured ions – Due to presence of unpaired electrons.
- (viii) Formation of complex compounds – Due to small size and high charge density of metal ions.
- (ix) They possess catalytic properties – Due to their ability to adopt multiple oxidation states.
- (x) Formation of interstitial compounds.
- (xi) Alloy formation.

They are called transition elements due to their incompletely filled d-orbitals in ground state or in any stable oxidation state and they are placed between s and p-block elements. Zn, Cd and Hg have fully filled d-orbitals in their ground state hence may not be regarded as the transition elements.

SUMMARY

1. The elements lying in the middle of Periodic Table between s-block and p-block elements (i.e between group 2 and 13) are known as **d-block or transition elements**.
2. There are three transition series each of 10 elements:
 - (i) **First transition series:** It involves filling of 3d-orbitals. It starts from scandium ($Z = 21$) and goes upto zinc ($Z = 30$).
 - (ii) **Second transition series:** It involves filling of 4d-orbitals. It starts from yttrium ($Z=39$) to cadmium ($Z = 48$).
 - (iii) **Third transition series:** It involves filling of 5d-orbitals. The first element of this series is lanthanum ($Z = 57$). It is followed by 14 elements called lanthanides which involve the filling of 4f-orbitals. The next nine elements from hafnium ($Z = 72$) to mercury ($Z = 80$) belong to third transition series.
3. The f-block elements are called **inner-transition elements**.
4. All the transition elements are metallic in nature, good conductors, of heat and electricity; show a gradual decrease in electropositive character in moving across a period. Due to strong metallic bonds, these metals are hard, possess high densities, high enthalpies of atomisation, high melting and boiling points and form alloys with other metals.
5. The melting point of these first increases to maximum and then gradually decreases towards the end of the series. The strength of metallic bonds is roughly related to number of half-filled d-orbitals.
6. The radii of ions, having the same charge and magnitude, in a given series decreases progressively with increase in atomic number. This is because of poor shielding effect of d-electrons.