8

The d & f-Block Elements

Electronic Configurations/(n–1) d^{1-10} ns^{1-2}.

Exceptions: 1. Cr = $4s^1$ $3d^5$

2. Cu = $4s^1$ $3d^{10}$

3. Pd = $5s^0 4d^{10}$

Transition Series

1st	3d series	Sc_{21} - Zn_{30}	9 + 1 = 10
2nd	4d series	Y_{39} - Cd_{48}	9 + 1 = 10
3rd	5d series	La_{57}, Hf_{72} - Hg_{80}	9 + 1 = 10
4th	6d series	Ac_{89}, Unq_{104}- Uub_{112}	9 + 1 = 10

General Properties of Transition Element

- The transition elements exhibit typical characteristic properties due to their small **atomic sizes, large nuclear charges and the presence of unpaired d - electrons**.
- **Enthalpy of atomization:** V > Ti > Ni > Co > Fe > Cr > Cu > Sc > Mn > Zn

(1) Trends in M.P of transition elements(TE)

- In any row the melting points of these metals rise to a maximum at d^5 except for anomalous values of Mn and Tc and fall regularly as the atomic number increases. They have high enthalpies of atomization. The maxima at about the middle of each series indicate that one unpaired electron per d orbital is particularly favorable for strong interatomic interaction.

Number of valence electrons increase

↓

strong bonding

↓

higher enthalpy of atomisation

↓

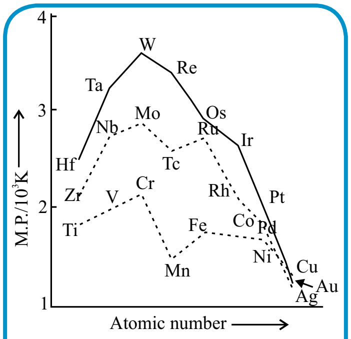
higher boiling point

↓

higher standard electronic potential

↓

More noble character



Trends in melting points of transition elements

After chromium, the number of unpaired electrons goes on decreasing. Accordingly, the melting points decrease after middle (Cr) because of increasing pairing of electrons.

(2) Size of atoms and ions

- The covalent radii of the elements **decreases from left to right across a row** in the transition series, until near the end when the size increases slightly.
- **Metallic radii:** Sc > Ti > Mn = Zn > V > Cr > Cu> Co = Ni

(3) Ionization Energies of 3d Series

- IP values generally **increase** from left to right in any series but the **increase is less than** that of s block elements due to increase in nuclear charge is opposed by screening effect.
- **Ionization Enthalpy:** Zn > Fe > Co > Cu > Ni > Mn > Ti > Cr > V >Sc

(4) Oxidation State

Transition elements exhibit variable oxidation state due to **small energy difference of ns and (n – 1)d electrons**.

- Sc(+3) and Zn(+2) exhibit only one oxidation state
- Common oxidation state is +2
- 3d series highest oxidation state is +7 (Mn)
- In d-block series highest oxidation state is +8 (Os, Ru)

> In carbonyl compound oxidation state of metals is zero due to synergic effects.
> The common examples are $[Ni(CO)_4]$, $[Fe(CO)_5]$ in which nickel and iron are in zero oxidation state.

- Their higher oxidation states are more stable in **fluoride** and **oxides**.
- Higher oxidation states in oxides are normally more stable than fluorides due to capability of oxygen to form multiple bonds.

Some more stable oxidation states of d-block elements			
Cu + 2	Mn + 2	Pt + 4	Ag + 1
Cu + 3	Sc + 3	Au + 3	Ni + 2

Common oxidation states			
Ti (+ 4)	V (+5)	Cr (+3, +5)	Mn (+2, +4, +7)
Fe(+2, +3)	Co (+2, +3)	Ni (+2)	Pt(+2, +4)

In p-block lower oxidation states of heavier elements are more stable while in d-block heavier element, higher oxidation state are more stable.

(5) Electrode potentials and chemical reactivity

Trends in the M^{2+}/M Standard electro potential

- S.R.P of M^{+2}/M values increases from left to right as IP values increases. (except Zn)

> Cu cannot displace H_2 from acids because it has highest S.R.P value which is +0.34 V.

- Mn, Ni and Zn have more negative S.R.P values than expected because.
- Reason: Mn & Zn have d^5 & d^{10} stable electronic configuration Ni has highest hydration energy. (ΔH_{Hyd} Ni^{+2} = –2121 kJ/mole)

Trends in the M^{3+}/M^{2+} Standard electro potential

- $E^0_{M^{+3}/M^{+2}}$ in the 3d series are observed for some metals are

> $Co^{+3}/Co^{+2} > Mn^{+3}/Mn^{+2} > Fe^{+3}/Fe^{+2} > Ti^{+3}/Ti^{+2} > Sc^{+3}/Sc^{+2} > V^{+3}/V^{+2}$

(6) Magnetic Property of Transition Metals

- Paramagnetic substances contain unpaired electron spins or unpaired electrons.
- Ex : $K_3[Fe(CN)_6]$, Sc^{2+}, Cr^{3+} etc
- Diamagnetic substances exhibit decrease in weight in the presence of magnetic field.
- Ex.: Ti^{+4}, V^{+5} , Sc^{3+}, Zn, Hg, Cd etc
- Diamagnetic substances contain electron pairs with opposite spins.
- **Ferromagnetic substances** are considered as a special case of paramagnetic substances.
- Paramagnetism of substances (molecules, atoms or ions)is due to the spins of the unpaired electrons and also due to angular orbital momentum.

SCAN (Special Cases Asked in NEET)

In terms of number of unpaired electrons (n), the magnetic moment is given by the formula.

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

Q. The magnetic moment of Ni^{2+} ion (atomic number of Ni = 28) in BM unit is:

a. 1.73 b. 4.81
c. 5.96 d. 2.84

Ans. (d) $Ni_{28} = [Ar]\ 3d^8\ ,\ 4s^2$

$Ni^{2+} = [Ar]\ 3d^8$ $\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow\downarrow}\boxed{\uparrow}\boxed{\uparrow}$

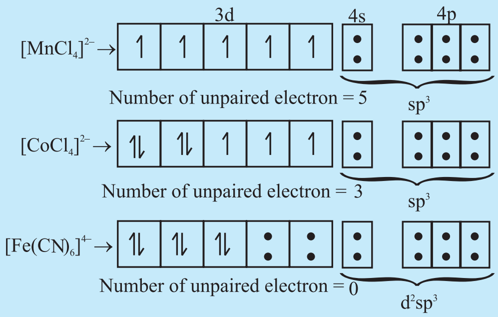
$\therefore\ n = 2$

$$\mu = \sqrt{n(n+2)} = \sqrt{2(2+2)} = \sqrt{2(4)} = \sqrt{8} = 2.84\,BM$$

Q. The correct order of magnetic moments (spin only values in B.M.) among is

a. $[Fe(CN)_6]^{4-} > [MnCl_4]^{2-} > [CoCl_4]^{2-}$
b. $[MnCl_4]^{2-} > [Fe(CN)_6]^{4-} > [CoCl_4]^{2-}$
c. $[MnCl_4]^{2-} > [CoCl_4]^{2-} > [Fe(CN)_6]^{4-}$
d. $[Fe(CN)_6]^{4-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$

Ans. (c)



(7) Colours of Transition Metal Ions

Colour in transition metal ions is associated with d-d transition of unpaired electron from t_{2g} to e_g set of energies.

(8) Formation of complexes

The great tendency of transition metal ions to form complexes is due to : small size of the atoms and ions, high nuclear charge and availability of vacant d-orbitals of suitable energy to accept lone pairs of electrons donated by ligands.

(9) Catalytic properties of transition metals

Good catalysts due to the presence of free valencies and also variable oxidation states.

(10) Formation of Interstitial Compounds

- From interstitial compounds: As they are able to entrap atoms of elements having small atomic size like H, C, N, B etc.
- The general characteristic physical and chemical properties of these compounds are :
  - **High melting points** which are higher than those of pure metals.
  - **Retain metallic conductivity** i.e. of pure metals.
  - Very hard and some borides have hardness as that of diamond.
  - **Chemically inert**.

(11) Alloy Formation

Solid mixture of metals in a definate ratio (15% difference in metallic radius)

They are hard and having high melting point.

eg., Brass (Cu + Zn)

Bronze (Cu + Sn) etc.

Hg when mix with other metals form semisolid amalgam except Fe, Co, Ni, Li.

Potassium Dichromate ($K_2Cr_2O_7$)

Properties

(a) Physical:

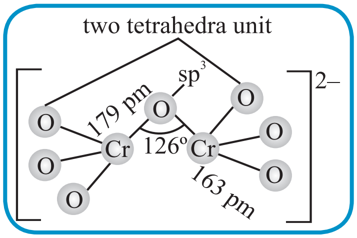


Fig.: Dichromate ion orange, red colour

☑ Key Note

$K_2Cr_2O_7$ is preferred over $Na_2Cr_2O_7$ as a primary standard in volumetric estimation because $Na_2Cr_2O_7$ is hygroscopic in nature but $K_2Cr_2O_7$ is not.

(b) Chemical:

- $$2K_2Cr_2O_7 \xrightarrow{\Delta} 2K_2CrO_4 + Cr_2O_3 + \frac{3}{2}O_2$$

$$K_2Cr_2O_7 + 2KOH \longrightarrow 2K_2CrO_4 + H_2O$$

$$\underset{\text{Orange}}{Cr_2O_7^{2-}} + 2OH^- \longrightarrow \underset{\text{Yellow}}{2CrO_4^{2-}} + H_2O$$

Yellow→ (color change in basic medium)

$$\underset{\text{Yellow}}{2CrO_4^{2-}} + 2H^+ \longrightarrow \underset{\text{Orange}}{Cr_2O_7^{2-}} + H_2O$$

Orange → (color change in acidic medium)

CrO_4^{2-} and $Cr_2O_7^{2-}$ exist in equilibrium and are interconvertable by **altering the pH** of solution.

$$2CrO_4^{2-} + 2H^+ \rightleftharpoons 2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$$

- It acts as a powerful oxidising agent in acidic medium (dilute H_2SO_4)

$$\overset{+6}{Cr}_2\,O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O.$$

(E° = 1.33 V)

SCAN (Special Cases Asked in NEET)

Reaction of Acidified potassium dichromate

$$K_2Cr_2O_7 + 3Na_2SO_3 + 4H_2SO_4 \longrightarrow Cr_2\,(SO_4)_3 + 3Na_2SO_4 + K_2SO_4$$

$$K_2Cr_2O_7 + 3SO_2(g) + H_2SO_4 \longrightarrow Cr_2\,(SO_4)_3 + K_2SO_4$$

Q. The reaction of acidified potassium dichromate with Na_2SO_3 produces a compound that show green colour. Identify the compound.

a. $Cr_2\,(SO_4)_3$
b. K_2SO_4
c. $Cr_2O_4{}^{2-}$
d. MnO_2

Ans. (a) $K_2Cr_2O_7 + 3Na_2SO_3 + 4H_2SO_4$

$$\longrightarrow \underset{\text{green colour}}{Cr_2\,(SO_4)_3} + 3Na_2SO_4 + K_2SO_4$$

Potassium Permanganate ($KMnO_4$)

Preparation

- Commercially it is prepared by fusion of MnO_2 with KOH followed by electrolytic oxidation of manganate.

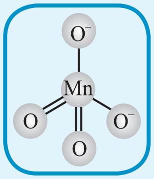
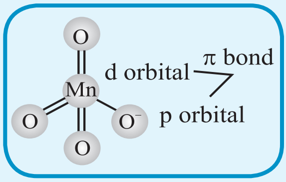
$MnO_4{}^{2-}$ (green) $\longrightarrow$ $MnO_4{}^-$ (purple) + e^-

- In the lab

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \longrightarrow 2MnO_4^- + 10SO_4^{2-} + 16H^+$$

Properties

(a) Physical:

	
Tetrahedral manganate (green) ion (Paramagnetic)	Terahedral permanganate (purple) ion (Diamagnetic)

SCAN (Special Cases Asked in NEET)

MnO_4^{2-} & MnO_4^- contains one and zero unpaired electron respectively

Q. Predict the magnetic nature of manganate and permanganate ion.

a. Paramagnetic, diamagnetic

b. Diamagnetic, Paramagnetic

c. Paramagnetic, Paramagnetic

d. Diamagnetic, Diamagnetic

Ans. (a) Manganate (MnO_4^{2-}) Paramanganate (MnO_4^-)
The green manganate is paramagnetic with one unpaired electron but the permanganate is diamagnetic.

(b) Chemical:

(i) Effect of heating

$$2KMnO_4 \xrightarrow{751K} K_2MnO_4 + MnO_2 + O_2$$

In alkaline & neutral medium:

$$\underset{\text{(conc.)}}{2KMnO_4 + 2KOH} \longrightarrow \underset{\text{manganate}}{2K_2MnO_4} + H_2O + [O]$$

If solution is dilute

$$2K_2MnO_4 + 2H_2O \longrightarrow \underset{\text{(Brown ppt)}}{2MnO_2} + 4KOH + 2[O]$$

This type of behaviour is shown by $KMnO_4$ itself in neutral medium

$$3e^- + 2H_2O + MnO_4^- \longrightarrow MnO_2 + 4OH^-$$

In alkaline or neutral medium $KMnO_4$ shows **oxidising properties**.

In acidic medium (in presence of dilute H_2SO_4):

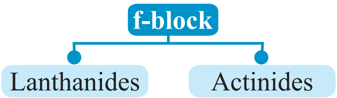
oxidised

$$MnO_4^- + \underset{\text{Green}}{5Fe^{2+}} + 8H^+ \longrightarrow \underset{\text{yellow}}{5Fe^{3+}} + Mn^{2+} + 4H_2O$$

oxidised

$$2MnO_4^- + 5SO_2 + 2H_2O \longrightarrow 5SO_4^{2-} + 2Mn^{2+} + 4H^+$$

The Inner Transition f-Block Elements



Lanthanides

Electronic configuration - $4f^{14}\ 5d^{0-1}\ 6s^2$

La to Lu
(57) (71)

Properties

Atomic sizes

- There is decrease in atomic and ionic radii from lanthanum to lutetium due to **lanthanoid contraction**. However, the shielding of one 4f electron by another is less than a d-electron by another with the increase in nuclear charge along the series.

SCAN (Special Cases Asked in NEET)

The net result of the lanthanoid contraction is that the second and the third d series exhibit similar radii (e.g., Zr 160 pm, Hf 159 pm) and have very similar physical and chemical properties much more than that expected on the basis of usual family relationship.

Q. The pair that is referred as 'chemical twins' is:

a. Ac, Cf b. Hf, Ta c. Tc, Re d.La, Ac

Ans. (c) Tc & Re belongs to same group. The atomic radius of elements of second transition series is similar to that of third transition elements, due to poor shielding of f-orbitals.(MnO_4^-)
The green manganate is paramagnetic with one unpaired electron but the permanganate is diamagnetic.

Physical Properties

Density: Increases with increase in atomic number.

Electropositive Character: Highly electropositive due to their low Ionisation energy.

Ionisation Energy: Low ionisation energies, IE_1 & IE_2 are equal to calcium ionisation enthalpy

- **Low IE_3**
  - $(f^0)La$
  - $(f^7)Gd$
  - $(f^{14})Lu$
- **Magnetic Behaviour**
  - M^{3+} ions are paramagnetic
  - Ions
    - La^{3+}, Ce^{+4} f^0
    - Yb^{2+}, Lu^{3+} f^{14}
    - Diamagnetic

Colour

- The colour is due to f-f transitions since they have partly filled f-orbitals.

Radioactivity

- All Lanthanides except promethium and samarium are non-radioactive

Oxidation States

- Common oxidation state + 3.
- +3 oxidations state stable in La, Gd and Lu.
- +3 oxidation state in Lanthanum, Gadolinium and Lutetium are especially stable because +3 ions of these elements have an empty (f^0), a halffilled [f^7] and completely filled (f^{14})] configurations.
- Al though the formation of **Eu^{2+}** is favoured by the extra stability of its **f^7 configurations**, but Eu^{2+} is a **strong reducing agent** and changes to Eu^{3+} in its reactions. Samarium (Sm) also shows +2 and +3 oxidation states.

> The E° Value for Ce^{4+}/Ce^{3+} is +1.74 V which suggests that it can oxidise water. However, the reaction rate is very slow and hence Ce(IV) is a **good analytical reagent**.

SCAN (Special Cases Asked in NEET)

> The formation of Ce^{IV} is favoured by its noble gas configuration.

Q. Although +3 is the characteristic oxidation state for lanthanoids but cerium also shows +4 oxidation state because:

a. It has variable ionisation enthalpy

b. It has a tendency to attain noble gas configuration

c. It has a tendency to attain f^0 configuration

d. It resembles Pb^{4+}

Ans. (b,c) Electronic configuration of $_{58}Ce = 54[Xe]4f^2 5d^0 6s^2$.

Therefore, electronic configuration of $Ce^{4+} = {}_{54}[Xe]4f^0$.

Thus, it has a tendency to attain noble gas configuration and attain f^0 configuration.

Chemical Reactivity of Lanthanides

- Earlier members of the series are quite reactive similar to calcium but, with increasing atomic number, they **behave more like Al**.
- Size of M^{+3} ion ↓ the covalent character in M-OH bond and their basic strength in their hydroxides ↓ gradually from $La(OH)_3$ to $Lu(OH)_3$ due to Lanthanide contraction

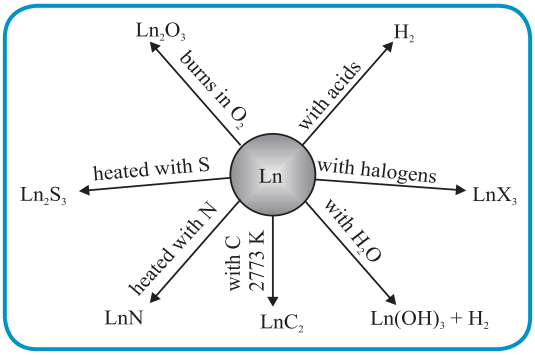


Fig.: Chemical reactions of the lanthanoids

Actinoids

- General electronic configuration → $5f^{1-4} 6d^{0-1} 7s^2$
- Ac_{89} to $Law_{(103)}$

Properties

Atomic Size

Decrease in size of M^{3+} across series due to **actinoid contraction** (poor shielding by 5f electron)

Oxidation States

> Large number of O.S due to comparable energy of 5f, 6d and 7s energy level.

- Common **+3** O.S
- Also exhibit +4, +5, +6, +7 O.S
- After uranium → elements knows as **transuranic element**

NEET REPLICA

1. Which of the following pair will have effective magnetic moment equal?

a. Cr^{+3} and Mn^{+2}
b. Cr^{+2} and Fe^{+2}
c. V^{+2} and Sc^{+3}
d. Ti^{+2} and V^{+2}

2. The number of d-electrons in Fe^{2+} (at no. of Fe = 2r) is not equal to that of the

a. p – electrons in Ne (at. no. = 10)
b. s – electrons in Mg (at. no. = 12)
c. d – electrons in Fe
d. p – electrons in Cl^{-} (at. no. of Cl = 17)

3. The stability of a particular oxidation state of a metal in aqueous solutions is determined by:

a. Enthalpy of sublimation
b. Ionisation enthalpy
c. Enthalpy of hydration
d. All of these

4. Which oxide of Mn is acidic in nature?

a. MnO
b. Mn_2O_7
c. Mn_2O_3
d. MnO_2

5. Which of the following element exhibits maximum oxidation state?

a. Mn
b. Co
c. Fe
d. Zn

6. Which one of the following transition metals ions is colourless in aqueous solution?

a. Ti^{4+}
b. V^{4+}
c. Mn^{2+}
d. Fe^{3+}

7. Which of the following has maximum unpaired d-electrons?

a. Zn^{2+}
b. Fe^{2+}
c. Ni^{2+}
d. Cu^{+}

8. The spin only magnetic moment of Fe^{3+} ion (in BM) is approximately:

a. 4
b. 7
c. 5
d. 6

9. Transition metal show paramagnetic behaviour. This is because of their:

a. High lattice energy
b. Variable oxidation state
c. Characteristic configuration
d. Unpaired electrons

10. The magnetic moment of a divalent ion in aqueous solution with atomic number 25 is:

a. 5.9 BM
b. 2.9 BM
c. 6.9 BM
d. 9.9 BM

11. The correct order of number of unpaired electron is:

a. $Cu^{2+} > Ni^{2+} > Cr^{3+} > Fe^{3+}$
b. $Ni^{2+} > Cu^{2+} > Fe^{3+} > Cr^{3+}$
c. $Fe^{3+} > Cr^{3+} > Ni^{2+} > Cu^{2+}$
d. $Cr^{3+} > Fe^{3+} > Ni^{2+} > Cu^{2+}$

12. Which of the following pairs magnetic moment is same?

a. $MnCl_2$, $CuSO_4$
b. $CuCl_2$, $TiCl_3$
c. TiO_2 , $CuSO_4$
d. $TiCl_3$, $NiCl_2$

13. Electronic configuration of a transition element X in +3 oxidation state is [Ar] $3d^5$. What is its atomic number?

a. 25
b. 26
c. 27
d. 24

14. The correct order of decreasing second ionization enthalpy of Ti (22), V(23), Cr(24), and Mn (25) is:

a. Ti > V > Cr > Mn
b. Cr > Mn > V > Ti
c. V > Mn > Cr > Ti
d. Mn > Cr > Ti > V

15. When calomel reacts with NH_4 OH, we get

a. $HgNH_2Cl$
b. $NH_2 – Hg – Hg – Cl$
c. Hg_2O
d. HgO

16. Which one of the following oxides is ionic?

a. MnO
c. Mn_2O_7
c. CrO_3
d. MnO

17. $KMnO_4$ in basic medium is reduced to

a. K_2MnO_4
d. MnO_2
c. $Mn(OH)_2$
d. Mn^{2+}

18. Which of the following statement is not true?

a. Colourless compounds of transition elements are paramagnetic.
b. Coloured compounds of transition elements are paramagnetic.
c. Colourless compounds of transition elements are diamagnetic.
d. Transition elements form the complex compounds.

19. Which of the following has diamagnetic character?

a. $[NiCl_4]^{2-}$ b. $[CoF_6]^{3-}$

c. $[Fe(H_2O_6)]^{2+}$ d. $[Ni(CN)_4]^{2-}$

20. 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

21. When $KMnO_4$ reacts with acidified $FeSO_4$:

a. Only $FeSO_4$ is oxidised

b. Only $KMnO_4$ is oxidised

c. $FeSO_4$ is oxidized and $KMnO_4$ is reduced

d. $KMnO_4$ and $FeSO_4$ oxidised

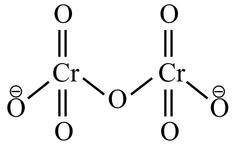
22. Acidified $K_2Cr_2O_7$ solution turns green when Na_2SO_3 is added to it. This is due to the formation of:

a. $CrSO_4$ b. $Cr_2\ (SO_4)_3$

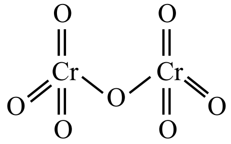
c. CrO_4^{2-} d. $Cr(SO_3)_3$

23. Identify the correct structure of dichromate ion:

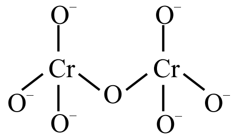
a.



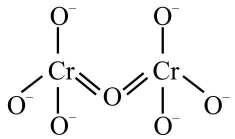
b.



c.



d.



24. The electronic configuration of cerium is:

a. $[Xe]4\ f^0 5d^1 6s^2$ b. $[Xe]4\ f^1 5d^1 6s^2$

c. $[Xe]4\ f^2 5d^0 6s^2$ d. Both (b) and (c)

25. Which of the following is not the configuration of lanthanoid?

a. $[Xe]4\ f^{10}.6s^2$ b. $[Xe]4\ f^1 5d^1.6s^2$

c. $[Xe]4\ f^{14} 5d^{10} 6s^1$ d. $[Xe]4\ f^{14} 5d^1 6s^2$

26. Zr and Hf have almost equal atomic and ionic radii because of:

a. Diagonal relationship

b. Lanthanoid Contraction

c. Actinoid contraction

d. Belong to the same group

27. Gd (64) gives an oxidation state of only +3 because:

a. It contains 3 unpaired electrons

b. In +3 oxidation state it has unstable configuration

c. In +3 oxidation state it has stable configuration

d. There are 3 electrons present in 4f in +3 oxidation state

28. Across the lanthanide series, the basicity of the lanthanoide hydroxides:

a. Increases

b. Decreases

c. First increases and then decreases

d. First decreases and then increases

29. $4K_2Cr_2O_7 \xrightarrow{\text{heat}} 4K_2CrO_4 + 3O_2 + X$. In the above reaction X is

a. CrO_3 b. Cr_2O_7

c. Cr_2O_3 d. CrO_5

30. Arrange Ce^{+3}, La^{+3}, Pm^{+3} and Yb^{+3} in increasing order of their ionic radii

a. $Yb^{+3} < Pm^{+3} < Ce^{+3} < La^{+3}$

b. $Ce^{+3} < Yb^{+3} < Pm^{+3} < La^{+3}$

c. $Yb^{+3} < Pm^{+3} < La^{+3} < Ce^{+3}$

d. $Pm^{+3} < La^{+3} < Ce^{+3} < Yb^{+3}$

31. When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because:

a. CO_2 is formed as the product

b. Reaction is exothermic

c. MnO_4^- catalyses the reaction

d. Mn^{2+} acts as autocatalyst

32. Gadolinium belongs to 4f series. Its atomic number is 64. Which of the following is the correct electronic configuration of gadolinium?

a. $[Xe]4f^7 5d^1 6s^2$ b. $[Xe]4f^6\ 5d^2\ 6s^2$

c. $[Xe]4f^8\ 6d^2$ d. $[Xe]4f^9\ 5s^1$

33. Interstitial compounds are formed when small atoms are trapped inside the crystal lattice of metals. Which of the following is not the characteristic property of interstitial compounds?

a. They have high melting points in comparison to pure metals

b. They are very hard

c. They retain metallic conductivity

d. The are chemically very reactive

34. Which of the following statements is not correct?

a. Copper liberates hydrogen from acids

b. In its higher oxidation states, manganese forms stable compounds with oxygen and fluorine

c. Mn^{3+} and Co^{3+} are oxidising agents in aqueous solution are reducing agents in aqueous solution

d. Ti^{2+} and Cr^{2+} are reducing agents in aqueous solution

35. Although Zirconium belongs to 4d transition series and Hafniun to 5d transition series even then they show similar physical and chemical properties because:

a. Both belong to d-block

b. Both have same number of electrons

c. Both have similar atomic radius

d. Both belong to the same group of the Periodic Table

36. In the form of dichromate, Cr(VI) is a strong oxidising agent in acidic medium but Mo(VI) in MoO_3 and W(VI) in WO_3 are not because:

a. Cr (VI) is more stable than Mo(VI) and W(VI)

b. Mo (VI) and W (VI) are more stable than Cr(VI)

c. Higher oxidation states of heavier members of group 6 of transition series are more stable

d. Lower oxidation states of heavier members of group-6 of transition series are more stable

37. General electronic configuration of actinoids is $(n-2)\,f^{1-14}\,(n-1)\,d^{0-2}\,ns^2$. Which of the following actinoids have one electron in 6d orbital?

a. U (Atomic numbr. 92)

b. Np (Atomic number. 93)

c. Pu (Atomic number. 94)

d. Am (Atomic number. 95)

EXPLANATIONS

1. (b) Cr^{+2} and Fe^{+2}

Cr^{+2} – $3d^4$ 4 unpaired electrons

Fe^{+2} – $3d^6$ 4 unpaired electrons

2. (d) p-electrons in Cl^- (atomic no. of Cl = 17)

$Cl^- \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

$Fe^{2+} \rightarrow 1s^2\ 2s^2\ 2p^2\ 3s^2\ 3p^6\ 3d^6$

In Fe^{+2} total number of de^- = 6 which is not equal to pe^- in Cl^- = 12.

3. (d) (Based on Facts)

4. (b) Mn_2O_7

5. (a)

6. (a) $Ti^{4+} = (22 - 4 = 18) \quad = [Ar]\ 3d^0$

$V^{4+} = (23 - 4 = 19) \quad = [\ Ar\ ]\ 3d^1$

$Mn^{2+} = (35 - 2 = 23) \quad = [Ar]\ 3d^5$

$Fe^{3+} = (26 - 3 = 23) \quad = [Ar]\ 3d^5$

$\therefore$ it is colourless in nature so $\because$ Ti is not having any unpaired electron.

7. (b) $Zn^{2+} = 3d^{10}$ = no unpaired electron

$Ni^{2+} = 3d^8$ = 2 unpaired electrons

$Fe^{2+} = 3d^6$ = 4 unpaired electrons

$Cu^+ = 3d^{10}$ = no unpaired electron

8. (d) $Fe = 26 = [\ Ar]\ 3d^6\ 4s^2$

$Fe^{3+} = [Ar]\ 3d^5$

$\therefore\ n = 5$

$$\mu = \sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{5(7)} = \sqrt{35}$$

$$= \sqrt{35} = 5.91 \approx 6\ BM$$

9. (d) Paramagnetic behaviour of transition metals is due to presence of unpaired electrons.

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

$25 = [Ar]\ 3d^5 = \begin{array}{|c|c|c|c|c|}\hline \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \hline\end{array}$

$\therefore\ n = 5$

$$\mu = \sqrt{5(5+2)} = \sqrt{5(7)} = \sqrt{35} = 5.9BM$$

11. (c) $Fe^{+3} = 3d^5 = \begin{array}{|c|c|c|c|c|}\hline \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \hline\end{array} = 5$

$Cr^{3+} = 3d^3 = \begin{array}{|c|c|c|c|c|}\hline \uparrow & \uparrow & \uparrow & & \\ \hline\end{array} = 3$

$Ni^{2+} = 3d^8 = \begin{array}{|c|c|c|c|c|}\hline \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow & \uparrow \\ \hline\end{array} = 2$

$Cr^{2+} = 3d^9 = \begin{array}{|c|c|c|c|c|}\hline \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow \\ \hline\end{array} = 1$

12. (b) a. $MnCl_2 = Mn^{2+} = [Ar]\ 3d^5 = \begin{array}{|c|c|c|c|c|}\hline \uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\ \hline\end{array} = 5$

$CuSO_4 = Cu^{2+} = [Ar]\ 3d^9 = \begin{array}{|c|c|c|c|c|}\hline \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow \\ \hline\end{array} = 1$

b. $CuCl_2 = Cu^{2+}\ [Ar]\ 3d^9\ 4s^0 = \begin{array}{|c|c|c|c|c|}\hline \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow\downarrow & \uparrow \\ \hline\end{array} = 1$

$TiCl_3 = Ti^{3+} = [Ar]\ 3d^1,\ 4s^0 = \begin{array}{|c|c|c|c|c|}\hline \uparrow & & & & \\ \hline\end{array} = 1$

$\therefore$ $CuCl_2$ and $TiCl_3$ has same number of unpaired electrons.

13. (b) The electronic configuration of X^{3+} is $[Ar]\ 3d^5$

$\therefore$ Atomic number of x = 18 + 5 + 3 = 26

14. (b) $Cr(24) \longrightarrow [Ar]\ 3d^5\ 4s^1$

Cr has higher second ionisation enthalpy as after removing one electron from Cr, the resulting configuration, i.e., $[Ar]\ 3d^5$ becomes more stable.

15. (a) $$\underset{\text{Calomel}}{Hg_2Cl_2} + 2NH_4OH \rightarrow NH_4Cl + 2H_2O + Hg + Hg(NH_2)Cl$$

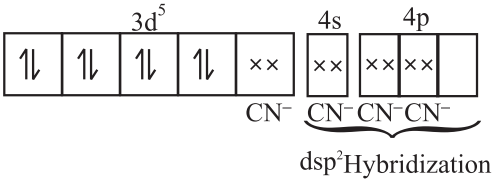
16. (a) MnO is ionic due to lower oxidation state.

17. (b) $KMnO_4$ is first reduced to manganate and then to insoluble manganese dioxide. Colour changes first from purple to green and finally becomes colourless.

18. (a) Colourless compounds are those which have no unpaired electrons and paramagnetic substance do have unpaired electrons. Therefore paramagnetic substance possess colour.

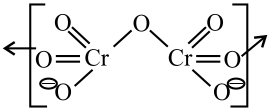
19. (d) Ni in presence of CN^-

$[Ni^{2+}$ in presence of $CN^- = [Ar]$



As $[Ni(CN)_4]^{2-}$ has no unpaired electron. It is diamagnetic.

20. (b) Resonance occurs



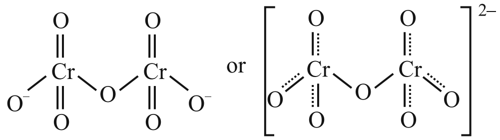
Resonance occurs

21. (c)

22. (b) $K_2Cr_2O_7 + 3Na_2SO_3 + 4H_2SO_4$

$\rightarrow 3Na_2\ SO_4 + K_2SO_4 + 4H_2O + Cr_2(SO_4)_3$

23. (a)



24. (b)

25. (c)

26. (b) The atomic and ionic radii of Zr and Hf are equal in size due to lanthanoid contraction.

27. (c) In + 3 oxidation state its configuration is $4f^7$, $5d^0$, $6s^0$, which is stable as per the rule of extra stability.

28. (b) Across lanthanoide series, due to lanthanoid contraction, size of cation decreases, increase covalent character and decrease ionic character. So; basicity of hydroxides decreases.

29. (c) Potassium dichromate, on heating gives oxygen and chromic oxide (Cr_2O_3).

30. (a) Due to Lanthanoid contraction order will be

$Yb^{+3} < Pm^{3+} < Ce^{+3} < La^{3+}$

31. (d) When $KMnO_4$ solution is added to oxalic acid solution, the decolourisation is slow in the beginning but becomes instantaneous after some time because Mn^{2+} acts as autocatalyst.

Reduction half

$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$

Oxidation half

$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-] \times 2$

Overall equation

$2MnO_4^- + 16H^+ + 5C_2O_4^{2-} \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

End point of this reaction Colourless to light pink

32. (a) Gadolinium belongs to 4f series and has atomic number 64. The correct electronic configuration of gadolinium is

${}_{64}Gd = {}_{54}[Xe]4f^7 5d^1 6s^2$

It has extra stability due to half-filled 4f subshell.

33. (d) When small atoms are trapped inside the crystal lattice of metals interstitial compounds are formed. Some of their important characteristics are as follows

(i) They are very hard and rigid.

(ii) They have high melting point which are higher than those of the pure metals.

(iii) They show conductivity like that of the pure metal.

(iv) They acquire chemical inertness.

34. (a) Copper does not liberate H_2 from acids as Copper lies below hydrogen in the electrochemical series. Therefore, option (a) is not correct. Other three options (b, c, d) are correct.

35. (c) Due to lanthanoide contraction, Zr and Hf possess nearly same atomic and ionic radii *i.e.,* Zr = 160 pm and Hf = 159 pm, $Zr^{4+} = 79$ pm and $Hf^{4+} = 78$ pm. Therefore, these two elements show similar properties (physical and chemical properties).

36. (b,c) In *d*-block elements, for heavier elements. the higher oxidation states are more stable. Hence, Mo(VI) and W(VI) are more stable than Cr (VI). That why, Cr (VI) in the form of dichromate is a stronger oxidising agent in acidic medium whereas MoO_3 and WO_3 are not.

37. (a,b) General electronic configuration of actinoids is $(n-1)^{1-14}(n-1)d^{0-2}ns^2$. U and Np each have one electron in 6d orbital.

NEET Past 5 Year Questions

Oxidation States

1. Which of the following processes does not involve oxidation of iron? (2015)

a. Decolourisation of blue $CuSO_4$ solution by iron

b. Formation of $Fe(CO)_5$ from Fe

c. Liberation of H_2 from steam by iron at high temperature

d. Rusting of iron sheets

Magnetic Property of Transition Metals

2. Which one of the following ions exhibits d-d transition and paramagnetism as well? (2018)

a. CrO_4^{2-} b. $Cr_2O_7^{2-}$

c. MnO_4^{2-} d. MnO_4^{-}

3. Match the metal ions given in Column I with the spin magnetic moments of the ions given in Column II and assign the correct code: (2018)

Column I	Column II
A. Co^{3+}	1. $\sqrt{8}$ B.M
B. Cr^{3+}	2. $\sqrt{35}$ B.M
C. Fe^{3+}	3. $\sqrt{3}$ B.M
D. Ni^{2+}	4. $\sqrt{24}$ B.M
	5. $\sqrt{15}$ B.M

a. A-4 B-5 C-2 D-1

b. A-1 B-2 C-3 D-4

c. A-3 B-5 C-1 D-2

d. A-4 B-1 C-2 D-3

4. Magnetic moment 2.84 B.M. is given by: (Atomic numbers, Ni = 28, Ti = 22, Cr = 24, Co = 27) (2015)

a. Ti^{3+} b. Cr^{2+}

c. Co^{2+} d. Ni^{2+}

Potassium Dichromate ($K_2Cr_2O_7$)

5. Which one of the following statements is correct when SO_2 is passed through acidified $K_2Cr_2O_7$ solution? (2016-I)

a. SO_2 is reduced

b. Green $Cr_2(SO_4)_3$ is formed

c. The solution turns blue

d. The solution is decolourised

Potassium Permanganate ($KMnO_4$)

6. The manganate and permanganate ions are tetrahedral, due to: (2019)

a. The p-bonding involves overlap of p-orbitals of oxygen with d-orbitals of manganese

b. There is no p-bonding

c. The p-bonding involves overlap of p-orbitals of oxygen with p-orbitals of manganese

d. The p-bonding involves overlap of d-orbitals of oxygen with d-orbitals of manganese

7. Name the gas that can readily decolourise acidified $KMnO_4$ solution: (2017-Delhi)

a. P_2O_5 b. CO_2

c. SO_2 d. NO_2

Lanthanides Electronic Configuration

8. The electronic configurations of Eu (Atomic Number 63) Gd (Atomic Number 64) and Tb (Atomic Number 65) are: (2016 - I)

a. $[Xe]4f^7 6s^2$, $[Xe]4f^7 5d^1 6s^2$ and $[Xe]4f^9 6s^2$

b. $[Xe]4f^7 6s^2$, $[Xe]4f^8 6s^2$ and $[Xe]4f^8 5d^1 6s^2$

c. $[Xe]4f^6 5d^1 6s^2$, $[Xe]4f^7 5d^1 6s^2$ and $[Xe]4f^9 5d^1 6s^2$

d. $[Xe]4f^6 5d^1 6s^2$, $[Xe]4f^7 5d^1 6s^2$ and $[Xe]4f^8 5d^1 6s^2$

Lanthanides Atomic Sizes

9. Because of lanthanoid contraction, which of the following pairs of elements have nearly same atomic radii? (Numbers in the parenthesis are atomic numbers) (2015)

a. Zr (40) and Nb (41)
b. Zr (40) and Hf (72)
c. Zr (40) and Ta (73)
d. Ti (22) and Zr (40)

Actinoids Oxidation States

10. The reason for greater range of oxidation states in actinoids is attributed to: (2017-Delhi)

a. $4f$ and $5d$ levels being close in energies
b. The radioactive nature of actinoids
c. Actinoid contraction
d. $5f$, $6d$ and $7s$ levels having comparable energies

ANSWER KEY

1	2	3	4	5	6	7	8	9	10
b	c	a	d	b	a	c	a	b	d