

## THE d & f BLOCK ELEMENTS

### 1. Why is zinc not regarded as a transition element?

It is because neither Zn nor  $Zn^{+2}$  ions have incompletely filled d-orbitals.

### 2. Copper atom has completely filled d-orbitals in its ground state but it is a transition element. Why?

It is because  $Cu^{+2}$  has  $3d^9$ , incompletely filled d-orbitals, therefore, it is a transition metal.

### 3. $Zn^{+2}$ salts are white while $Cu^{+2}$ salts are coloured. Why?

$Zn^{+2}$  salts are white because it does not have unpaired electron, whereas  $Cu^{+2}$  salts are coloured because it has **unpaired electron** and undergoes **d-d transition** by **absorbing light from visible region and radiate blue colour**.

### How is the variability in oxidation states of d-block different from that of the p-block elements?

It is due to similar energy of  $(n - 1)d$  and  $ns$  orbitals, electrons from both can be lost. In p-block, lower oxidation state is more stable due to inert pair effect, whereas in d block elements higher oxidation states are more stable. In d-block, oxidation states differ by one, whereas in p-block, it differs by two.

### 4. What are the transition elements? Write two characteristics of the transition elements.

Those elements which either themselves or their ions have incompletely filled electronic configuration.

- (i) They show variable oxidation state.
- (ii) They form coloured ions.

### 5. Why do transition elements show variable oxidation states?

Transition elements show variable oxidation states because electrons from both  $s$  and  $d$  orbital take part in bond formation.

### In 3d series (Sc to Zn), which element shows the maximum number of oxidation states and why?

In 3d series, 'Mn' shows maximum number of oxidation states because it has maximum number of electrons in  $s$  as well as in  $d$  orbital which can take part in bond formation.

### 6. (i) $E^\circ$ value for the $Mn^{+3}/Mn^{+2}$ couple is positive (+1.5 V) whereas that of $Cr^{+3}/Cr^{+2}$ is negative (-0.4 V). Why? ‘

### (ii) Transition metals form coloured compounds. Why?

(i)  $Mn^{+2}$  is more stable than  $Mn^{+3}$  due to half filled d-orbitals ( $3d^5$ ), whereas  $Cr^{+3}$  is more stable than  $Cr^{+2}$  due to half filled orbitals.

(ii) It is due to presence of unpaired electrons which undergo d-d transition by absorbing light from visible region and radiate complementary colour.

**7.(i) MnO is basic whereas Mn<sub>2</sub>O<sub>7</sub> is acidic in nature. Why?**

**(ii) Transition metals form alloys. Why?**

(i) In MnO, Mn has +2 oxidation state, whereas in Mn<sub>2</sub>O<sub>7</sub>, Mn has +7 oxidation state. Higher the oxidation state, more will be acidic nature, e.g. Mn<sub>2</sub>O<sub>7</sub>. Lower the oxidation state, more will be basic nature, e.g. MnO.

(ii) It is due to similar atomic size, they can replace one another in metallic bond.

**8. Account for the following:**

**(i) Cu<sup>+</sup> is unstable in an aqueous solution.**

**(ii) Transition metals form complex compounds**

(i) It is because hydration energy of Cu<sup>2+</sup> overcomes 2nd ionisation enthalpy, that is why Cu<sup>+</sup> changes to Cu<sup>2+</sup> and Cu.



(ii) It is due to their small size, high charge and availability of vacant d-orbitals

**How would you account for the following:**

**(i) Highest fluoride of Mn is MnF<sub>4</sub> whereas the highest oxide is Mn<sub>2</sub>O<sub>7</sub>**

**(ii) Transition metals and their compounds show catalytic properties.**

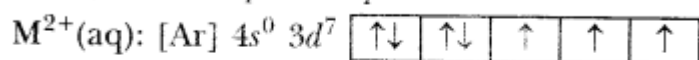
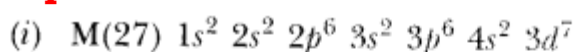
(i) Oxygen can form double bond, therefore, it can form Mn<sub>2</sub>O<sub>7</sub> whereas 'F' cannot form double bonds, so, it can form MnF<sub>4</sub>.

(ii) Transition metals show variable oxidation states, therefore, they and their compounds act as catalyst.

**9.(i) Calculate the spin magnetic moment of M<sup>2+</sup>(aq) ion.**

**Atomic number (Z) = 27.**

**(ii) Chromium is typical hard metal while mercury is liquid, explain.**



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

$$\mu = \sqrt{3 \times 5} = \sqrt{15} = 3.87 \text{ BM.}$$

(ii) Cr is typically hard metal due to presence of large number of unpaired electrons, metal-metal interaction is strong whereas mercury does not have unpaired electrons and has large size, therefore, forms weak metallic bond.

**10. Account for the following:**

**(a) (i) Transition elements form interstitial compounds.**

**(ii)  $\text{Mn}^{3+}(3d^4)$  is strongly oxidising, whereas  $\text{Cr}^{2+}(3d^4)$  is strongly reducing.**

**(iii) Transition metals have high melting points.**

**(b) What is misch metal? Write its one use.**

(a) (i) Small size atoms B, C, H can occupy voids present in transition metals.

(ii)  $\text{Mn}^{3+}$  gains one electron to form  $\text{Mn}^{2+}$  since  $3d^5$  is more stable, whereas  $\text{Cr}^{2+}$  loses one electron to form  $\text{Cr}^{3+}(t_{2g}^3)$  which is more stable), so, it acts as reducing agent.

(iii) It is due to involvement of unpaired d electrons to form strong metallic bond.

(b) It contains 95% lanthanoid metal, 5% iron and traces of S, C, Ca and Al.

Use: Its magnesium based alloy is used to produce bullets, shells, flints.

**11.(a) What are the different oxidation states exhibited by the lanthanoids?**

**(b) Write two characteristics of the transition elements.**

**(c) Which of the 3d-block elements may not be regarded as the transition elements and why?**

(a) Lanthanoids, mostly show **+3** oxidation state but some of them show +2 and +4 oxidation states also due to the stability of electronic configuration ( $4f^0$ ,  $4f^7$  and  $4f^{14}$ ), e.g. Eu shows +2, whereas **Ce shows +4 oxidation state.**

(b) (i) They show variable oxidation states.

(ii) They form coloured compounds.

(c) Zn may not be regarded as transition metal because neither 'Zn' nor  $\text{Zn}^{2+}$  ions have incompletely filled d-orbital.

**12. Assign suitable reasons for the following:**

**(a) The  $\text{Mn}^{2+}$  compounds are more stable than  $\text{Fe}^{2+}$  towards oxidation to their +3 state.**

**(b) In the 3d series from Sc (Z = 21) to Zn (Z = 30), the enthalpy of atomization of Zn is the lowest.**

**(c) Sc<sup>3+</sup> is colourless in aqueous solution, whereas Ti<sup>3+</sup> is coloured.**

(a) Mn<sup>2+</sup> has 3d<sup>5</sup> (stable electronic configuration), therefore, it does not get oxidised to Mn<sup>3+</sup>, whereas Fe<sup>2+</sup> has 3d<sup>6</sup> which readily changes to Fe<sup>3+</sup> (3d<sup>5</sup>), which has stable electronic configuration.

(b) Zinc does not have unpaired electrons and larger in size, therefore, it has weak metallic bonds. That is why it has least enthalpy of atomisation.

(c) Sc<sup>3+</sup> is colourless as it does not have unpaired electron and cannot undergo d-d transition, whereas Ti<sup>3+</sup> is coloured due to presence of unpaired electrons and undergoes d-d transition by absorbing light from visible region and radiate complementary colour.

**13.(i) Name the element of 3d transition series which shows maximum number of oxidation states. Why does it show so?**

**(ii) Which transition metal of 3d series has positive E° (M<sup>2+</sup>/M) value and why?**

**(iii) Out of Cr<sup>3+</sup> and Mn<sup>3+</sup>, which is a stronger oxidizing agent and why?**

**(iv) Name a member of the lanthanoid series which is well known to exhibit + 2 oxidation state.**

(i) Mn because it has five unpaired electrons and 2 electrons in s-orbital which can take part in bond formation, therefore, it shows maximum number of oxidation states.

(ii) E°Cu<sup>2+</sup>/Cu has +ve value due to high ionisation enthalpies and sublimation energies and lower hydration energy.

(iii) Mn<sup>3+</sup> is stronger oxidising agent because it can gain electrons to become Mn<sup>2+</sup> which is more stable due to 3d<sup>5</sup> (half filled d-orbitals), whereas Cr<sup>3+</sup> is stable due to t<sub>2g</sub><sup>3</sup> (half filled orbitals).

(iv) Europium shows +2 oxidation state. Ytterbium (Yb) also shows +2 oxidation state.

**14. Transition metals form a large number of complexes.**

It is due to small size, higher charge and presence of vacant d-orbitals of suitable energy.

**Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.**

Ce shows +4 oxidation state.

**Out of Mn<sup>3+</sup> and Cr<sup>3+</sup>, which is more paramagnetic and why? (Atomic nos.: Mn = 25, Cr = 24)**

Mn<sup>3+</sup> (3d<sup>4</sup>) has 4 unpaired electrons, therefore, it is more paramagnetic than Cr<sup>3+</sup> which has three unpaired electrons.

**15.(a) Which metal in the first transition series (3d series) exhibits +1 oxidation state most frequently and why?**

**(b) Which of the following cations are coloured in aqueous solutions and why?**

**Sc<sup>3+</sup>, V<sup>3+</sup>, Ti<sup>4+</sup>, Mn<sup>2+</sup>**

**(At. Nos. Sc = 21, V = 23, Ti = 22, Mn = 25)**

**Answer:**

(a) Copper exhibits +1 oxidation state frequently due to stable electronic configuration.

(b) V<sup>3+</sup> and Mn<sup>2+</sup> are coloured, due to the presence of unpaired electrons, they can undergo d-d transitions. Others are colourless due to the absence of unpaired electrons and cannot undergo d-d transitions.

**16. How would you account for the following?**

**(i) Transition metals exhibit variable oxidation states.**

**(ii) Zr (Z = 40) and Hf (Z = 72) have almost identical radii.**

**(iii) Transition metals and their compounds act as catalyst.**

**Answer:**

It is because electrons from (n - 1)d and ns take part in bond formation.

(ii) It is due to lanthanoid contraction which is due to poor shielding effect of f-electrons, due to which effective nuclear charge increases, therefore, Zr and Hf have almost identical radii.

(iii) It is because they show variable oxidation states and form unstable intermediates which readily change into products.

17.

Give reasons for the following:

- (i)  $\text{Mn}^{3+}$  is a good oxidising agent.
- (ii)  $E_{\text{M}^{2+}/\text{M}}^\circ$  values are not regular for first row transition metals (3d series).
- (iii) Although 'F' is more electronegative than 'O', the highest Mn fluoride is  $\text{MnF}_4$ , whereas the highest oxide is  $\text{Mn}_2\text{O}_7$ .

- (i) It is because  $\text{Mn}^{3+}$  can gain one electron to form  $\text{Mn}^{2+}$  which is stable due to half-filled  $d$ -orbitals ( $3d^5$ ).
- (ii) It is due to irregular variations of ionisation enthalpies ( $\Delta_i H_1 + \Delta_i H_2$ ) and sublimation enthalpies in 3d transition series.
- (iii) It is because oxygen can form multiple bonds with 'Mn', whereas 'F' cannot.

**18. The value for copper is positive (+ 0.34 V).**

**$\text{Cr}^{2+}$  is a very good reducing agent.**

It is because of high ionisation enthalpy of Cu which is not compensated by hydration energy.

It is because  $\text{Cr}^{2+}$  loses an electron to form  $\text{Cr}^{3+}$  which is more stable as  $t_{2g}$  orbitals are half-filled, i.e. more stable.

**19.(i) Name the element showing maximum number of oxidation states among the first series of transition metals from Sc ( $Z = 21$ ) to Zn ( $Z = 30$ ).**

**(ii) Name the element which shows only +3 oxidation state.**

**(b) Name an important alloy which contains some of the lanthanoid metals.**

(i) 'Mn' shows maximum number of oxidation states; +2, +3, +4, +6, +7.

(ii) Sc shows only +3 oxidation state.

(b) Misch metal is an important alloy which contains some of the lanthanoid metals.

**20.(a) What is meant by the term lanthanoid contraction?**

**What is it due to and what consequences does it have on the chemistry of elements following lanthanoids in the periodic table**

**(b) Although  $\text{Co}^{2+}$  ion appears to be stable, it is easily oxidised to  $\text{Co}^{3+}$  ion in the presence of a strong ligand.**

(a) The decrease in atomic and ionic size with increase in atomic number is called lanthanoid contraction. It is due to poor shielding effect of 4f electron due to which effective nuclear charge increases.

Consequences:

- The lanthanoids have similar ionic size and resemble with each other closely in their properties.
- Their separation becomes difficult.

Strong ligand provides energy which overcomes third ionisation energy to form  $\text{Co}^{3+}$  ion which forms more stable complex than  $\text{Co}^{2+}$ .

## 21.State reasons for the following observations:

**The enthalpies of atomisation of transition elements are quite high.**

(i) It is due to smaller size of transition metals and strong metallic bonds due to presence of large number of unpaired electrons.

How would you account for the following:

(i) The oxidising power of oxoanions are in the order  $\text{VO}_2^+ < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$ .

(ii) The third ionization enthalpy of manganese ( $Z = 25$ ) is exceptionally high.

(iii)  $\text{Cr}^{2+}$  is a stronger reducing agent than  $\text{Fe}^{2+}$ . [Foreign]

(i) It is because V in lower oxidation state is less stable than Cr which is less stable than Mn. That is why  $\text{MnO}_4^-$  is best oxidising agent and  $\text{VO}_2^+$  is least.

(ii) Mn (25) has electronic configuration  $[\text{Ar}]4s^23d^5$ . Electronic configuration of  $\text{Mn}^{2+}$  is  $[\text{Ar}]4s^03d^5$ . After losing 2 electrons, it has half filled  $d$ -orbital, which is more stable, that is why  $\text{Mn}^{2+}$  has exceptionally high third ionization energy, *i.e.* the energy required to remove third electron is very high.

(iii) It is because in  $\text{Cr}^{3+}$ ,  $d^3$  (half filled  $t_{2g}$  orbitals) is more stable in aqueous solution than  $\text{Fe}^{3+}$  ( $d^5$ ) *i.e.*,  $\text{Cr}^{3+}$  is more stable than  $\text{Fe}^{3+}$ .

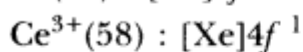
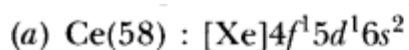
**(a) Write the electronic configuration of  $\text{Ce}^{3+}$  ion, and calculate the magnetic moment on the basis of 'spin-only' formula. [Atomic No. of Ce = 58]**

**(b) Account for the following:**

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

**(iii) Cobalt (II) is stable in aqueous solution but in the presence of complexing agents, it is easily oxidised.**

**Answer:**



**Spin only formula**

$$\begin{aligned}\text{Magnetic moment} &= \sqrt{4S(S+1)} = \sqrt{4 \times \frac{1}{2} \left( \frac{1}{2} + 1 \right)} = \sqrt{2 \times \frac{3}{2}} = \sqrt{3} \\ &= 1.732 \text{ B.M.}\end{aligned}$$

where 'S' is spin quantum number, Ce<sup>3+</sup> has one unpaired electron which has spin quantum number equal to 1/2.

(b) (i) It is because transition metals in lowest oxidation state are more metallic and in higher oxidation state are least metallic, therefore, oxides in lower oxidation state are basic, whereas in higher oxidation state are amphoteric/acidic.

(iii) Strong oxidising agents provide energy for loss of one more electron from Co<sup>2+</sup>.

**(a) Describe the following characteristics of the first series of the transition metals and their trends in the series (Sc to Zn):**

**(i) Atomic radii (ii) Oxidation states (iii) Ionisation enthalpies**

(a) (i) Atomic and covalent radii: The atomic radii decrease from Sc to Cr because number of unpaired electrons increases, therefore, effective nuclear charge increases. The atomic size of Fe, Co, Ni is almost same because pairing of electrons takes place in d-orbitals causing repulsion and effective nuclear charge does not increase appreciably. Cu and Zn have bigger size because repulsion between paired electrons increases. Ionic radii of bivalent cations decrease from Sc to Cu due to increase in number of protons.

(ii) Oxidation state: Transition metals show variable oxidation states due to tendency of 'd' as well as 's' electrons to take part in bond formation. The highest oxidation state is equal to the total number of electrons in 's' as well as of-orbitals.

The maximum oxidation state shown by the elements of first transition series increases from Sc to Mn and then decreases to Zn. Sc shows maximum + 3 and Mn shows + 7, V(+ 5), Cr(+ 6), Fe(+ 3), Ni(+ 2), Co(+ 3), Cu(+ 2) and Zn(+ 2) oxidation state.

(iii) Ionisation enthalpies: There is slight and irregular variation in ionisation energies of transition metals due to irregular variation of atomic size. The I.E. of 5d transition series is higher than 4d transition series because of lanthanoid contraction, so, effective nuclear charge increases.

**(i)  $\text{La}^{3+}$  ( $Z = 57$ ) and  $\text{Lu}^{3+}$  ( $Z = 71$ ) do not show any colour in solutions:**

**(ii) Among the divalent cations in the first series of transition elements, manganese exhibits the maximum paramagnetism.** (i) It is because they do not have unpaired electrons and cannot undergo f-f- transitions.

(ii) It is due to maximum number of unpaired electrons(s).

**Explain the following:**

**(i) There is a gradual decrease in the atomic sizes of transition elements in the series with increasing atomic numbers.**

**(iii) Lanthanum and Lutetium do not show colouration in solutions. (At. No. : La = 57, Lu = 71)**

(i) It is due to increase in effective nuclear charge gradually because unpaired electrons increase in the beginning and then decrease. There is repulsion between paired electrons.

(iii) It is due to absence of unpaired electrons, they do not absorb light from visible region and do not radiate colour.

**How would you account for the following?**

**(i) The atomic radii of the metals of the third (5d) series of transition elements are virtually the same as those of the corresponding members of the second (4d) series.**

**(ii) The  $E^\circ$  value for the  $\text{Mn}^{3+}/\text{Mn}^{2+}$  couple is much more positive than that for  $\text{Cr}^{3+}/\text{Cr}^{2+}$  couple or  $\text{Fe}^{3+}/\text{Fe}^{2+}$  couple.**

**(iii) The highest oxidation state of a metal is exhibited in its oxide or fluoride.**

(i) It is due to lanthanoid contraction which is due to poor shielding effect of f-electrons.

(ii) It is because  $\text{Mn}^{2+}$  is more stable than  $\text{Mn}^{3+}$  due to stable half filled  $3d^5$  configuration:

(iii) It is because oxygen and fluorine are strong oxidising agents, highly electronegative, small size and can provide energy for formation of transition metal ion in higher oxidation state

**Give reasons for the following observations:**

**(i)  $\text{Mn}(\text{II})$  ion shows maximum paramagnetic character amongst the divalent ions of first transition series.**

**(ii) Scandium (At. no. 21) salts are white.**

(i) It is due to presence of five unpaired electrons.

(ii)  $\text{Sc}^{3+}$  does not have unpaired electrons, therefore, cannot undergo d-d transition by absorbing light from visible region. Therefore, its salts are white.

**Explain the following observations:**

**(i) Generally there is an increase in density of elements from titanium (Z = 22) to copper (Z = 29) in the first series of transition elements.**

(ii) Transition elements and their compounds are generally found to be good catalysts in chemical reactions.

(i) It is because atomic mass increases more than atomic volume, therefore, density increases from titanium (Z = 22) to copper (Z = 29).

(ii) It is because they show variable oxidation states and have vacant d-orbitals forming unstable intermediates which readily change into products

**There occurs much more frequent metal-metal bonding in compounds of heavy transition metals (i.e. 3rd series)** It is due to presence of unpaired electrons which participate in metal-metal bonding in 5d series (3rd series).

**There is a greater horizontal similarity in the properties of the transition elements than of the main group elements.**

It is due to similarity in atomic and ionic size, there is more horizontal similarity. Secondly, in transition elements, incoming electron goes to inner shell (d-orbitals), whereas in main group elements, the incoming electron goes to outermost shell.

**Explain the following observations:**

**Zinc is not regarded as a transition element** (i) It is because neither Zn nor  $\text{Zn}^{2+}$  ions have incompletely filled d-orbitals.