

THE D- AND F- BLOCK ELEMENTS

CHAPTER 08

INTRODUCTION

The series of elements, that are formed by filling the 3d, 4d and 5d shells of electrons, comprise the d-block elements. They are often called as transition elements because their position in the periodic table is between s-block and p-block elements.

Their properties are transitional between the highly reactive metallic elements of the s-block, which form ionic compounds and elements of p-block which form covalent compounds. In s and p blocks electrons add to the last shell, in d-block electrons are added to the penultimate shell.

Typically the transition elements have an incompletely filled d level. The zinc group has d^{10} configuration and compounds of these elements show some differences from other transition elements. The elements make up three complete rows of ten elements and an incomplete fourth row. The position of the incomplete fourth series is discussed along with the f-block elements.

ELECTRONIC CONFIGURATION

The general electronic configuration is $(n-1)^{1-10} ns^{1-2}$ where n is the outermost shell. The number of electrons in their outermost subshell remains two while their penultimate shell of electrons expands from 8 to 18 electrons.

Electronic configuration of 3d series

Sc	Ti	V	Cr	Mn	Fe	CO	Ni	Cu	Zn
$3d^1 4s^2$	$3d^2 4s^2$	$3d^3 4s^2$	$3d^5 4s^1$	$3d^5 4s^2$	$3d^6 4s^2$	$3d^7 4s^2$	$3d^8 4s^1$	$3d^{10} 4s^1$	$3d^{10} 4s^2$

Anomalous configuration of Cu and Cr : Copper and chromium have a single electron in 4s-orbital. This is due to the gain of additional stability by the atom having either half-filled (5 electrons) or completely filled (10 electrons) d-shell.

GENERAL CHARACTERISTICS OF TRANSITION ELEMENTS

- Except for mercury, which is a liquid at room temperature all other elements are solid metals exhibiting all the characteristics of a metal.
- They show variable oxidation states unlike s and p block elements.
- They, and some of their compounds, show catalytic properties.
- Their compounds are colored.
- They have great tendency to form complex compounds.
- They form alloys and interstitial compounds.

Conductivity

All the transition metals are good conductors of heat and electricity. Silver is the best conductor of electricity.

Density

Because of small size of their atoms and strong metallic bonding the density and hardness of transition elements are high.

Ionization Energy

The ionization energy (IE) of transition elements are higher than those of s-block elements but lower than p-block elements. In a particular transition series, ionization energy although increases gradually as we move from left to right but this increase is not appreciable.

The increase in ionization energy is due to increase in nuclear charge, the effect of increase in nuclear charge is partly balanced by the increase in screening effect. Consequently, the increase in ionization energy along the period of d-block elements is very small.

VARIABLE OXIDATION STATES

Transition elements usually exist in several different oxidation states and the oxidation states changes in units of one, e.g. Fe^{2+} and Fe^{3+} , Cu^{+1} and Cu^{+2} .

Scandium can have an oxidation number of (+II) if both s electrons are used for bonding and (+III) when two s and one d electrons are involved. Similarly all the elements show variable oxidation states depending upon the number of electrons available for bonding in their s and d sub-shells.

COMPLEXES AND THEIR PROPERTIES

The transition elements have an unparalleled tendency to form coordination compounds with the Lewis bases, which are called as ligands.



s and p block elements form very few complexes. The reason transition elements are so good at forming complex is that they have small, highly charged ions and have vacant low energy orbitals to accept lone pairs of electrons donated by ligands.

Size of Atoms and Ions

The covalent radii of the elements decrease from left to right across a row in the transition series. This is because of the poor screening by the d electrons due to which, the nuclear charge attracts all of the electrons more strongly, hence a contraction in size occurs.

The elements in the first group in the d-block show the expected increase (due to the addition of extra shell) in size $\text{Sc} \rightarrow \text{Y} \rightarrow \text{La}$. However in the subsequent groups there is an increase between first and second members, but hardly any increase between second and third elements. This is due to lanthanide contraction (discussed in f-block elements).

Colour

Many compounds of transition elements are colored in contrasts to those of s and p block elements. In compound state due to the surrounding groups (ligands), the d-orbitals of transition elements are not degenerate but split into two groups of different energy. Thus it is possible to promote electrons from one group to another group. This corresponds to fairly small amount of energy difference and so light is absorbed in visible region. Some compounds of transition metals are white, for example $ZnSO_4$ and TiO_2 . In these compounds it is not possible to promote the electrons within the d-level.

Magnetic Properties

On the basis of behaviors in a magnetic field, substances are classified as paramagnetic, diamagnetic and ferromagnetic. Those substances which are attracted by the applied magnetic field are called paramagnetic whereas those which are repelled by the magnetic field are called diamagnetic. Substances which are very strongly attracted by the applied field are called ferromagnetic.

Paramagnetism is a property due to the presence of unpaired electrons. Thus most of the transition metals are paramagnetic. As the number of unpaired electrons increases, the paramagnetic character also increases.

The magnetic moment is calculated from the following formula $\mu = \sqrt{n(n + 2)} B.M$

Where n is the number of unpaired electrons and B.M stands for Bohr magneton.

Catalytic Properties

Many transition metals and their compounds have catalytic properties. For e.g. V_2O_5 , Fe, $FeCl_3$, Ni, Pd etc.

This property of transition elements is due to their variable oxidation states. In some cases the transition metals with their variable valency may form variable unstable intermediate compounds. In other cases the transition metal provides a suitable reaction surface.

NON STOICHIOMETRY

Another feature of the transition elements is that they sometimes form non stoichiometry compounds. These are compounds of indefinite structure and proportions. For example $Fe_{0.94}O$. It is mostly due to the variable valency of transition elements. Sometimes, non stoichiometry is caused by defects in the solid structures.

ALLOY FORMATION

Alloys are homogenous solid solutions of two or more metals obtained by melting the components and then cooling the melt. These are formed by metals whose atomic radii differ by not more than 15% so that the atoms of one metal can easily take up the positions in the crystal lattice of the other. Since transition metals have similar atomic radii, they form alloys very readily.

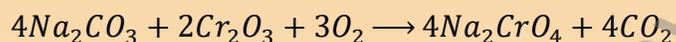
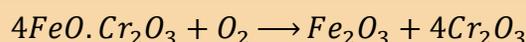
STUDY OF SOME IMPORTANT COMPOUNDS

➤ Potassium Dichromate, $K_2Cr_2O_7$

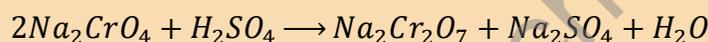
Preparation

It is prepared from the ore called chromate or ferrochrome or chrome iron, $FeO.Cr_2O_3$. The various steps involved are

(a) Preparation of sodium chromate



(b) Conversion of sodium chromate into sodium dichromate.



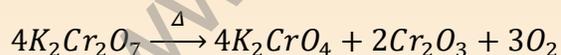
(c) Conversion of sodium dichromate into potassium dichromate.



Properties : It forms orange red crystals. It is moderately soluble in cold water but freely soluble in hot water.

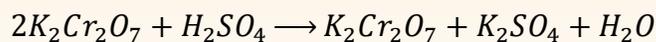
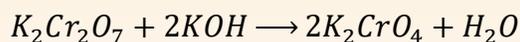
1. Action of heat

When heated, it decomposed to its chromate

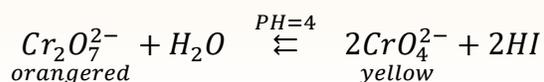


2. Action of alkalis

With alkalis it is converted into chromate which on acidifying gives back dichromate.



In dichromate solution the $Cr_2O_7^{2-}$ ions are in equilibrium with CrO_4^{2-} ions at pH = 4.



3. Action of conc. H₂SO₄ solution

(a) In cold conditions



(b) In hot conditions



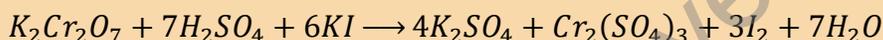
4. Oxidising properties

It is a powerful oxidising agent. In the presence of dil. H₂SO₄ it furnishes 3 atoms of available oxygen.



Some of the oxidizing properties of K₂Cr₂O₇ are

(a) It liberates I₂ from KI



(b) It oxidises ferrous salts to ferric salts



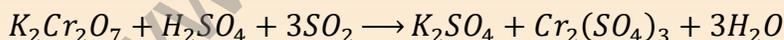
(c) It oxidises S⁻² to S



(d) It oxidises nitrites to nitrates



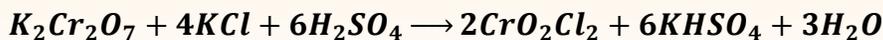
(e) It oxidises SO₂ to SO₄²⁻



(f) It oxidises ethyl alcohol to acetaldehyde and acetic acid.

5. Chromyl chloride test

When heated with conc. HCl or with a chloride in the presence of sulphuric acid, reddish brown vapors of chromyl chloride are obtained.



Thus, reaction is used in the detection of chloride ions in qualitative analysis.

Uses

1. In volumetric analysis for the estimation of Fe^{2+} and I^- .
2. In chrome tanning in leather industry.
3. In photography and in hardening gelatin film.

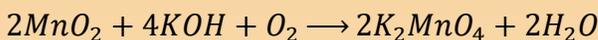
➤ Potassium Permanganate, KMnO_4

Preparation on a large scale

It is prepared from the mineral pyrolusite, MnO_2 . The preparation involves the following steps

(i) Conversion of MnO_2 into potassium manganate.

When finely powdered MnO_2 is fused with KOH . K_2MnO_4 is obtained.



(ii) Oxidation of potassium manganate into permanganate

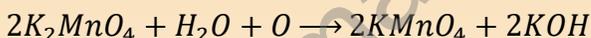
(a) Chemical oxidation

K_2MnO_4 is oxidised to KMnO_4 by bubbling CO_2 or Cl_2 or ozone into the former.



(b) Electrolytic oxidation

The manganate solution is electrolysed between iron electrodes. The oxygen evolved at anode converts manganate into permanganate.



Properties

KMnO_4 exists as deep purple prisms. It is moderately soluble in water at room temperature and its solubility in water increases with temperature.

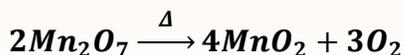
(i) Action of heat

When heated it decomposes to K_2MnO_4 .



(ii) Action of conc. H_2SO_4

With cold conc. H_2SO_4 it gives Mn_2O_7 which on warming decomposes to MnO_2 .



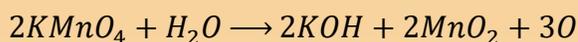
With hot Conc. H_2SO_4 O_2 is evolved



(iii) Oxidising properties

$KMnO_4$ is a powerful oxidizing agent. The actual oxidizing action depends upon the medium i.e., acidic, basic or neutral.

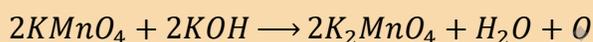
(a) In neutral solution, it acts as moderate oxidizing agent.



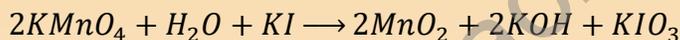
Some oxidizing properties of $KMnO_4$ in neutral medium are



(b) In strong alkaline solution, it is converted into MnO_4^{2-}



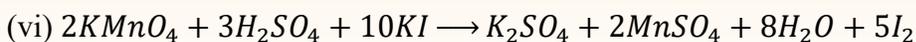
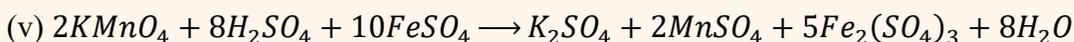
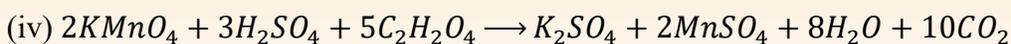
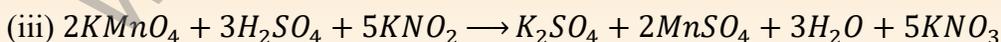
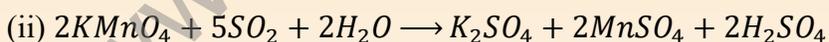
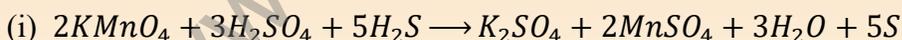
Some reactions in alkaline medium are



(c) In acidic medium, Mn^{+7} is converted into Mn^{+2}



Some other reactions are



Uses

- (i) It is used in volumetric analysis for the estimation of ferrous salts, oxalates, iodides and H_2O_2 .
- (ii) It is used as oxidizing agent in the laboratory as well as in industry.
- (iii) It is also used as disinfectant and germicide.

f – BLOCK ELEMENTS (Inner Transition Elements): -

The elements in which the differentiating electron enters the anti-penultimate energy level i.e. $(n - 2)f$, are called f – block elements. These are often called as inner transition elements or rare earth elements. The differentiating electron in transition elements may enter either 4f or 5f orbitals based upon which they are differentiated into lanthanides and actinides.

Lanthanides

In lanthanides the differentiating electron enters 4f orbital. These are cerium to lutetium. The name lanthanides is because they come immediately after lanthanum.

Actinides

In actinides the differentiating electron enters 5f orbitals. These are thorium to lawrencium. These elements come immediately after actinium.

Electronic configuration

General electronic configuration of f – block elements is $(n - 2)f^{1-14}(n - 1)d^{0-1}ns^2$

Lanthanides $[Xe]4f^{1-14}5d^{0-1}6s^2$

Actinides $[Rn]5f^{1-14}6d^{0-1}7s^2$

CHARACTERISTICS OF LANTHANIDES

1. Oxidation states

Lanthanides show only one stable oxidation state, which is not in the case of actinides. The typical oxidation state of lanthanides is +3. Some elements show +2 and +4 also, when they lead to

- (a) a noble gas configuration e.g. $Ce^{4+}(f^0)$
- (b) a half-filled f shell e.g. $Eu^{2+}(f^7)$
- (c) a completely filled f shell e.g. $Yb^{2+}(f^{14})$

2. Lanthanide contraction

In lanthanide series with increasing atomic number there is a progressive decrease in the atomic as well as ionic radii. This regular decrease is known as lanthanide contraction. This is due to the poor shielding off orbitals, which are unable to counter balance the effect of increasing nuclear charge. Net result is contraction in size.

3. Complex formation

The lanthanides do not have much tendency to form complexes due to low charge density because of their size. However, the tendency to form complex and their stability increases with increasing atomic number.

4. Chemical Behavior

The first few members of the series are quite reactive like calcium. However with increasing atomic number, their behaviors becomes similar to that of aluminum.

- They combine with H_2 on gentle heating. When heated with carbon, they form carbides. On burning in the presence of halogens, they form halides.
- They react with dilute acids to liberate H_2 .
- They form oxides and hydroxides of the type M_2O_3 and $M(OH)_3$ which are basic alkaline earth metal oxides and hydroxides.

GENERAL CHARACTERISTICS OF ACTINIDES

1. Oxidation states

The dominant oxidation state of these elements is +3 (similar to lanthanides). Besides +3 state, they also exhibit +4 oxidation state. Some actinides show still higher oxidation states. The maximum oxidation state first increases up to the middle of the series and then decreases i.e., it increases from +4 for Th to +5, +6 and +7 for Pa, V and Np but decreases in the succeeding elements.

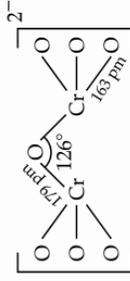
2. Chemical behaviors

The ability of actinides to exist in different oxidation states has made their chemistry more complex. Moreover, most of these elements are radioactive and the study of their chemistry in the laboratory is difficult.

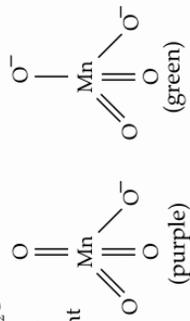
- They react with boiling water to give a mixture of oxide and hydride.
- The combine with most of the non – metals at moderate temperature.
- All these metals are attacked by HCl but the effect of HNO_3 is very small due to the formation of a protective oxide layer on their surface.

- **Position** : Between *s*- and *p*-blocks.
- **Electronic configuration** : $(n-1)d^{1-10}ns^{1-2}$
- **Physical properties** : Show typical metallic properties, melting and boiling point are high; High enthalpies of atomization.
- Decrease in radius with increasing atomic number. Lanthanoid contraction is due to filling of 4f before 5d orbitals, hence 2nd, 3rd d-series exhibit similar radii. Also due to imperfect shielding of one e^- by another in the same set of orbitals in same set of orbitals.
- **Ionisation enthalpies** : Increases from left to right.
- **Oxidation states** : Variable; higher oxidation number stable.
- Trends in $M^{2+}/M E^\circ$: E° for Mn, Ni and Zn are more negative than expected.
- Trends in $M^{3+}/M^{2+} E^\circ$: Variable.
- **Chemical reactivity and E° values** : Variable; Ti^{2+} , V^{2+} and Cr^{2+} are strong reducing agents.
- **Magnetic properties** : Diamagnetism and paramagnetism. Magnetic moment increases with increasing atomic number.
- **Formation of coloured ions** : Form coloured compounds due to d-d transitions.
- **Formation of complex compounds** : Form a large number of complex compounds.
- **Catalytic properties** : Due to variable oxidation states and ability to form complexes.
- **Forms interstitial compounds** : Non-stoichiometric and are neither ionic nor covalent.

- Potassium dichromate $K_2Cr_2O_7$
Preparation : $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$
 $2Na_2CrO_4 + 2H^+ \rightarrow Na_2Cr_2O_7 + 2Na^+ + H_2O$
 $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$
Properties : $Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$
Oxidises iodides to iodine, H_2S to S , SO_3^{2-} to SO_4^{2-} , NO_2^- to NO_3^-



- Potassium permanganate $KMnO_4$
Preparation : $2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$
 $3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$
 $2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \rightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$
Properties : Intense colour, weak temperature dependent paramagnetism
 $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$
Oxidizes I^- to I_2 , Fe^{2+} to Fe^{3+} , $C_2O_4^{2-}$ to CO_2 , S^{2-} to S , SO_3^{2-} to SO_4^{2-} , NO_2^- to NO_3^-



- Helps in production of iron and steels.
- TiO_2 in pigment industry.
- MnO_2 in dry battery cells.
- As catalysts in industry.
- Ni complexes useful in the polymerization of alkenes and other organic compounds such as benzene.
- AgBr in photographic industry.

d-Block transition elements groups 3-12

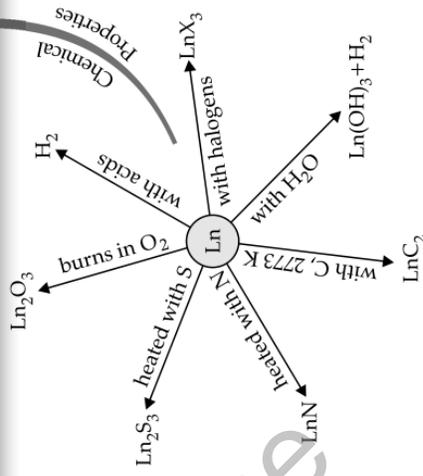
f-Block Transition Elements

Lanthanoid contraction is progressive decrease in atomic/ionic radii from La^{3+} to Lu^{3+}

- Electronic configuration: $[Rn]5f^{1-14}6d^{0-1}7s^2$
- Ionic sizes : Gradual decrease along the series.
- Oxidation states : Most common is +3. They show oxidation number of +4, +5, +6 and +7.
- **General characteristics** :
 - Silvery in appearance.
 - Display variety of structures.
 - Highly reactive metals.
 - Irregularities in metallic radii, greater than in lanthanoids.
 - Magnetic properties more complex than lanthanoids.

Lanthanoids

- Electronic configuration : $4f^{1-14}5d^{0-1}6s^2$
- Atomic and ionic sizes : Decrease from La to Lu
- Oxidation states : Most common is +3. Some elements exhibit +2 and +4.
- **General characteristics** :
 - Silvery white soft metals and tarnish rapidly in air.
 - Hardness increases with increasing atomic number.
 - Metallic structure and good conductors of heat and electricity.
 - Variable density.
 - Trivalent lanthanoid ions are coloured.
 - Ionisation Enthalpies : Low third ionisation enthalpies.
 - Good reducing agents.



d and f-Block Elements

Trace the Mind Map

- First Level
- Second Level
- Third Level

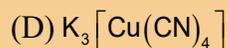
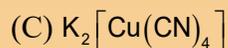
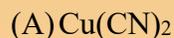
8. Which element exhibits oxidation states ranging from +4 to +6?
a) Fe b) Mg c) Co d) Cr
9. Among the following identify the transition metal species with an atom in +6 oxidation state
a) MnF b) $[\text{Cr}(\text{CN})_6]$ c) NiF d) CrO_2Cl_2
10. The number of electrons transferred in each case when KMnO_4 acts as oxidising agent to give MnO , Mn^{2+} , $\text{Mn}(\text{OH})_2$, and MnO_2 , are respectively
a) 3, 5, 4, 1 b) 4, 3, 1, 5 c) 1, 3, 4, 5 d) 5, 4, 3, 1
11. The correct order of $E_{M^{2+}/M}$ values with negative sign for the four successive elements Cr, Mn, Fe and Co is
a) $\text{Mn} > \text{Cr} > \text{Fe} > \text{Co}$
b) $\text{Cr} > \text{Fe} > \text{Mn} > \text{Co}$
c) $\text{Fe} > \text{Mn} > \text{Cr} > \text{Co}$
d) $\text{Cr} > \text{Mn} > \text{Fe} > \text{Co}$
12. Which is wrong with regard to actinoids
a) Chemistry of actinoids is not so smooth as that of Ln
b) Am and Cm have 5f configuration
c) They display different crystal structure due to irregular metallic radii
d) The actinoids resembles lanthanoids in having more compounds in +2 state
13. Which is a correct statement?
a) $\Delta H_{\text{atomization}}$ is abnormally low for Cr and Cu
b) K_1 , $[\text{PtCl}_6]^{2-}$ is thermodynamically unstable
c) In the d-block, ionisation enthalpy is lowest for La and highest for Hg
d) The oxidising power: $\text{VO}_2^+ > \text{CrO}_2 > \text{MnO}_2$

20. On addition of small amount of KMnO_4 to concentrated H_2SO_4 a green oily compound is obtained which is highly explosive in nature. Identify the compound from the following
- a) Mn_2O_7 b) MnO_2 c) MnSO_4 d) Mn_2O_3
21. The magnetic nature of elements depends on the presence of unpaired electrons. Identify the configuration of transition element, which shows highest magnetic moment
- a) $3d^7$ b) $3d^5$ c) $3d^8$ d) $3d^2$
22. Which of the following oxidation state is common for all lanthanoids?
- a)+3 b)+2 c)+4 d)+5
23. What would happen when a solution of potassium chromate is treated with an excess of dilute nitric acid
- a) Cr and Cr_2O are formed
b) CrO and HO are formed
c) Cr_2O is reduced to +3 state of Cr
d) Cr_2O is oxidised to +7 state of Cr
24. When MnO , is fused with KOH , a colored compound is formed, the product and its color is
- a) KMnO_4 green b) KMnO_4 purple
c) MnO , brown d) MnO , black
25. The number of moles of acidified KMnO_4 , required to convert sulphite ion into sulphate ion is:
- a) $\frac{2}{5}$ b) $\frac{4}{5}$ c) $\frac{3}{5}$ d) 1

26. Cerium ($Z=58$) is the first Ln present in monazite. Which is incorrect w.r.t cerium
- Common oxidation state possible are +3 and +4
 - +4 is unknown in solution
 - Ce is the best oxidant and analytical reagent
 - Most useful Ln
27. The Lanthanoid contraction is responsible for the fact that
- Zr and Y have about the same radius
 - Zr and Nb have similar oxidation state
 - Zr and Hf have about the same radius
 - Zr and Zn have the same oxidation state
28. The highest oxidation state achieved by a transition metal is given by
- | | |
|--------------------------|-------------------------------|
| (A) ns electrons | (B) $(n - 1)d$ electrons |
| (C) $(n + 1)d$ electrons | (D) $ns + (n - 1)d$ electrons |
29. Among the following outermost configurations of transition metals, which allows the highest oxidation state?
- | | |
|----------------|----------------|
| (A) $3d^24s^2$ | (B) $3d^54s^1$ |
| (C) $3d^54s^2$ | (D) $3d^64s^2$ |
30. Which one of the following characteristics of transition metals is associated with their catalytic activity?
- | | |
|-------------------------------|----------------------------------|
| (A) paramagnetic behaviors | (B) color of hydrated ions |
| (C) variable oxidation states | (D) high enthalpy of atomisation |
31. The highest magnetic moment is shown by the transition metal ion with the outer electronic configuration
- | | |
|------------|------------|
| (A) $3d^2$ | (B) $3d^5$ |
| (C) $3d^7$ | (D) $3d^9$ |

32. The atomic numbers of N, Cr, Mn and Fe are 23, 24, 25 & 26 respectively. Which one of these may be expected to have the highest second ionisation enthalpy?
- (A) V (B) Cr
(C) Mn (D) Fe
33. In nitroprusside ion, iron and NO exists as Fe^{2+} and NO^+ rather than Fe^{+3} and NO. These forms can be differentiated by
- (A) estimating the concentration of iron
(B) measuring the concentration of CN^-
(C) measuring the solid-state magnetic moment
(D) thermally decomposing the compound
34. Which of the following compounds is expected to be colored?
- (A) Ag_2SO_4 (B) CuF_2
(C) MgF_2 (D) CuCl
35. Pick up the transition metal which forms green compounds in +3 oxidation state and yellow to orange compounds in +6 oxidation state
- (A) chromium (B) cobalt
(C) Iron (D) nickel
36. The basic character of the transition metal monoxides follows the order
- (A) $\text{CrO} > \text{VO} > \text{FeO} > \text{TiO}$ (B) $\text{TiO} > \text{FeO} > \text{VO} > \text{CrO}$
(C) $\text{TiO} > \text{VO} > \text{CrO} > \text{FeO}$ (D) $\text{VO} > \text{CrO} > \text{TiO} > \text{FeO}$
37. Identify the statement which is not correct regarding CuSO_4
- (A) It reacts with KI to give I_2
(B) It reacts with KCl to give Cu_2Cl_2
(C) It reacts with NaOH and glucose to give Cu_2O
(D) It gives CuO on strong heating in air

38. Which compound is formed when excess of KCN is added to an aqueous solution of copper sulphate?



39. An aqueous solution of FeSO_4 , $\text{Al}_2(\text{SO}_4)_3$ and chrome alum is heated with excess of Na_2O_2 and filtered. The material obtained is

(A) a colorless filtrate and a green residue

(B) a yellow filtrate and a green residue

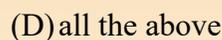
(C) a yellow filtrate and a brown residue

(D) a green filtrate and a brown residue

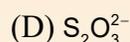
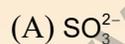
40. Which of the following compounds does not dissolve in hot dilute HNO_3 ?



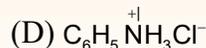
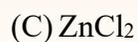
41. Which of the following exists in liquid state at room temperature?



42. Which of the following finally gives black ppt. with Ag^+ ions?



43. Which of the following does not give positive chromyl chloride test?



44. Ammonium dichromate is used in fireworks. The green colored power blown in the air is
- (A) CrO_3 (B) Cr_2O_3
(C) Cr (D) $\text{CrO}(\text{O}_2)$
45. In the dichromate dianion
- (A) 4 Cr — O bonds are equivalent
(B) 6 Cr — O bonds are equivalent
(C) all Cr — O bonds are equivalent
(D) all Cr — O bonds are non – equivalent
46. The chemical composition of slag formed during the smelting process in the extraction of copper is
- (A) $\text{Cu}_2\text{O} + \text{FeS}$ (B) FeSiO_3
(C) CuFeS_2 (D) $\text{Cu}_2\text{S} + \text{FeO}$
47. Which of the following metal is leached by cyanide process?
- (A) Ag (B) Na
(C) Al (D) Cu
48. KI and CuSO_4 solutions when mixed give
- (A) $\text{CuI}_2 + \text{K}_2\text{SO}_4$ (B) $\text{Cu}_2\text{I}_2 + \text{K}_2\text{SO}_4$
(C) $\text{K}_2\text{SO}_4 + \text{Cu}_2\text{I}_2 + \text{I}_2$ (D) $\text{K}_2\text{SO}_4 + \text{CuI}_2 + \text{I}_2$
49. The form of iron having the highest carbon content
- (A) cast iron (B) wrought iron
(C) stainless steel (D) mild steel
50. Which of the following compounds is not colored?
- (A) Na_2CuCl_4 (B) Na_2CdCl_4
(C) $\text{K}_4[\text{Fe}(\text{CN})_6]$ (D) $\text{K}_3[\text{Fe}(\text{CN})_6]$

51. When calomel reacts with NH_4OH , we get?
- (A) HgNH_2Cl (B) $\text{NH}_2\text{—Hg—hg—Cl}$
(C) Hg_2O (D) HgO
52. An anion solution gives a white ppt with AgNO_3 solution. The ppt dissolves in dil. ammonia due to the formation of
- (A) AgNO_3 (B) $[\text{Ag}(\text{NH}_3)\text{Cl}]$
(C) $[\text{Ag}(\text{NH}_3)_2]\text{Br}$ (D) NH_4NO_3
53. Which of the following oxides of chromium is amphoteric in nature?
- (A) CrO (B) Cr_2O_3
(C) CrO_3 (D) CrO_5
54. CrO_3 dissolves in aqueous NaOH to give
- (A) CrO_4^{2-} (B) $\text{Cr}(\text{OH})_3$
(C) $\text{Cr}_2\text{O}_7^{2-}$ (D) $\text{Cr}(\text{OH})_2$
55. A red solid is insoluble in water. However, it becomes soluble if some KI is added to water. Heating the red solid in a test tube results in liberation of some violet colored fumes and droplets of a metal appear on the cooler parts of the test tube. The red solid is
- (A) HgI_2 (B) HgO
(C) Pb_3O_4 (D) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$
56. The colorless species is
- (A) VCl_3 (B) VOSO_4
(C) Na_3VO_4 (D) $[\text{V}(\text{H}_2\text{O})_6.\text{SO}_4]\cdot\text{H}_2\text{O}$
57. In Nessler's reagent for the detection of NH_3 , the active species is
- (A) Hg_2Cl_2 (B) HgI_2
(C) Hg_2I_2 (D) HgI_4^{-2}

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1. (A) +7

Explanation: The electron configuration of manganese in the given form suggests that it can have a maximum oxidation state of +7. This corresponds to the oxidation state in which all the 3d orbitals are half-filled.

2. (A) an oxide layer is formed on their surface.

Explanation: Many transition metals form a protective oxide layer on their surface, which prevents them from reacting further with dilute acids. This oxide layer inhibits the release of hydrogen gas.

3. (C) unpaired electrons

Explanation: Transition elements have unpaired electrons in their partially filled d-orbitals. These unpaired electrons are responsible for their ability to form complexes and undergo hydrolysis reactions.

4. (A) Mn_2O_7

Explanation: The acid anhydride of permanganic acid (H_2MnO_4) is obtained by removing water (H_2O) from it. The resulting compound is Mn_2O_7 .

5. (C) exchange energy of Cu^{2+} is high.

Explanation: Cu^{2+} ion is more stable than Ag^{2+} ion due to the higher exchange energy of Cu^{2+} . This higher exchange energy contributes to the stability of the Cu^{2+} ion compared to Ag^{2+} . Certainly, here are the correct options and explanations for each question:

6. (c) $Dy < Gd < Pm < Ce^{3+}$

Explanation: The ionic radii of lanthanoids decrease across a period with increasing atomic number due to the lanthanoid contraction. In the +3 oxidation state, the ionic radii follow the reverse order of the atomic numbers.

7. (c) $5f^{14}$

Explanation: The actinoids are believed to have the electronic configuration with the $5f^{14}$ electrons.

8. (d) Cr

Explanation: Chromium (Cr) can exhibit oxidation states ranging from +4 to +6.

9. (b) $[\text{Cr}(\text{CN})_6]^{3-}$

Explanation: The compound $[\text{Cr}(\text{CN})_6]^{3-}$ has chromium in the +3 oxidation state.

10. (a) 3, 5, 4, 1

Explanation: When KMnO_4 acts as an oxidizing agent, the number of electrons transferred in each case are: 3 electrons for MnO , 5 electrons for Mn_2O_7 , 4 electrons for $\text{Mn}(\text{OH})_4^-$, and 1 electron for MnO_2 .

11. (b) $\text{Cr} > \text{Fe} > \text{Mn} > \text{Co}$

Explanation: The EMF series (EM2M values) indicates the reduction potential, with more positive values being easier to reduce. Among the given elements, Cr has the highest negative EMF value, followed by Fe, Mn, and then Co.

12. (d) The actinoids resemble lanthanoids in having more compounds in +2 state

Explanation: This statement is incorrect. Actinoids, unlike lanthanoids, have a wider range of oxidation states and can exhibit more diverse chemistry.

13. (a) AH, is abnormally low for Cr and Cu

Explanation: The enthalpy of atomization (AH) is abnormally low for chromium (Cr) and copper (Cu) due to their stable half-filled and fully-filled d-orbitals, respectively.

14. (b) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$

Explanation: Among the given options, $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ has the d^3 electron configuration, which has no unpaired electrons and exhibits the minimum paramagnetic behavior.

15. (b) $[\text{Cr}]_2 (\text{SO}_4)_3$

Explanation: When acidified potassium chromate solution reacts with sodium sulfate, green chromium(III) sulfate, $[\text{Cr}]_2 (\text{SO}_4)_3$, is formed.

16. (b) $K[Cu(CN)]$ (potassium cuprocyanide)

Explanation: $K[Cu(CN)]$ is a colored compound due to the presence of the copper ion.

17. (c) Ti, V, Cr

Explanation: Among the given options, the series Ti, V, Cr consists of transition metal ions with 3d electronic configuration.

18. (a) 25

Explanation: The atomic number of an element is determined by the number of protons in its nucleus. The given electronic configuration $[Ar] 4s^2 3d^6$ corresponds to atomic number 25, which is manganese (Mn).

19. (c) Cu(I) and Cu(II) are equally stable

Explanation: Cu(I) and Cu(II) are equally stable due to the filled $3d^{10}$ configuration in both oxidation states.

20. (a) Mn_2O_7 (Manganese heptoxide)

Explanation: When potassium permanganate ($KMnO_4$) is added to concentrated sulfuric acid, it forms a green oily compound known as manganese heptoxide (Mn_2O_7), which is highly explosive.

21. (b) $3d^5$

Explanation: Among the given options, the configuration $3d^5$ has the maximum number of unpaired electrons, leading to the highest magnetic moment.

22. (a) +3

Explanation: The common oxidation state for all lanthanoids is +3.

23. (d) Cr_2O is oxidised to +7 state of Cr

Explanation: In the presence of excess nitric acid, chromate ions (CrO_4^{2-}) get oxidized to dichromate ions ($Cr_2O_7^{2-}$) in the +7 oxidation state.

24. (a) KMnO_4 (green)

Explanation: When MnO_2 is fused with KOH , it forms potassium manganate (KMnO_4), which is green in color.

25. (a) 2/5

Explanation: The balanced redox equation for converting sulphite (SO_3^{2-}) ion to sulfate (SO_4^{2-}) ion involves the transfer of 2 electrons for each SO_3^{2-} ion.

26. (b) +4 is unknown in solution

Explanation: Cerium (Ce) can exist in both +3 and +4 oxidation states, but +4 is not stable in aqueous solution.

27. (c) Zr and Hf have about the same radius

Explanation: The Lanthanoid contraction affects the similarity in atomic radii between zirconium (Zr) and hafnium (Hf).o Ag^{2+} ion.

28. (C) $(n + 1)d$ electrons

Explanation: The highest oxidation state achieved by a transition metal is given by the $(n + 1)d$ electrons, where "n" is the principal quantum number of the outermost electron shell.

29. (B) $3d^54s^1$

Explanation: Among the given configurations, $3d^54s^1$ allows the highest oxidation state. The presence of unpaired electrons in the 3d orbitals provides the possibility for multiple oxidation states.

30. (C) variable oxidation states

Explanation: The catalytic activity of transition metals is associated with their ability to change oxidation states during a reaction. Transition metals can readily switch between different oxidation states, which allows them to participate in redox reactions and facilitate catalysis.

31. (C) $3d^7$

Explanation: The highest magnetic moment is shown by the transition metal ion with the outer electronic configuration of $3d^7$, as it has the maximum number of unpaired electrons.

32. (D) Fe

Explanation: Among the given elements (N, Cr, Mn, Fe), Fe (iron) has the highest atomic number (26), and higher atomic number generally correlates with higher second ionization enthalpy.

33. (B) measuring the concentration of CN^-

Explanation: Nitroprusside ion forms colored complexes with various ions, including Fe^{2+} and NO^+ . The presence of CN^- ions in solution can be determined by measuring the concentration of CN^- using its complexation with the formed Fe^{2+} ions.

34. (B) CuF_2

Explanation: Copper(II) fluoride (CuF_2) is expected to be colored. Transition metal compounds often exhibit color due to the presence of unpaired electrons in their partially filled d-orbitals.

35. (A) chromium

Explanation: Chromium (Cr) forms green compounds in +3 oxidation state and yellow to orange compounds in +6 oxidation state.

36. (A) $CrO > VO > FeO > TiO$

Explanation: The basic character of transition metal monoxides follows the order $CrO > VO > FeO > TiO$, where the oxides of chromium (CrO) and vanadium (VO) are more basic compared to the oxides of iron (FeO) and titanium (TiO).

37. (C) It reacts with NaOH and glucose to give Cu_2O

Explanation: $CuSO_4$ reacts with sodium hydroxide (NaOH) and glucose to give copper(I) oxide (Cu_2O).

38. (B) CuCN

Explanation: When excess KCN is added to an aqueous solution of copper sulfate (CuSO_4), copper(I) cyanide (CuCN) is formed.

39. (C) a yellow filtrate and a brown residue

Explanation: When FeSO_4 , $\text{Al}_2(\text{SO}_4)_3$, and chrome alum are heated with excess Na_2O_2 , a yellow filtrate (containing the dissolved aluminum ions) and a brown residue (iron hydroxide) are obtained.

40. (A) HgS

Explanation: Mercury(II) sulfide (HgS), also known as cinnabar, does not dissolve in hot dilute HNO_3 .

41. (B) Hg

Explanation: Mercury (Hg) exists in the liquid state at room temperature.

42. (B) Br^-

Explanation: Br^- ions do not give a positive chromyl chloride test. This test involves the formation of a red chromyl chloride complex when chloride ions are present.

43. (B) HgCl_2

Explanation: Among the given options, HgCl_2 does not give a positive chromyl chloride test. This test is usually used to identify the presence of chloride ions using chromyl chloride (CrO_2Cl_2).

44. (A) CrO_3

Explanation: Ammonium dichromate $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ is used in fireworks. When heated, it decomposes to form Cr_2O_3 (chromium(III) oxide) along with nitrogen and water vapor.

45. (B) 6 Cr-O bonds are equivalent

Explanation: In the dichromate ion ($\text{Cr}_2\text{O}_7^{2-}$), 6 Cr-O bonds are equivalent.

46. (D) $\text{Cu}_2\text{S} + \text{FeO}$

Explanation: The chemical composition of slag formed during the smelting process in the extraction of copper is $\text{Cu}_2\text{S} + \text{FeO}$.

47. (A) Ag

Explanation: The cyanide process is used to leach silver (Ag) from its ores.

48. (B) $\text{Cu}_2\text{I}_2 + \text{K}_2\text{SO}_4$

Explanation: When KI and CuSO_4 solutions are mixed, they give $\text{Cu}_2\text{I}_2 + \text{K}_2\text{SO}_4$ as a result.

49. (A) cast iron

Explanation: Cast iron typically contains the highest carbon content among the given options.

50. (C)

Explanation: The options provided for this question are not complete, so it's not possible to determine the correct answer.

51. (B) HgI_2

Explanation: When calomel (Hg_2Cl_2) reacts with NH_4OH , it forms HgI_2 , which is a yellowish substance.

52. (B) HgI_2

Explanation: The white precipitate formed in the presence of AgNO_3 dissolves in dilute ammonia due to the formation of the soluble complex $\text{HgI}_2 \cdot \text{NH}_3$.

53. (B) Cr_2O_3

Explanation: Chromium(III) oxide (Cr_2O_3) is amphoteric in nature, meaning it can act as both an acid and a base in reactions.

54. (C) CrO_3

Explanation: CrO_3 dissolves in aqueous NaOH to give sodium chromate (Na_2CrO_4) and water.

55. (D) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$

Explanation: $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$, also known as ammonium dichromate, is a red solid that liberates violet-colored fumes and droplets of chromium oxide (Cr_2O_3) upon heating.

56. (A) VCl_3

Explanation: Among the given options, VCl_3 is colorless.

57. (C) Hg_2I_2

Explanation: In Nessler's reagent, the active species responsible for detecting NH_3 is Hg_2I_2 , which forms a brown color complex upon reacting with ammonia.