

d-Block Elements

Topics Covered

- Transition Elements
- General Characteristics of *d*-Block Elements
- Potassium Dichromate
- Potassium Permanganate

Transition Elements

The elements in which last electron enters in $(n - 1)$ *d*-orbital are called *d*-block elements. These elements are generally known as **transition elements** due to their position in the periodic table in between *s*-block (electropositive) and *p*-block elements. These elements make up three complete rows, i.e. *3d*, *4d*, *5d*, and an incomplete fourth row, i.e. *6d*.

Occurrence

Various *d*-block elements are found in nature in combined form. Soft metals of *d*-block found in sulphide, whereas hard ones in the form of oxides. Titanium is present in coal and clay. Vanadium is observed as vanadates of lead, copper and zinc.

Chromium is found as chromite (FeO , Cr_2O_3). Ore of manganese is pyrolusite. Cobalt is associated with nickel and arsenic. Important ore of copper are cuprite and malachite. Zn is found with silver, copper and platinum.

Position of *d*-Block Elements in the Periodic Table

The *d*-block occupies the large middle section flanked between *s*- and *p*-blocks in the periodic table. The name 'transition' given to the elements of *d*-block is only because of their position between *s*- and *p*-block elements.

The *d*-orbitals of the penultimate energy level in their atoms receive electrons giving rise to the four rows of the transition metals, i.e. *3d*, *4d*, *5d* and *6d*.

- First transition series** or **3*d*-series** Scandium ($_{21}\text{Sc}$) to zinc ($_{30}\text{Zn}$).
- Second transition series** or **4*d*-series** Yttrium ($_{39}\text{Y}$) to cadmium ($_{48}\text{Cd}$).
- Third transition series** or **5*d*-series** Lanthanum ($_{57}\text{La}$) to mercury ($_{80}\text{Hg}$).
Omitting ($_{58}\text{Ce}$ to $_{71}\text{Lu}$).
- Fourth transition series** or **6*d*-series** Actinium ($_{89}\text{Ac}$) to copernicium ($_{112}\text{Cn}$).
Omitting ($_{90}\text{Th}$ to $_{103}\text{Lu}$).

General Characteristics of d-Block Elements

(i) Electronic Configuration

General electronic configuration of transition metals is $(n-1)d^{1-10}ns^{1-2}$. Some of the exceptions are observed in electronic configuration due to very little energy difference between $(n-1)d$ and ns orbital such as Cr: $3d^5 4s^1$; Cu: $3d^{10} 4s^1$. However, zinc (Zn), cadmium (Cd), mercury (Hg) are represented by a general formula $(n-1)d^{10} ns^2$. These are not regarded as transition metals due to completely filled d -orbitals.

(ii) Atomic and Ionic Radii

From Sc to Cr, atomic radii decreases because effective nuclear charge increases. The atomic sizes of Fe, Co and Ni are almost same because pairing of electrons in d -orbitals causes repulsion and hence, effective nuclear charge does not increase appreciably.

(iii) Ionisation Enthalpy

Ionisation enthalpy increases with increase in nuclear charge along each series. However, the first ionisation energy of Cr is low because loss of one electron gives stable configuration and the value for Zn is higher because it represents an ionisation from the completely filled $4s$ level.

(iv) Metallic Properties

Nearly, all the transition elements exhibit metallic properties. They (except Zn, Cd and Hg) are very much hard and have low volatility. Their melting and boiling points are high due to strong metallic bonding. Greater the number of valence electrons, stronger is the resultant bonding. They have high enthalpy of atomisation.

(v) Density

Density of the transition metals from Sc to Cu increases due to high atomic mass and small atomic volume.

(vi) Melting and Boiling Points

Transition elements possess higher melting and boiling points due to the presence of strong metallic bonding (inter-atomic bonding) involving the participation of ns and $(n-1)d$ -orbitals electrons. Larger the number of unpaired d -electrons, stronger is the inter-atomic or metallic bonding and higher will be the boiling and melting points.

(vii) Enthalpy of Atomisation

Transition elements possess high enthalpy of atomisation because their atoms are closely packed and held together by strong metallic bonds.

(viii) Oxidation States

Transition metals show variable oxidation states due to the participation of $(n-1)d$ as well as ns electrons in bond formation. The maximum oxidation states are shown by Mn, i.e. from +2 to +7 (in first series). Sc shows only +3 oxidation state. High oxidation state is shown by their fluorides and oxides because fluorine and oxygen are strong oxidising agents.

(ix) Formation of Coloured Compound

Most of the compounds formed by the transition elements are coloured in nature. The colour arises due to the excitation of electron from d -orbitals of lower energy to d -orbitals of higher energy ($d-d$ transition). Atoms or ions having d^1 to d^9 configuration are coloured. While, atoms or ions having d^0 or d^{10} configurations are colourless due to the absence of $d-d$ transition.

(x) Complex Formation

Due to the presence of vacant d -orbitals, smaller size and high positive charge density, transition elements form coordination complexes by accepting lone pair of electrons donated by negatively charged or neutral molecules (ligands).

(xi) Magnetic Properties

The presence of unpaired electrons in transition metals is responsible for their magnetic behaviour. The transition elements containing unpaired electrons are paramagnetic in nature and, hence show magnetic properties. Each unpaired electron possess a magnetic moment which is related to their spin and orbital angular momentum. Hence, the magnetic moment is determined only from spin formula

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

where, $n \rightarrow$ number of unpaired electrons

BM \rightarrow Bohr magneton (unit for magnetic moment)

The transition elements which contains electrons are called diamagnetic.

(xii) Catalytic Property

Most of the transition metals and their compounds show catalytic behaviour. Transition metals and their compounds can act as catalyst due to the presence of unpaired electrons in d -orbitals and presence of variable oxidation states.

(xiii) Alloy Formation

An alloy is the homogeneous mixture of either two or more metals or a metal and non-metal. Transition metals form a number of alloys due to the tendency of replacing each other from their lattice and form solid solutions because of similar radii of these elements. Alloys are hard and have high melting point as compared to the host metal.

(xiv) Formation of Interstitial Compounds

Transition elements possess a tendency to trap atoms like H, B, C, N in their interstitial spaces of their lattices, e.g. $\text{TiH}_{1.7}$, $\text{VH}_{0.56}$. These compounds are very hard and chemically inert and have higher melting points than those of pure metals.

(xv) Standard Electrode Potential and Chemical Reactivity

The E° values of all the transition metals (except Cu) is lower (negative) than that of hydrogen (taken as zero). Thus, all the transition elements with negative reduction potential liberate hydrogen from dilute acids. E° value for copper is positive because energy to transform Cu(s) to $\text{Cu}^{2+}(\text{aq})$ is not balanced by its hydration enthalpy.

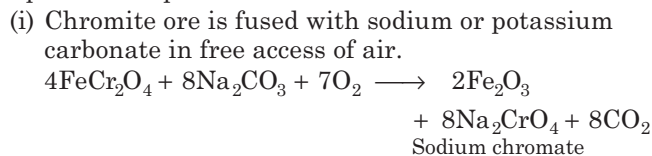
The comparative high value of E° for $\text{Mn}^{3+}/\text{Mn}^{2+}$ indicates the stability of $\text{Mn}^{2+}(d^5)$, whereas comparatively low value for Fe indicates the extra stability of $\text{Fe}^{3+}(d^5)$. Similarly, the comparative low value for $\text{V}^{3+}/\text{V}^{2+}$ indicates the stability of V^{2+} .

Potassium Dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$)

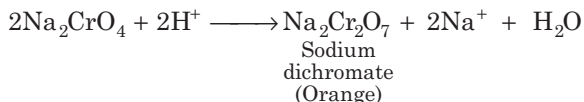
It is used in leather industry and acts as an oxidant for the preparation of many azo compounds.

Preparation

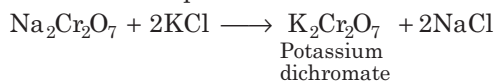
Potassium dichromate is prepared by chromite ore (FeCr_2O_4). Following steps are involved during the preparation of potassium dichromate.



(ii) Yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give orange coloured sodium dichromate solution.



(iii) $\text{K}_2\text{Cr}_2\text{O}_7$ is prepared by treating the solution of $\text{Na}_2\text{Cr}_2\text{O}_7$ with KCl because sodium dichromate is more soluble than potassium dichromate.



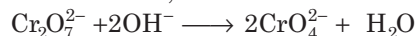
Orange coloured crystals of $\text{K}_2\text{Cr}_2\text{O}_7$ separates out.

In the solution, chromate ions exist in equilibrium with dichromate ions.

Depending on the pH of solution, equilibrium shifts in the forward and backward direction. The oxidation

state of chromium in chromate and dichromate ion is same.

In alkaline medium,



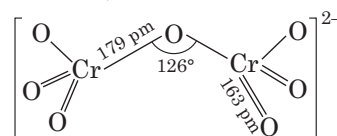
In acidic medium,



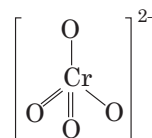
Structure of $\text{Cr}_2\text{O}_7^{2-}$ and CrO_4^{2-}

The structure of chromate ion is tetrahedral and dichromate ion consists of two tetrahedral sharing one corner with Cr—O—Cr having bond angle of 126° .

Dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$)



Chromate ion (CrO_4^{2-})



Physical Properties

- (i) Potassium dichromate is an orange red crystal solid which melts at 671K.
- (ii) Potassium dichromate is a strong oxidising agent.

Chemical Properties

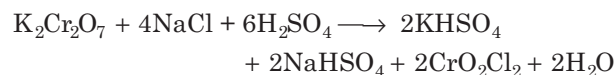
- (i) On heating, it slowly decomposes as follows with evolution of O_2 .



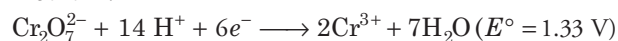
- (ii) On reaction with hydrochloric acid, chlorine gas is liberated.



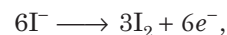
- (iii) On reaction with conc. sulphuric acid and sodium chloride, orange-red fumes of chromyl chloride (CrO_2Cl_2) is liberated.

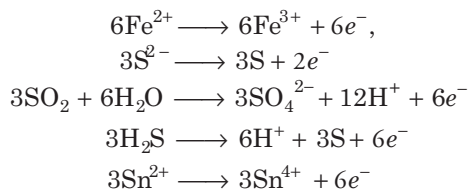


- (iv) Potassium dichromate is used as a primary standard solution in volumetric analysis in acidic medium.

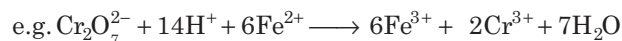


Thus, acidified potassium dichromate oxidises iodides to iodine, sulphides to sulphur, iron (II) salts to iron (III), tin (II) to tin (IV), H_2S to S and SO_2 to H_2SO_4 .

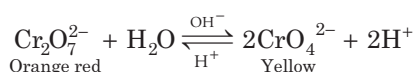




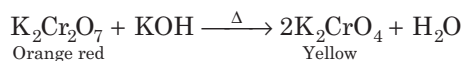
The full ionic equation may be obtained by adding half-reaction for potassium dichromate ($\text{K}_2\text{Cr}_2\text{O}_7$) to half-reaction for reducing agent.



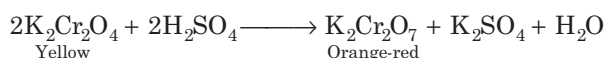
(v) $\text{Cr}_2\text{O}_7^{2-}$ ions are in equilibrium with CrO_4^{2-} ions.



With alkali, it gives K_2CrO_4 which is yellow coloured.

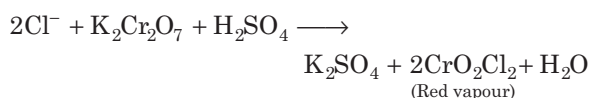


The yellow solution again changes to orange red solution on acidification.



(vi) **Chromyl chloride test** It is a test used to detect Cl^- ions. Chloride salt is heated with $\text{K}_2\text{Cr}_2\text{O}_7$ and conc. H_2SO_4 to give red vapours of CrO_2Cl_2 .

When these vapours are passed through NaOH , a yellow solution of Na_2CrO_4 is obtained. The reactions are:



Uses

- (i) In volumetric analysis, it is used as primary standard for estimating Fe^{2+} and I^- .
- (ii) It is used in leather industry in chrome tanning and in preparation of chrome alum.
- (iii) It is used as oxidising agent in organic chemistry.
- (iv) In photography.
- (v) It is used as cleansing agent ($\text{K}_2\text{Cr}_2\text{O}_7$ + conc. H_2SO_4) for glassware.

Potassium Permanganate (KMnO_4)

It is the potassium salt of permanganate acid (HMnO_4).

Preparation

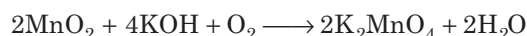
Following methods are used in the preparation of potassium permanganate.

(i) It is prepared by the action of dil. H_2SO_4 on potassium manganate.



MnO_2 can be removed by filtration. KMnO_4 is less soluble, hence crystallises out first.

(ii) Potassium permanganate is prepared by pyrolusite (MnO_2) ore. When pyrolusite ore is fused with alkali metal hydroxide in the presence of air or an oxidising agent like KNO_3 , potassium permanganate is formed.

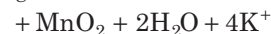


Potassium
manganate

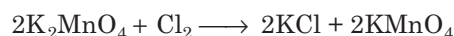
Potassium manganate (K_2MnO_4) is of green colour which disproportionates in a neutral or acidic solution to produce potassium permanganate.



Potassium
permanganate

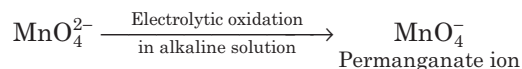
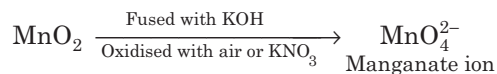


Chlorine gas can also be passed through green solution of potassium manganate to produce potassium permanganate.



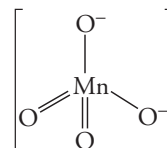
KMnO_4 is less soluble than KCl . Therefore, on concentrating KMnO_4 separates out.

(iii) Commercially, it is prepared by alkaline oxidative fusion of MnO_2 followed by electrolytic oxidation of manganate (VI) using Ni anode and iron cathode.

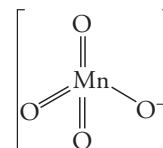


Structure

The manganate, MnO_4^{2-} and permanganate, MnO_4^- are tetrahedral, the green MnO_4^{2-} is paramagnetic with one unpaired electron but the purple MnO_4^- is diamagnetic.



Tetrahedral manganate ion
(green)
(Paramagnetic)



Tetrahedral permanganate ion
(purple)
(Diamagnetic)

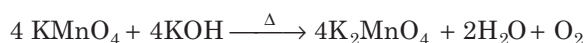
The π -bonding takes place by overlapping of p -orbitals of oxygen with d -orbitals of manganese.

Physical Properties

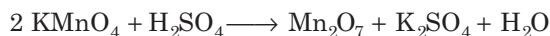
- (i) It is dark purple coloured (the deep purple colour of KMnO_4 is due to charge transfer from O to Mn) crystalline solid. It is moderately soluble in water (6.4 g/100 g of H_2O at 293 K).
- (ii) It is stored in dark coloured bottles because it gets decomposed in the presence of sunlight.
- (iii) Its paramagnetism depends upon temperature.

Chemical Properties

- (i) It decomposes evolving oxygen when heated alone or with alkali.

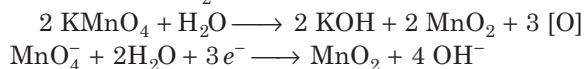


- (ii) On reaction with conc. H_2SO_4 , it produces Mn (VII) oxide which decomposes explosively when heated.

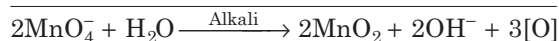
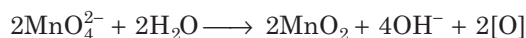
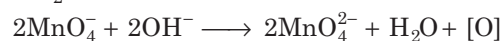


- (iii) Potassium permanganate is a powerful oxidising agent in neutral, alkaline or acidic solutions because, it liberates nascent oxygen.

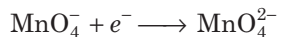
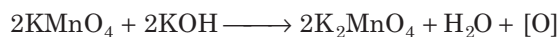
- (a) In neutral solution, potassium permanganate is reduced to MnO_2 .



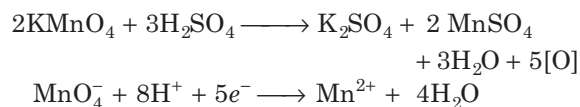
- (b) In alkaline medium, KMnO_4 is first reduced to K_2MnO_4 , which is finally reduced to insoluble MnO_2 as follows :



The colour of the solution changes from purple to green and finally, it becomes colourless.



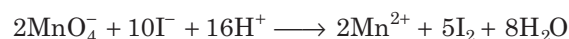
- (c) In acidic solution, MnO_4^- is reduced to Mn(II) ion.



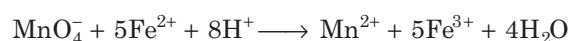
For titration sulphuric acid is preferred over hydrochloric acid because HCl is oxidised to Cl_2 during titration. The colour of the solution changes from purple to colourless.

Important oxidation reactions of acidified KMnO_4 are :

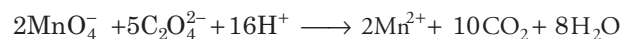
- (i) Iodide to iodine



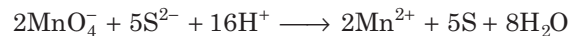
- (ii) Ferrous to ferric



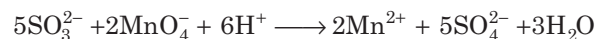
- (iii) Oxalate to carbon dioxide



- (iv) Hydrogen sulphide to sulphur



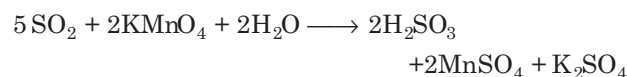
- (v) Sulphite to sulphate



- (vi) Nitrite to nitrate



- (vii) SO_2 to SO_3^{2-} and SO_4^{2-}



Uses

- (i) In analytical chemistry, it acts as an oxidant in the preparation of organic compounds, bleaching of wool, cotton, silk, decolourisation of oils. (Volumetric titrations involving KMnO_4 are carried out only in the presence of dil. H_2SO_4).
- (ii) It is used in cleaning surgical instruments in hospitals.
- (iii) It is used as disinfectant.
- (iv) It is used in the manufacture of saccharine, benzoic acid, acetaldehyde, etc.

PRACTICE QUESTIONS

Exams', Textbook's Other Imp. Questions

1 MARK Questions

Exams' Questions

- Q.1** A transition metal ion having configuration $[\text{Ar}]3d^4$ is in tripositive oxidation state. Its atomic number is
(a) 25 (b) 26 (c) 32 (d) 19 [2018]

Sol (a) A transition metal ion having configuration $[\text{Ar}]3d^4$ is in tripositive oxidation state.

$$M^{3+} = [\text{Ar}]3d^4 \text{ So, } M = [\text{Ar}]3d^5 4s^2$$

Therefore, the atomic number of the transition metal is 25.

- Q.2** The transition elements are paramagnetic due to the presence of [2012]

Sol unpaired electrons in d -orbitals.

- Q.3** The colour of the transition metal or its ion is due to [2011]

- (a) $d-d$ transition (b) $p-p$ transition
(c) paired electrons (d) None of these

Sol (a) The colour of the transition metal or ion is due to $d-d$ transition.

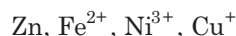
- Q.4** Write the electronic configuration of Fe^{2+} . [2007]

Sol $_{26}\text{Fe} - 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

$$_{26}\text{Fe}^{2+} - 1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 = [\text{Ar}]3d^6$$

Thus, the configuration of Fe^{2+} is $[\text{Ar}]3d^6$.

- Q.5** Out of the following, which one has more number of unpaired electrons? [2007]



Sol The number of electrons in the outermost shell of given elements are:

$$_{30}\text{Zn}: 3d^{10} 4s^2, \text{ }_{26}\text{Fe}^{2+}: 3d^6, \text{ }_{28}\text{Ni}^{3+}: 3d^7, \text{ }_{29}\text{Cu}^+: 3d^{10}$$

Fe^{2+} has four unpaired electrons which is maximum in the given set. Zinc and copper have no unpaired electrons, while nickel has three unpaired electrons.

- Q.6** Which of the following is a transition metal? [2006]



Sol Fe is the transition metal among these.

- Q.7** What is the oxidation number of Mn in K_2MnO_4 ?

Sol The oxidation number of Mn in K_2MnO_4 is +6, [2006]

$$\text{i.e. } 2 + x - 8 = 0 \Rightarrow x = +6$$

- Q.8** Out of the following, identify the d -block element. [2006]

- (a) Ca (b) U (c) Mn (d) Al

Sol (c) Mn is a d -block element, due to presence of outermost electron in $3d$ -subshell.

- Q.9** Which of the following ion is not coloured? [2006]

- (a) Cu^+ (b) Cr^{2+} (c) Co^{2+} (d) Cr^{3+}

Sol (a) Cu^+ ion is not coloured as, it does not possess any unpaired electrons.

- Q.10** What is the oxidation number of Mn in MnO_4^- ?

[2001, Textbook]

Sol +7 is the oxidation number of Mn in MnO_4^- .

$$\text{i.e. } x + 4(-2) = -1$$

$$\therefore x = +7$$

Important Questions

- Q.11** Which of the following is a transition element?

[Textbook]

- (a) Ca (b) Al (c) Co (d) Na

Sol (c) Co is a transition metal due to the presence of outermost electron in $3d$ -subshell.

- Q.12** The d -block elements form alloys among themselves, because

- (a) their atomic sizes are nearly same
(b) they have unpaired electrons
(c) their ionisation enthalpies are similar
(d) they are all metals [Textbook]

Sol (a) The d -block elements form alloys among themselves, because their atomic sizes are nearly same.

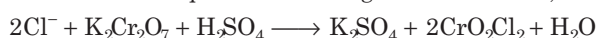
- Q.13** Which of the following statement(s) is/are correct regarding the following statements?

When a mixture of NaCl and $\text{K}_2\text{Cr}_2\text{O}_7$ is gently warmed with conc. H_2SO_4 ,

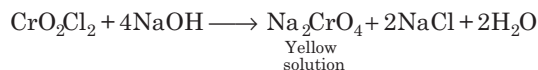
- (a) a deep red vapour is evolved.
(b) the vapour when passed into NaOH solution gives a yellow solution of Na_2CrO_4 .
(c) chlorine gas is evolved.
(d) chromyl chloride is formed. [Textbook]

Sol (a, b, d)

The chemical equation for the given reaction is,



Chromyl
chloride
(Red vapours)



- Q.14** Which of the following statements about transition metals is wrong? [Textbook]
 (a) They form coloured compounds.
 (b) All their compounds are diamagnetic.
 (c) They exhibit variable valency.
 (d) They contain partially filled *d*-orbitals.

Sol (b) Transition metals may be paramagnetic or diamagnetic. If the metal contains unpaired electrons in *d*-subshell, then it is paramagnetic, whereas if all the electrons are paired, then the metal is diamagnetic.

- Q.15** Acidified potassium permanganate solution is decolourised by [Textbook]
 (a) bleaching powder (b) white vitriol
 (c) Mohr's salt (d) microcosmic salt

Sol (c) Acidified KMnO_4 solution is decolourised by Mohr's salt.

- Q.16** Which one of the following metals does not form amalgam? [Textbook]
 (a) Zn (b) Ag
 (c) Cu (d) Fe

Sol (d) Fe does not form amalgam as the metallic bonds in Fe are very strong and it does not allow mercury to diffuse into it.

- Q.17** Paramagnetic behaviour in transition metal is due to the presence of [Textbook]
 (a) lone pair of electrons
 (b) even number of electrons
 (c) unpaired electrons
 (d) odd number of electrons

Sol (c) Paramagnetic behaviour in transition metals is due to the presence of unpaired electrons.

- Q.18** The general electronic configuration of transition elements is [Textbook]
 (a) $(n-1)d^{1-5}$ (b) $(n-1)d^{1-10}ns^1$
 (c) $(n-1)d^{1-10}ns^1 \text{ or } 2$ (d) None of these

Sol (c) The general electronic configuration of transition elements is $(n-1)d^{1-10}ns^1 \text{ or } 2$.

- Q.19** The correct statement for *d*-block elements is/are
 (a) they are all metals
 (b) they form coloured ions and complex salts
 (c) they show variable valency
 (d) All the given statements are correct

Sol (d) All the given statements are correct.

- Q.20** Which one of the following *d*-block element has half-filled penultimate *d*-subshell as well as half-filled valence *s*-subshell?
 (a) Pd (b) Au
 (c) Cr (d) Pt

Sol (c) ${}_{24}\text{Cr} - 1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$.

Here, Cr has half-filled penultimate *d*-subshell as well as half-filled valence *s*-subshell.

- Q.21** All transition elements have unpaired electrons. (Correct the Sentence)

Sol All transition elements do not have unpaired electrons.

- Q.22** The *d*-block elements are also known as (Fill in the blanks)

Sol transition elements

- Q.23** Silver atom has completely filled *d*-orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition element?

Sol Silver in its +1 oxidation state exhibits $4d^{10} 5s^0$ configuration.

But in some compounds, it also shows +2 oxidation state, so the configuration becomes $4d^9 5s^0$.

Here, *d*-orbital is not completely filled.

Therefore, silver is a transition element.

- Q.24** Why are Mn^{2+} compounds more stable than Fe^{2+} towards oxidation to their +3 state?

Sol Mn^{2+} compounds are more stable due to half-filled *d*-orbitals. Fe^{2+} compounds are comparatively less stable as they have six electrons in their orbital. So, they tend to lose one electron (to form Fe^{3+}) and attain stable $3d^5$ configuration.

- Q.25** Define transition elements. [Textbook]

Sol The elements in which last electron enters in $(n-1)d$ -subshell are known as transition elements.

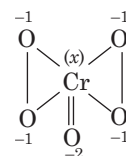
- Q.26** Mention two characteristic features of transition elements. [Textbook]

Sol The two characteristic features of transition elements are

- Transition elements have variable oxidation states.
- Transition elements form interstitial compounds.

- Q.27** What is the oxidation number of Cr in CrO_5 ?

Sol



$$\therefore -2 + 4(-1) + x = 0 \text{ or } x = +6$$

Thus, oxidation number of Cr in CrO_5 is +6.

Q.28 What is the oxidation number of Cr in $\text{Cr}_2\text{O}_7^{2-}$?

Sol $\text{Cr}_2\text{O}_7^{2-}$ [Textbook]

$$2x + 7(-2) = -2$$

$$2x - 14 = -2$$

$$x = +6$$

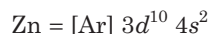
\therefore The oxidation number of Cr in $\text{Cr}_2\text{O}_7^{2-}$ is +6.

Q.29 What is the reason of paramagnetism in transition metals? [Textbook]

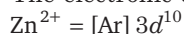
Sol The presence of unpaired electrons in d -subshell imparts paramagnetic behaviour in transition metals.

Q.30 What is the magnetic property of dipositive zinc ion? [Textbook]

Sol The electronic configuration of $\text{Zn}(Z = 30)$ is,



The electronic configuration of Zn^{2+} is,



Since, the $3d$ -orbital in Zn^{2+} are completely filled (no unpaired electrons),

\therefore Zn^{2+} is diamagnetic in nature.

Q.31 What is the maximum oxidation state of manganese? [Textbook]

Sol The maximum oxidation state of Mn is +7 as, it contains a total of seven electrons in $3d$ and $4s$ -orbitals.



Q.32 Name a transition element, which is not a solid. [Textbook]

Sol A transition element, which is not a solid is mercury (Hg).

Q.33 What happens when acid is added to the yellow coloured potassium chromate solution? [Textbook]

Sol When an acid is added to yellow coloured potassium chromate solution, it changes to orange coloured potassium dichromate solution.

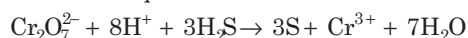


Q.34 What happens, when KMnO_4 is heated alone or with alkali? [Textbook]

Sol Refer to text on page 175.

Q.35 What happens, when H_2S gas is passed through acidified $\text{K}_2\text{Cr}_2\text{O}_7$? [Textbook]

Sol The ionic equation for the above reaction is,



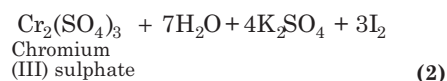
Therefore, when H_2S gas is passed through acidified $\text{K}_2\text{Cr}_2\text{O}_7$, hydrogen sulphide (H_2S) gets oxidised to sulphur.

2 MARK Questions

Exams' Questions

Q.36 What happens, when KI solution is added to acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution? [2019]

Sol When KI solution is added to acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution, it gives Cr^{3+} and I_2 as follows :



Q.37 Why do transitional elements form complex compounds? [2015]

Sol Transition elements form complex compounds due to

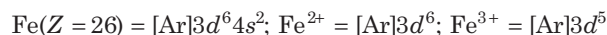
(i) small size of cation.

(ii) high nuclear charge of their cation.

(iii) availability of empty inner d -orbitals (of nearly same energy) for bonding to ligands. (2)

Q.38 Why, Fe^{3+} is more stable than Fe^{2+} ? [2009]

Sol The electronic configuration of Fe, Fe^{2+} and Fe^{3+} are shown below:

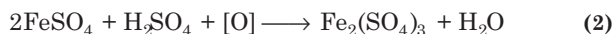
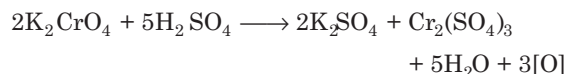


Here, the electronic configuration of Fe^{3+} is more stable ($3d$ -orbitals are all half-filled).

Hence, Fe^{3+} is more stable than Fe^{2+} . (2)

Q.39 What happens, when potassium chromate is treated with ferrous sulphate solution in the presence of dilute sulphuric acid? [2007]

Sol An acidified solution of K_2CrO_4 acts as an oxidising agent. Therefore, ferrous sulphate is oxidised to ferric sulphate. When potassium chromate is treated with ferrous sulphate solution in presence of $\text{dil. H}_2\text{SO}_4$. The reaction is as follows:



Q.40 Explain, why copper exhibits variable valency? [2006]

Sol Copper exhibits variable valency because, it contains electrons in d -subshell. Copper can easily lose one or two electrons. (2)

Q.41 Why chromium has higher boiling point than zinc? [2006]

Sol It is because of the presence of unpaired electrons in chromium which allows d - d overlap in addition to metallic bonding. Whereas, zinc does not have any unpaired electrons in it. (2)

Q.42 Define transition elements. Give their general outer electronic configuration. [2003]

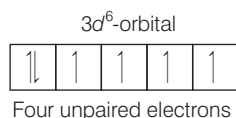
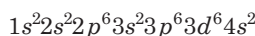
Sol Transition elements contain the outermost electron in the penultimate d -orbital. Their general electronic configuration is $(n-1)d^{1-10} ns^{1-2}$. (2)

Q.43 Why are most of the transition elements and their compounds paramagnetic? Give an example. [2003]

Sol Most of the transition elements and their compounds are paramagnetic due to the presence of unpaired electrons in their d -subshell.

e.g. Iron

Electronic configuration of ${}_{26}\text{Fe}$



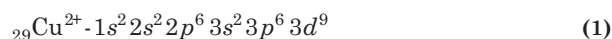
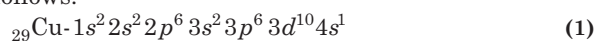
(2)

Q.44 Distinguish between alloy and amalgam. [2003]

Sol An alloy is a homogeneous mixture of two or more metals, while in amalgam, mercury is present as one of the constituents. (2)

Q.45 Write down the electronic configuration of Cu and Cu^{2+} . [2001]

Sol The electronic configuration of Cu and Cu^{2+} are as follows:



Important Questions

Q.46 Transition elements form alloys easily. Give reason. [Textbook]

Sol An alloy is a homogenous solid solution. Due to almost similar size, atoms of transition metals can easily occupy a place in the crystal lattice of another metal in the molten state and are miscible with each other forming alloys. (2)

Q.47 Why zinc salts are colourless? [Textbook]

Sol Zn exists as Zn^{2+} in its salts. The electronic configuration of Zn^{2+} is $[\text{Ar}] 3d^{10}$, i.e. there are no unpaired electrons in Zn^{2+} . Therefore, zinc salts are colourless. (2)

Q.48 Why Cu^+ salts are colourless? [Textbook]

Sol The electronic configuration of Cu^+ is $[\text{Ar}] 3d^{10}$, i.e. there are no unpaired electrons in Cu^+ . Therefore, Cu^+ salts are colourless. (2)

Q.49 Write the structure of chromate and dichromate ions. [Textbook]

Sol Refer to text on page 173. (2)

Q.50 What happens when potassium dichromate is heated? [Textbook]

Sol Refer to text on page 173. (2)

Q.51 Mention two uses of potassium dichromate. [Textbook]

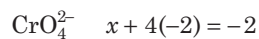
Sol Refer to text on page 174. (2)

Q.52 Write the structure of manganate and permanganate. [Textbook]

Sol Refer to text on page 174. (2)

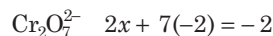
Q.53 Explain, why conversion of chromate ion to dichromate ion is not a redox reaction? [Textbook]

Sol The oxidation state of Cr in CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ is +6 as shown below :



$$x - 8 = -2$$

$$x = +6$$



$$2x - 14 = -2$$

$$x = +6$$

Since, the conversion of chromate ion to dichromate ion does not involve any change in oxidation number, it is not considered as a redox reaction. (2)

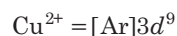
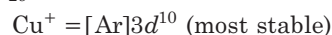
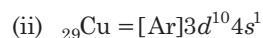
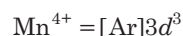
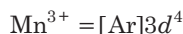
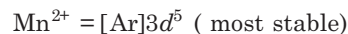
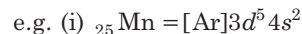
Q.54 Mention two important uses of potassium permanganate. [Textbook]

Sol Refer to text on page 175. (2)

Q.55 To what extent, does the electronic configuration decide the stability of oxidation states in the first series of the transition elements?

Illustrate your answer with examples.

Sol If orbital is half-filled or completely filled, it imparts stability to an atom or ion. (1)



In manganese, Mn^{2+} ion is most stable due to symmetry and half-filled d -orbitals. In the same way in copper, Cu^+ ion is most stable due to symmetry and completely filled d -orbitals. (1)

- Q.56** In 3d-series, it is easier to form M^{3+} ion from iron onwards. Why?
- Sol** The electron is being removed from M^{2+} ion of iron and all other subsequent members of the series. This electron is coming from paired d-orbital, so electron-electron repulsion assists removal of electron from M^{2+} ion to form M^{3+} ion. (2)

- Q.57** How would you account for the following?
- Transition metals exhibit variable oxidation states.
- Sol** ns and (n – 1)d electrons of transition metals participate in bonding, which results in variable oxidation states. When ns electrons take part in bonding, they exhibit lower oxidation states, whereas when (n – 1) d-electrons alongwith ns electrons participate in bonding, they exhibit higher oxidation states. (2)

3 MARK Questions

Exams' Question

- Q.58** Explain, why transition metal ions are usually coloured?
[2018, 2013, 2011, 2009 Instant, 2006, 2001, Textbook]
- Sol** Transition metal ions are usually coloured because of the absorption of radiation from visible region of light to promote an electron from a lower energy d-orbital to a higher energy d-orbital. The energy of excitation corresponds to the frequency of light absorbed. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of light absorbed is determined by the nature of ligand.
- When ligands have free electrons, the transfer of electron from anion to cation takes place. In this case, energy is absorbed during this process which is responsible for colour.
- Thus, most of the compounds of transition metals are coloured due to d-d transition. Transition metal ions having d^0 configuration are colourless. (3)

- Q.59** Why transition metal compounds are paramagnetic? [2014, 2005, 2003]
- Sol** Transition metal compounds are paramagnetic in nature due to the presence of unpaired electrons in d-subshell. More is the number of unpaired electrons in a substance, greater is its paramagnetic character or magnetic moment (μ).
- $$\mu_{\text{eff}} = \sqrt{n(n+2)} \text{ BM}$$
- where, n = number of unpaired electrons (3)

Important Questions

- Q.60** Explain, why CuSO_4 is paramagnetic, while ZnSO_4 is diamagnetic? [Textbook]
- Sol** In CuSO_4 and ZnSO_4 , the oxidation numbers of copper and zinc are +2. The electronic configurations of Cu^{2+} and Zn^{2+} are:
- $$\text{Cu}^{2+} = [\text{Ar}] 3d^9$$
- $$\text{Zn}^{2+} = [\text{Ar}] 3d^{10}$$
- Cu^{2+} ion contains one unpaired electron, whereas Zn^{2+} ions does not contain any unpaired electron. Therefore, CuSO_4 is paramagnetic, while ZnSO_4 is diamagnetic. (3)
- Q.61** Why do transition metal ions form complexes? [Textbook]
- Sol** Refer to text on page 172. (3)
- Q.62** Transition metals and their compound act as catalysts. Explain. [Textbook]
- Sol** Refer to text on page 172. (3)
- Q.63** What is the equivalent mass of KMnO_4 alkaline solution? Explain. [Textbook]
- Sol** The reaction of KMnO_4 with an alkali is given as follows:
- $$2\text{KMnO}_4 + 2\text{KOH} \longrightarrow 2\text{K}_2\text{MnO}_4 + \text{H}_2\text{O} + [\text{O}]$$
- $$\Rightarrow \text{MnO}_4^- + e^- \longrightarrow \text{MnO}_4^{2-}$$
- In an alkaline medium, the oxidation number of Mn changes from +7 to +6. Therefore, one electron is required for reduction.
- The molecular mass of KMnO_4 is 158 g/mol.
- \therefore The equivalent mass of KMnO_4 is,
- $$= \frac{\text{Molecular mass}}{1} = \frac{158}{1} = 158 \text{ eq}^{-1} \quad (3)$$
- Q.64** 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?
- Sol** The electronic configurations of the given ions are as follows:
- $$\text{Mn}^{3+} (Z = 25) = [\text{Ar}] 3d^4$$
- $$\text{Cr}^{3+} (Z = 24) = [\text{Ar}] 3d^3$$
- $$\text{V}^{3+} (Z = 23) = [\text{Ar}] 3d^2$$
- $$\text{Ti}^{3+} (Z = 22) = [\text{Ar}] 3d^1$$
- \therefore Number of unpaired electrons in Mn^{3+} , Cr^{3+} , V^{3+} , Ti^{3+} are 4, 3, 2 and 1 respectively.
- Cr^{3+} is the most stable among these in aqueous solution because it has half-filled t_{2g} level ($= t_{2g}^3$) (3)

7 MARK Questions

Exams' Questions

Q.65 Define transition elements. Discuss their following characteristic properties.

- (i) Formation of coloured compounds
- (ii) Magnetic property [2016]

Sol **Transition elements** The elements in which last electron enters in $(n-1)$ d -orbital are called d -block elements. These elements are generally known as transition elements as their position in periodic table is in between that of s -block (electropositive) and p -block elements. These elements make up three complete rows, i.e. $3d$, $4d$, $5d$, and an incomplete fourth row, i.e. $6d$. Their given characteristic properties are discussed below: (2)

- (i) **Formation of coloured compounds** The compounds formed by the transition elements are mainly coloured in nature. The colour arises due to the excitation of electron from d -orbitals of lower energy to d -orbitals of higher energy ($d-d$ transition).

Atoms or ions having d^1 to d^9 configuration are coloured, while atoms or ions having d^0 or d^{10} configurations are colourless. (2½)

- (ii) **Magnetic properties** The presence of unpaired electrons in transition metals is responsible for their magnetic behaviour. The transition elements containing unpaired electrons are paramagnetic in nature and, hence show magnetic properties. Each unpaired electron possesses a magnetic moment which is related to their spin and orbital angular momentum.

Hence, the magnetic moment is determined only from spin formula which is given below.

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

where, $n \rightarrow$ number of unpaired electrons

BM \rightarrow Bohr magneton. (2½)

Q.66 What are transition elements? Explain any four characteristic properties of transition elements. [2013, 2010, 2005, 2003, 2001, Textbook]

Sol Refer to the text on pages 171 and 172. (7)

Important Questions

Q.67 Describe the preparation of potassium permanganate. How does acidified potassium permanganate solution react with [Textbook]

- (i) SO_2
- (ii) iron (II)

Sol Refer to text on pages 174 and 175. (3 + 1 + 1 + 1 + 1)

Q.68 Discuss the oxidising action of KMnO_4 in acidic, alkaline and neutral solutions with suitable examples. [Textbook]

Sol Refer to text on page 175. (2 + 3 + 2)

Q.69 Describe the preparation of potassium dichromate from iron chromite ore. Discuss the effect of pH on a solution of potassium dichromate. [Textbook]

Sol Refer to text on page 173. (5 + 2)

Q.70 Discuss the oxidising action of $\text{K}_2\text{Cr}_2\text{O}_7$ and write the ionic equations for its reaction with (i) Fe^{2+} (ii) H_2S [Textbook]

Sol Refer to text on pages 173 and 174. (7)

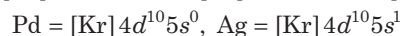
Q.71 Compare the general characteristics of the first series of the transition metals with those of the second and third series of metals in the respective vertical columns. Give special emphasis on the following points.

- (i) Electronic configuration
- (ii) Oxidation states
- (iii) Ionisation enthalpies and
- (iv) Atomic size

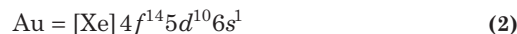
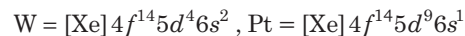
Sol (i) **Electronic configuration** The elements in the same vertical column generally have similar electronic configuration. Although the first series has only two exceptions.



Second transition series has five exceptions.



Third transition series has three exceptions.



- (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. (1)

- (iii) **Ionisation enthalpies** The first ionisation enthalpies in each series generally increase gradually as we move from left to right. Though, some exceptions are observed in each series. The first ionisation 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. (2)

- (iv) **Atomic size** Generally, ions of the same charge or atoms in a given series show progressive 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 of $4d$ -series due to lanthanoid contraction. (2)

Q.72 (i) Give reasons for the following;

- (a) Mn^{3+} is a good oxidising agent.
 (b) $E_{M^{2+}/M}^\circ$ values are not regular for first row of transition metals ($3d$ -series).
 (c) Although, 'F' is more electronegative than 'O', yet Mn forms MnF_4 with flourine, while it forms Mn_2O_7 with oxygen.

- (ii) Which of the following cations are coloured in aqueous solutions and why?

Sc^{3+} , V^{3+} , Ti^{4+} , Mn^{2+}

(Atomic number of Sc = 21, V = 23, Ti = 22, Mn = 25)

- Sol** (i) (a) $\text{Mn}^{3+}/\text{Mn}^{2+}$ has large positive E° value. Hence, Mn^{3+} can be easily reduced to Mn^{2+} . Therefore, it is a good oxidising agent. Also, Mn^{2+} has half-filled electronic configuration, so it is more stable as compared to Mn^{3+} . (2)

- (b) There is decreasing negative electrode potentials of M^{2+}/M in the first transition series due to increase in the sum $\text{IE}_1 + \text{IE}_2$. It shows that in general, the stability of +2 oxidation state decreases from left to right (exceptions are Mn and Zn) in which the greater stability of +2 state for Mn is due to half-filled d -subshell (d^5) in Mn^{2+} and that of Zn is due to completely filled d -subshell (d^{10}) in Zn^{2+} . (2)

- (c) It is because oxygen can form multiple bonds, whereas fluorine can only form single bonds with metals. (1)

- (ii) The colour of any cation depends on the number of unpaired electrons present in d -orbital. (1)

Cation	Configuration	Atomic number	Number of unpaired e^- in d -orbital	Colour
Sc	$3d^1 4s^2$	21	01	
Sc^{3+}	$3d^0 4s^0$	21	00	Colourless
V	$3d^3 4s^2$	23	03	
V^{3+}	$3d^2 4s^0$	23	02	Green
Ti	$3d^2 4s^2$	22	02	
Ti^{4+}	$3d^0 4s^0$	22	00	Colourless
Mn	$3d^5 4s^2$	25	05	
Mn^{2+}	$3d^5 4s^0$	25	05	Pink

(1)

Chapter Test

1 MARK Questions

- Write the formula of a compound, where transition metal is in +7 oxidation state.
- When acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution is added to Sn^{2+} salt, then Sn^{2+} changes to
(a) Sn (b) Sn^{3+} (c) Sn^{4+} (d) Sn^+
[Ans. (c)]
- Why is copper (I) ion not known in aqueous solution?
- What is the oxidation state of Cr in $\text{K}_2\text{Cr}_2\text{O}_7$?
- Which one of the following characteristics of the transition metal is associated with their catalytic property?
(a) Variable oxidation states
(b) Colour of hydrated ions
(c) High enthalpy of atomisation
(d) Paramagnetic behaviour [Ans. (a)]
- The trivalent cation having largest size in the lanthanoid series is [Ans. La^{3+}]
- Cr^{2+} ion is a strong agent, whereas Mn^{3+} with the same (d^4) configuration is agent. [Ans. reducing, oxidising]
- Transition elements show high melting points. Why?
- Why are transition elements known as d -block elements?

2 MARK Questions

- Chromium is typical hard metal, while mercury is a liquid. Why?
- Why is there striking similarities (horizontal and vertical) in successive members of the transition series?
- Why is the copper ($Z = 29$) considered as a transition metal?
- The atomic sizes of Fe, Co and Ni are nearly the same. Explain with reason.

- What happens when chromates are kept in acidic solution and dichromates in the alkaline solution?
- Calculate the spin magnetic moment of $\text{M}^{2+}(\text{aq})$ ($Z = 27$).

3 MARK Questions

- Complete the following chemical equations:
(i) $\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \longrightarrow$
(ii) $2\text{CrO}_4^{2-} + 2\text{H}^+ \longrightarrow$
(iii) $2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \longrightarrow$
- Explain the following about transition metals.
(i) Metallic character (ii) Oxidation states
(iii) Magnetic behaviour
- Account the following:
(i) The d^1 -configuration is very unstable in ions.
(ii) The IE_1 of Cr is low, whereas IE_1 for Zn is very high.
(iii) Copper (I) is diamagnetic whereas copper (II) is paramagnetic.

7 MARK Questions

- Give reasons for the following observations:
(a) Scandium ($Z = 21$) salts are white.
(b) The oxidising power of oxoanions are in the order: $\text{VO}_2^+ < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$
(c) The third ionisation enthalpy of manganese ($Z = 25$) is exceptionally high.
(d) The enthalpies of atomisation of transition elements are high.
(e) The lowest oxide of a transition metal is basic, the highest is amphoteric or acidic.
- Describe the commercial preparation of KMnO_4 from pyrolusite ore.
- Mn(II) ion shows maximum paramagnetic character amongst the bivalent ions of first transition series.
(ii) Describe the reactions involved in the preparation of $\text{K}_2\text{Cr}_2\text{O}_7$ from chromite ore.
(iii) The third ionisation enthalpy of manganese ($Z = 25$) is exceptionally high.