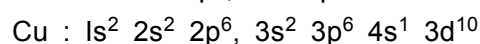
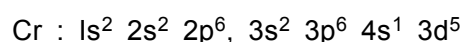


d – AND f – BLOCK ELEMENTS

Electronic Configuration of Transition Metal/Ions

The d-block element is called transition metal if it has partly filled d-orbitals in the ground state as well as in its oxidised state.

The general electronic configuration of transition metal is $(n-1) d^{1-10} ns^{1-2}$. Exceptions in electronic configuration are due to (a) very little energy difference between $(n-1) d$ and ns orbitals and (b) extra stability of half filled and completely filled orbitals in case of Cr and Cu in 3d series.



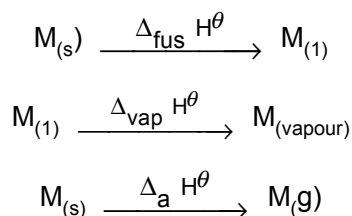
To write the electronic configuration of M^{n+} , the electrons are first removed from ns orbital and then from $(n-1) d$ orbitals of neutral atom (if required). For example, the electronic configuration of Cu^+ , Cu^{2+} and Cr^{3+} are respectively $3d^{10} 4s^0$, $3d^9 4s^0$ and $3d^3 4s^0$.

The following questions can be answered with the help of above.

- (i) Scandium ($Z = 21$) is a transition element but zinc ($Z = 30$) is not.
- (ii) Copper ($Z = 29$) and silver ($Z = 47$) both have fully filled d-orbitals i.e., $(n-1) d^{10}$. why are these elements are regarded as transition elements?
- (iii) Which of the d-block elements are not regarded as transition elements?

UNDERSTANDING $\Delta_{\text{fus}} H^\theta$, $\Delta_{\text{vap}} H^\theta$, AND $\Delta_a H^\theta$

In transition metals unpaired $(n-1)d$ electrons as well as ns electrons take part in interatomic bonding. Larger the number of unpaired $(n-1) d$ electrons, the stronger is the interatomic bonding and large amount of energy is required to overcome the interatomic interaction.



These enthalpies are related as

$$\Delta_{\text{fus}} H^\theta < \Delta_{\text{vap}} H^\theta < \Delta_a H^\theta$$

The following questions can be explained using the above reasoning.

- (i) Which has higher m.p.? V ($Z = 23$) or Cr ($Z = 24$) ?
- (ii) Explain why Fe ($Z = 26$) has higher m.p. than cobalt ($Z = 27$).

Metals of second (4d) and third (5d) transition series have greater enthalpies of atomisation than corresponding elements of first transition series on account of more frequent metal metal bonding due to greater spatial extension of 4d and 5d orbitals than 3d orbitals.

LANTHANOID CONTRACTION AND ITS CONSEQUENCE

The 4f orbitals screen the nuclear charge less effectively because they are large and diffused. The filling of 4f orbitals before 5d orbitals results in the gradual increase in effective nuclear charge resulting in a regular decrease in atomic and ionic radii. This phenomenon is called lanthanoid contraction. The corresponding members of second and third transition series have similar radii because the normal size increase down the group of d-block elements almost exactly balanced by the lanthanoid contraction.

This reasoning is applied in answering the following questions.

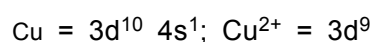
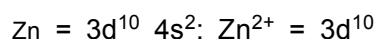
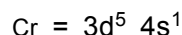
- (i) Elements in the following pairs have identical (similar) radii : Zr/Hf, Nb/Ta and Mo/W. Explain why?
- (ii) Why do Zr and Hf have very similar physical and chemical properties and occur together in the same mineral?

VARIATION IN IONISATION ENTHALPY

With the filling of $(n - 1)$ d orbitals effective nuclear charge increases resulting in the increase in first ionisation enthalpy. There are some irregular variations.

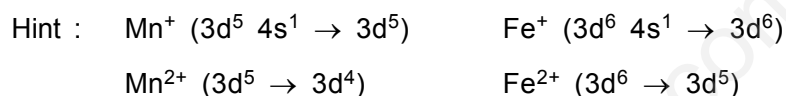
The first ionisation enthalpy of chromium is lower because the removal of one electron produces extra stable d^5 configuration and that of zinc is higher because the removal of electron takes place from fully filled 4s orbital.

Second ionization enthalpy of Zn ($\Delta_i H_2 = 1734$ kJ/mol) is lower than second ionization enthalpy of Cu (1958 kJ/mol). This is because removal of second electron in Zn produces stable d^{10} configuration while the removal of second electron in Cu disrupts the d^{10} configuration with a considerable loss in exchange energy to form less stable d^9 configuration.



Now the following questions can be accounted for :

- (i) Why is second ionization enthalpy of Cr ($Z = 24$) more than that Mn ($Z = 25$) (Hint. $\text{Cr}^+ (d^5 \rightarrow d^4)$, $\text{Mn}^+ (3d^5 4s^1 \rightarrow 3d^5)$).
- (ii) Which has more second ionisation enthalpy?
Cu ($Z = 29$) or Zn ($Z = 30$) (Hint. $\text{Cu}^+ (d^{10} \rightarrow d^9)$, $\text{Zn}^+ (3d^{10} 4s^1 \rightarrow 3d^{10})$).
- [iii] Second ionization enthalpy of Mn ($Z = 25$) is less than that of Fe ($Z=26$) but third ionisation enthalpy of Mn is more than that of Fe. Why?

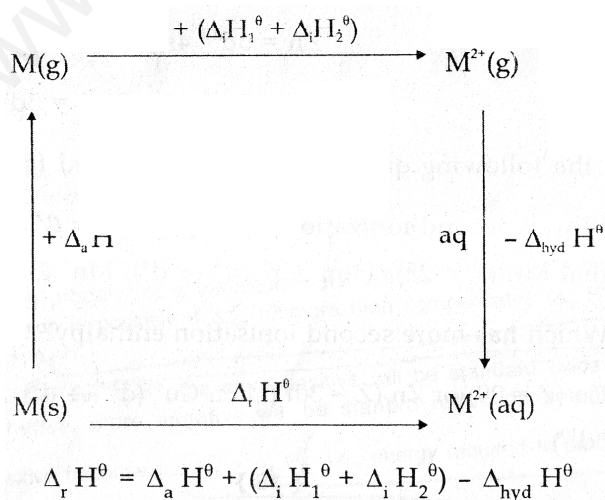


Relationship between E_{red}^\ominus and stability of various oxidation states.

Transition metals show variable oxidation states due to incompletely filled d-orbitals. These variable oxidation states differ from each other by unity, e.g., Mn (II), Mn (III), Mn (IV), Mn (V), Mn (VI) and Mn (VII). Scandium is the only transition element which exclusively shows the oxidation state of +3.

Standard Electrode potential $E_{\text{M}^{2+}/\text{M}}^\ominus$ can be calculated from the following parameters :

The reducing property of a transition metal will be higher if $\Delta_r H^\ominus$ has a large negative value which is possible if $\Delta_{\text{hyd}} H^\ominus$ more than compensates ($\Delta_a H^\ominus + \Delta_i H_1 + \Delta_i H_2$).



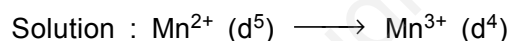
More negative the $\Delta_r H^\theta$, the more positive will be standard oxidation potential and hence, more negative will be standard reduction potential. $E^\ominus_{\text{Cu}^{2+}/\text{Cu}}$ is positive because $(\Delta_i H_1 + \Delta_i H_2)$ i.e., energy required to produce Cu^{2+} is not balanced by $\Delta_{\text{hyd}} H^\theta$ of Cu^{2+} .

Since the sum of $\Delta_i H_1$ and $\Delta_i H_2$ generally increases with the increase in the atomic number of the transition metal, therefore $E^\ominus_{\text{M}^{2+}/\text{M}}$ value becomes less and less negative.

$E^\ominus_{\text{M}^{2+}/\text{M}}$ values for Mn, Zn and Ni are more negative than expected trend. This is because $\Delta_i H_2$ for Mn and Zn produces stable d^5 configuration (Mn^{2+}) and d^{10} configuration (Zn^{2+}) are produced and therefore requirement of energy is less.

whereas $E^\ominus_{\text{Ni}^{2+}/\text{Ni}}$ is more negative due to highest negative $\Delta_{\text{hyd}} H^\theta$ which is -2121 kJ/mol for Ni^{2+} .

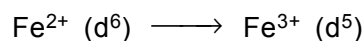
Example : Why is E^\ominus value for $\text{Mn}^{3+} / \text{Mn}^{2+}$ couple much more positive than for $\text{Cr}^{3+} / \text{Cr}^{2+}$ or $\text{Fe}^{3+} / \text{Fe}^{2+}$.



has much larger third ionisation energy due to disruption of extrastability of half filled d^5 configuration.

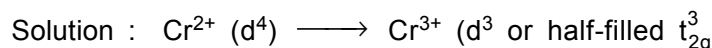


Cr^{3+} has half-filled t_{2g} level. Hence Cr^{2+} is oxidised easily to stable Cr^{3+} ion. Hence E^\ominus value is comparatively less.



Comparatively low value of E^\ominus is also due to extra stability of d^5 configuration of Fe^{3+} .

Example : Which is stronger reducing agent Cr^{2+} or Fe^{2+} and why?



In water medium $[\text{Cr} (\text{H}_2\text{O})_6]^{3+}$ has more CFSE than $[\text{Fe} (\text{H}_2\text{O})_6]^{3+}$. Hence Cr^{2+} is a stronger reducing agent.

Stability of Higher Oxidation States :

Higher oxidation states are shown by transition metals in fluorides, oxides, oxocations and oxoanions. The ability of fluorine to stabilise the highest oxidation state is due to either higher lattice energy as in case of CoF_3 or higher bond enthalpy terms for higher covalent compounds, e.g., VF_5 and CrF_6 .

Transition metals show highest oxidation state in oxides and oxocations and oxoanions, e.g., VO_4^+ and VO_4^- . The ability of oxygen to stabilise these high oxidation states exceeds that of fluorine due to its ability to form multiple bonds to metals.

The following questions can be explained using the above concepts.

- (i) All Cu (II) halides are known except the iodides. Why?

[Hint : $2\text{Cu}^{2+} + 4\text{I}^- \longrightarrow \text{Cu}_2\text{I}_2 + \text{I}_2$]

- (ii) Why do Cu (I) compounds undergo disproportionation in water?

[Hint : $\Delta_{\text{hyd}} H^\theta$ of Cu^{2+} more than compensates the $\Delta_1 H_2$ of copper]

- (iii) Highest fluoride of Mn is MnF_4 but the highest oxide is Mn_2O_7 .

- (iv) E^θ values of 3d series varies irregularly.

- (v) Why is Cr^{2+} is reducing and Mn^{3+} oxidising when both have d^4 configuration?

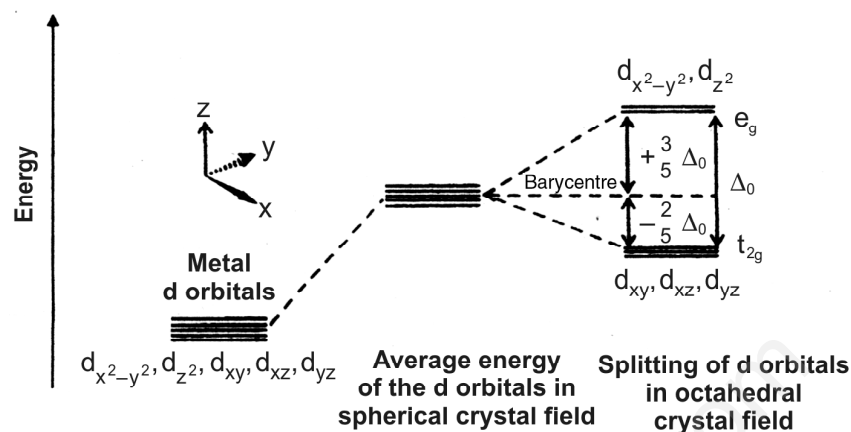
[Hint : $\text{Cr}^{2+} (d^4) \longrightarrow \text{Cr}^{2+} (t_{2g}^3; \text{half filled } t_{2g} \text{ level})$

$\text{Mn}^{3+} (d^4) + e^- \longrightarrow \text{Mn}^{2+} (d^5; \text{half filled d-level})$

- (vi) Why is highest oxidation state shown in oxocations and oxoanions?

Properties of Transition Elements

Transition metals with partly filled d-orbitals exhibit certain characteristic properties. For example they display a variety of oxidation states, form coloured ions and enter into complex formation. Transition metals and their compounds exhibit catalytic properties and are generally paramagnetic in nature.

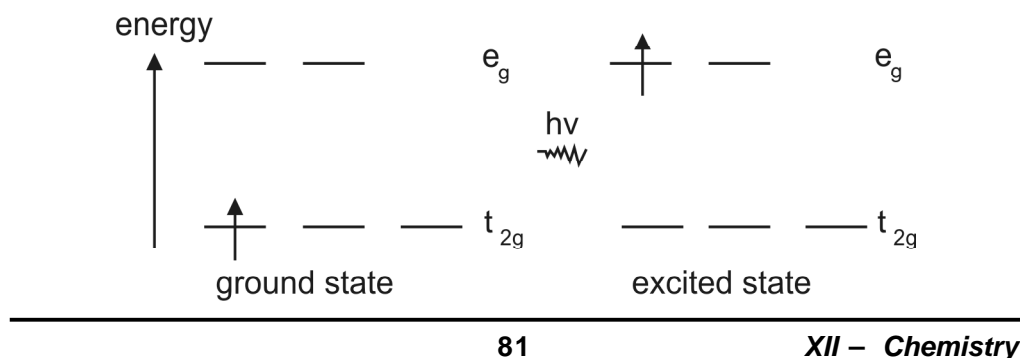
Crystal Field Theory :**d orbitals splitting in an octahedral crystal-field**

Calculation of CFSE : Each electron occupying t_{2g} orbital results in the lowering of energy by $-0.40 \Delta_0$ and each electron occupying the e_g orbital increases the energy by $+0.60 \Delta_0$. If x is the no. of electrons occupying t_{2g} orbitals and ' y ' is the no. of electrons occupying the e_g orbitals, then CFSE is given by

$$\begin{aligned} \text{CFSE} &= (-0.40 \Delta_0 x + 0.60 \Delta_0 y) \\ &= (-0.40 x + 0.60 y) \Delta_0 \end{aligned}$$

Formation of Coloured Ions : Degeneracy of d-orbitals is lifted in presence of the field of ligands approaching the central metal ion. For example, in the octahedral crystal field of ligands, the d-orbitals are split into two set of d-orbitals (i) t_{2g} orbitals of lower energy : these are d_{xy}, d_{yz}, d_{xz} and (ii) e_g orbitals of higher energy i.e., $d_{x^2-y^2}$ and d_{z^2} .

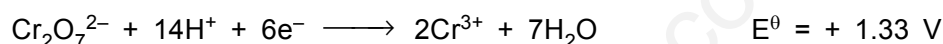
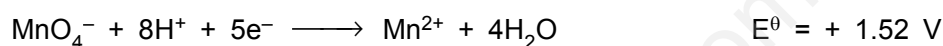
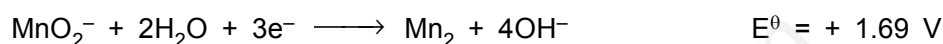
When visible light is incident on the octahedral transition metal complex, an electron is excited from t_{2g} level to e_g level. During this d-d transition, a characteristic wave length of visible light is absorbed and therefore transmitted light appears coloured. The colour of complex is complementary to the colour absorbed by the transition metal complex.



No d-d transition occurs if d-orbitals are empty or fully filled and therefore, such ions may be colourless.

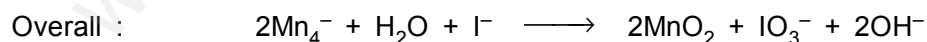
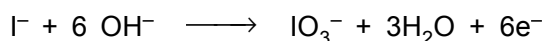
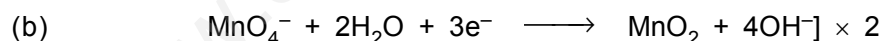
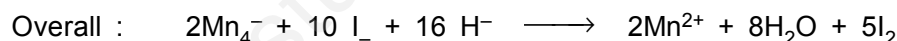
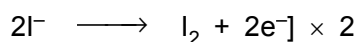
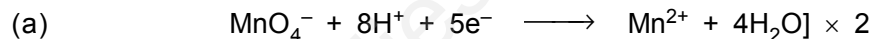
Exceptions : AgBr, AgI, have fully filled d-orbitals but are coloured due to transference of electron cloud from Br⁻ or I⁻ to Ag⁺ (d¹⁰) when white light is incident on AgBr / AgI. During this process also characteristic wave length of visible light is absorbed. Similarly MnO₄⁻ (purple), CrO₄²⁻ (yellow) and Cr₂O₇²⁻ (orange) are coloured due to charge transfer from oxide ions to the central metal ions although they have no d-electrons.

Comparison of oxidising powers of KMnO₄ and K₂Cr₂O₇



Electrode potential values shows that acidified KMnO₄ is a stronger oxidising agent than acidified K₂Cr₂O₇. But KMnO₄ in faint alkaline medium is a stronger oxidising agent than acidified KMnO₄.

For example, KMnO₄ oxidises KI to I₂ in acidic medium but to KIO₃ in alkaline medium.



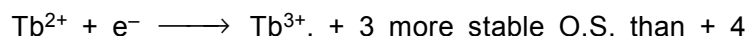
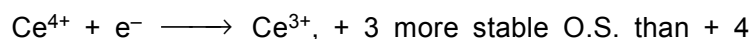
Following questions involving the oxidising actions of KMnO₄ and K₂Cr₂O₇ may be answered

- How do acidified KMnO₄ and acidified K₂Cr₂O₇ reacts separately with (a) SO₂, (b) H₂S (c) FeSO₄?
- Write the ionic equations of KMnO₄ (acidified) with (a) oxalate ion (b) Mohr salt (c) NO₂⁻ and (d) Iron (II) oxalate.

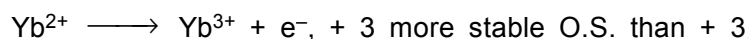
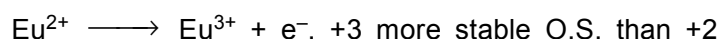
[Hint : (d) Both Fe²⁺ and C₂O₄²⁻ are oxidised to Fe³⁺ and CO₂ respectively.]

Oxidation States of Lanthanoids and Actinoids

The most common and most stable oxidation state of lanthanoids is +3. They also show oxidation states of +2, and +4 if the corresponding lanthanoid ions have extra stable $4f^0$, $4f^7$ and $4f^{14}$ configuration.



Hence Ce^{4+} and Tb^{4+} are strong oxidants.



Hence, Eu^{2+} and Yb^{2+} are strong reducing agents.

Actinoids also show most common O.S. of + 3 but it is not always most stable. Actinoids also show higher oxidation states, e.g., Th (+4), Pa (+5), U (+ 6) and Np (+ 7).

Example : La ($5d^1 6s^2$), Gd ($4f^7 5d^1 6s^2$) and Lu ($4f^{14} 5d^1 6s^2$) have abnormally low third ionisation enthalpies. Why?

Solution : La^{3+} , Gd^{3+} and Lu^{3+} have stable configurations $4f^0$, $4f^7$ and $4f^{14}$ respectively.

Answer the following question –

- Name the two members of lanthanoid series which show + 2 oxidation state
- Name the lanthanoid element which shows +4 O.S.

Participation of 5f electrons of actinoids in bonding.

5f orbitals in actinoids are not as buried as 4f orbitals in lanthanoids and hence 5f electrons can participate in bonding to a far greater extent.

There is a gradual decrease in the size of atoms or M^{3+} ions across the actinoid series. Since 5f orbitals are larger and more diffuse than 4f orbitals, their penetration towards the inner core of electrons is less than the penetration of 4f electrons. Hence 5f electrons screen the nuclear charge less effectively than 4f electrons in lanthanoids. Consequently effective nuclear charge in actinoids increases at faster rate as compared with lanthanoids. Hence actinoid contraction from element to element is more than the lanthanoid contraction.

The following question can be explained with the above reasoning :

Explain why Actinoid contraction from element to element is greater than lanthanoid contraction.

VERY SHORT ANSWER TYPE QUESTIONS**(1 - MARK QUESTIONS)**

1. Write the electronic configuration of Cr^{3+} ion (atomic number of Cr = 24)?
3. Explain $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is blue while ZnSO_4 and CuSO_4 are colourless?
4. Why is the third ionisation energy of Manganese ($Z = 25$) is unexpectedly high?
[Hint : The third electron is to be removed from stable configuration Mn^{2+} ($3d^5$). It requires higher energy.]
5. Which element among 3d- transition elements, exhibit the highest oxidation state?
[Hint : Mn (+7)]
6. Silver (Ag) has completely filled d-orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition element.
7. In 3d series ($\text{Sc} \rightarrow \text{Zn}$), the enthalpy of atomisation of Zn is low. Why?
[Hint : Poor interatomic bonding in zinc.]
8. Out of the following elements, identify the element which does not exhibit variable oxidation state?
Cr, Co, Zn.
9. The +3 oxidation state of lanthanum ($Z = 57$), gadolinium ($Z = 64$) and lutetium ($Z = 71$) are especially stable. Why?
10. Mention one consequence of Lanthanoid Contraction?
11. The first ionization enthalpies of 5d- series elements is higher than those of 3d and 4d series elements why?
[Hint : Increasing value of effective nuclear charge due to lanthanoid contraction.]
12. Why Mn^{2+} compounds are more stable than Fe^{2+} compounds towards oxidation to their +3 state?

14. Calculate the magnetic moment of Cu^{2+} ($Z = 29$) on the basis of "spin-only" formula.

[Hint : $\mu = \sqrt{n(n+2)}$ B.M.]

15. What is the shape of chromate ions?

[Hint : Tetrahedral]

16. Why does vanadium pentoxide act a catalyst?

[Hint : In V_2O_5 , Vanadium shows variable oxidation sates.]

17. What are interstitial compounds?

18. The transition metals and their compounds are known for their catalytic activity. Give two specific reasons to justify the statement.

19. Write the chemical equation for the reaction of thiosulphate ions and alkaline potassium permanganate.

[Hint : $8\text{MnO}_4^- + 3\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow 8\text{MnO}_2 + 2\text{OH}^- + 6\text{SO}_4^{2-}$].

20. Mention the name and formula of the ore from which potassium dichromate is prepared.

[Hint : FeCr_2O_4 (Chromite)].

21. Write the electronic configuration of Lu^{3+} (At. No. = 71).

22. What is the most common oxidation state of actinoids?

23. Write the names of the catalyst used in the :

- Manufacture of sulphuric acid by contact process.
- Manufacture of polythene.

24. Mention the name of the element among lanthanoids known to exhibit +4 oxidation state.

25. Name one ore each of manganese and chromium.

26. Why is Cd^{2+} ion white?

- *27. Draw the structure of dichromate anion.

- *28. Arrange the following monoxides of transition metals on the basis of decreasing basic character TiO , VO , CrO , FeO . [Hint : $\text{TiO} > \text{VO} > \text{CrO} > \text{FeO}$]

SHORT ANSWER TYPE QUESTIONS (2 - MARK QUESTIONS)

1. Write the chemical equation, when the yellow colour of aqueous solution of Na_2CrO_4 changes to orange on passing CO_2 gas?
2. The stability of Cu^{2+} (aq) is more than that of Cu^+ (aq). Why?
3. Indicate the steps in the preparation of
 - (a) $\text{K}_2\text{Cr}_2\text{O}_7$ from Chromite ore.
 - (b) KMnO_4 from Pyrolusite ore.
4. Give reason for : –
 - (a) In permanganate ions, all bonds formed between manganese and oxygen are covalent.
 - (b) Permanganate titrations in presence of hydrochloric acid are unsatisfactory.
5. Write complete chemical equations for
 - (a) oxidation of Fe^{2+} by $\text{Cr}_2\text{O}_7^{2-}$ in acidic medium
 - (b) oxidation of Mn^{2+} by MnO_4^- in neutral or faintly alkaline medium.
6.
 - (a) Why do transition metals show high melting points?
 - (b) Out of Fe and Cu, which one would exhibit higher melting point?

[Hint. (i) Strong interatomic bonding arising from the participation of ns and unpaired $(n - 1)$ d -electrons.
 (ii) Fe has higher melting point due to presence of more unpaired electrons $3d$ -orbitals.
7. Describe giving reason which one of the following pairs has the property indicated :
 - (a) Cr^{2+} or Fe^{2+} (stronger reducing agent).
 - (b) Co^{2+} or Ni^{2+} (lower magnetic moments).
8. Of the ions Co^{2+} , Sc^{3+} , Cr^{3+} which one will give colourless aqueous solution and how will each of them respond to magnetic field and why?
[Hint : Co^{2+} ($3d^7$); Cr^{3+} ($3d^4$); Sc^{3+} ($3d^0$)]
9. Complete the following equations :
 - (a) $\text{MnO}_2 + \text{KOH} + \text{O}_2 \longrightarrow$
 - (b) $\text{Na}_2\text{Cr}_2\text{O}_7 + \text{KCl} \longrightarrow$

10. Transition metals show low oxidation states with carbon monoxide.

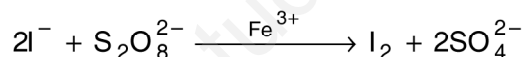
[Hint : CO is a π acceptor ligand capable of forming a π bond by accepting π electrons from the filled d-orbitals of transition metal and CO also form σ bond by donating σ electrons to transition metal orbital.

11. For the first row transition metals the enthalpy of atomisation value are :

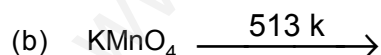
	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
$\Delta_a H^\circ / \text{kJ mol}^{-1}$	326	473	515	397	281	416	425	430	339	26

Assign reason for the following :

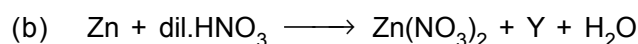
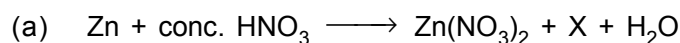
- Transition elements have higher values of enthalpies of atomisation.
 - The enthalpy of atomisation of zinc is the lowest in 3d - series.
12. Account for the following :
- Copper shows its inability to liberate hydrogen gas from the dilute acids.
 - Scandium ($Z = 21$) does not exhibit variable oxidation states.
13. Copper (I) compounds undergo disproportionation. Write the chemical equation for the reaction involved and give reason.
14. Iron (III) catalyses the reaction :



15. Complete the equations :



16. The following two reactions of MnO_3 with Zn are given.



Identify X and Y and write balanced equations.

[Hint : X is NO_2 and Y is N_2O].

17. Titanium shows magnetic moment of 1.73 BM in its compound. What is the oxidation number of Ti in the compound?
[Hint : O.N. of Ti = +3].
18. Account for the following :
(a) Transition metals and majority of their compounds act as good catalysts.
(b) From element to element, actinoid contraction is greater than lanthanoid contraction
19. Calculate the number of electrons transferred in each case when KMnO_4 acts as an oxidising agent to give
(i) MnO_2 (ii) Mn^{2+} (iii) $\text{Mn}(\text{OH})_3$ (iv) MnO_4^{2-} respectively.
[Hint : 3, 5, 4, 1].]
20. Calculate the number of moles of KMnO_4 that is needed to react completely with one mole of sulphite ion in acidic medium.
[Hint : $2/5$ moles].

SHORT ANSWER TYPE QUESTIONS (3 - MARK QUESTIONS)

1. Account for the following :
(a) $\text{La}(\text{OH})_3$ is more basic than $\text{Lu}(\text{OH})_3$
(b) Zn^{2+} salts are white.
(c) $\text{Cu}(\text{I})$ compounds are unstable in aqueous solution and undergo disproportionation.
2. Describe the oxidising action of potassium dichromate with following. Write ionic equations for its reaction with.
(a) Iodide ion (b) Iron (II) (c) H_2S .
3. (a) Deduce the number of 3d electrons in the following ions : Fe^{3+} , Cu^{2+} and Sc^{3+} .
(b) Why do transition metals form alloys.
(c) Write any two characteristics of interstitial compounds.
- *4. In the following reaction, Mn(VI) changes to Mn(VII) and Mn(IV) in acidic solution.



- (a) Explain why Mn(VI) changes to Mn(VII) and Mn(IV).
 (b) What special name is given to such type of reactions?
5. What happens when
 (a) thiosulphate ions react with alkaline KMnO_4 .
 (b) ferrous oxalate reacts with acidified KMnO_4 .
 (c) sulphurous acid reacts with acidified KMnO_4
 Write the chemical equations for the reactions involved.
7. Name the catalysts used in the
 (a) manufacture of ammonia by Haber's Process
 (b) oxidation of ethyne to ethanol
 (c) photographic industry.
- *8. Among TiCl_4 , VCl_3 and FeCl_2 which one will be drawn more strongly into a magnetic field and why?
[Hint : Among these halides the transition metal ion having maximum number of unpaired electrons will be drawn strongly into the magnetic field.
- | | | |
|-------------------------|---------------------------|-------------------------|
| $\text{Ti}^{4+} = 3d^0$ | no. of unpaired $e^- = 0$ | $\mu = 0$ |
| $\text{V}^{3+} = 3d^2$ | no. of unpaired $e^- = 2$ | $\mu = 2.76 \text{ BM}$ |
| $\text{Fe}^{2+} = 3d^6$ | no. of unpaired $e^- = 4$ | $\mu = 4.9 \text{ BM}$ |
9. Complete the following equations
 (a) $\text{MnO}_4^{2-} + \text{H}^+ \longrightarrow \dots\dots + \dots\dots + \dots\dots$
 (b) $\text{KMnO}_4 \xrightarrow{\text{Heat}}$
 (c) $\text{H}^+ + \text{MnO}_4^- + \text{Fe}^{2+} + \text{C}_2\text{O}_4^{2-} \longrightarrow$
10. How do you account for the following?
 (a) With the same d-orbital configuration (d^4), Cr^{2+} is a reducing agent while Mn^{3+} is an oxidising agent.
 (b) The actinoids exhibit a larger number of oxidation states than the corresponding members in the lanthanoid series.
 (c) Most of transition metal ions exhibit characteristic colours in aqueous solutions.

LONG ANSWER TYPE QUESTIONS (5 - MARK QUESTIONS)

1. A green compound 'A' on fusion with NaOH in presence of air forms yellow compound 'B' which on acidification with dilute acid, gives orange solution of compound 'C'. The orange solution when reacted with equimolar ammonium salt gives compound 'D' which when heated liberates nitrogen gas and compound 'A'. Identify compounds A to D and write the chemical equation of the reactions involved.

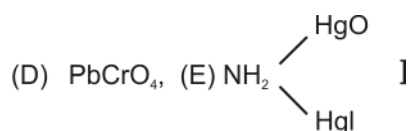
[Hint : 'A' = CrO_3 ; 'B' = Na_2CrO_4 ; 'C' = $\text{Na}_2\text{Cr}_2\text{O}_7$ 'D' = $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$]

2. Assign reasons for the following :
- There is no regular trends in E° values of M^{2+}/M systems in 3d series.
 - There is gradual decrease in the ionic radii of M^{2+} ion in 3d series.
 - Majority of transition metals form complexes.
 - Ce^{3+} can be easily oxidised to Ce^{4+}
 - Tantalum and palladium metals are used to electroplate coinage metals.
3. Account for the following :
- Actinoids display a variety of oxidation states.
 - Yb^{2+} behaves as a good reductant.
 - Cerium (iv) is a good analytical reagent.
 - Transition metal fluorides are ionic in nature while chlorides and bromides are covalent in nature.
 - Hydrochloric acid attacks all the actinoids.
- *4. Explain by giving suitable reason :
- Co(II) is stable in aqueous solution but in the presence of complexing agent it is readily oxidised.
 - Eu^{2+} , Yb^{2+} are good reductants whereas Tb^{4+} is an oxidant.
 - AgCl dissolves in ammonia solution
 - Out of Cr^{2+} or Fe^{2+} , which one is a stronger reducing agent?
 - The highest oxidation state is exhibited in oxoanions of a transition metal.

5. When a white crystalline compound A is heated with $K_2Cr_2O_7$ and conc. H_2SO_4 , a reddish brown gas B is evolved, which gives a yellow coloured solution C when passed through NaOH. On adding CH_3COOH and $(CH_3COO)_2Pb$ to solution C, a yellow coloured ppt. D is obtained. Also on heating A with NaOH and passing the evolved gas through K_2HgI_4 solution, a reddish brown precipitate E is formed.

Identify A, B, C, D and E and write the chemical equations for the reactions involved.

[Hint : (A) NH_4Cl , (B) CrO_2Cl_2 (g), (C) Na_2CrO_4



- *6. (a) Describe the preparation of potassium dichromate ($K_2Cr_2O_7$). Write the chemical equations of the reactions involved.
- (b) "The chromates and dichromates are interconvertible by the change in pH of medium." Why? Give chemical equations in favour of your answer.
7. Explain giving reasons :
- (a) Transition metals are less reactive than the alkali metals and alkaline earth metals.
- (b) $E^\ominus_{Cu^{2+}/Cu}$ has positive value
- (c) Elements in the middle of transition series have higher melting points.
- (d) The decrease in atomic size of transition elements in a series is very small.
8. (a) Compare the chemistry of the actinoids with that of lanthanoids with reference to—
- electronic configuration
 - oxidation states
 - chemical reactivity.

- (b) How would you account for the following :
- of the d^4 species, Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidising.
 - the lowest oxide of a transition metal is basic whereas highest is amphoteric or acidic.
9. (a) What is meant by disproportionation of an oxidation state. Give one example.
- (b) Explain why europium (II) is more stable than Ce(II)?
- [Hint : (a) When particular state becomes less stable relative to other oxidation states, one lower and one higher, it is said to undergo disproportionation, for example,
- $$3\overset{\text{VI}}{\text{MnO}}_4^{2-} + 4\overset{+}{\text{H}} \longrightarrow 2\overset{\text{VII}}{\text{MnO}}_4^- + \overset{\text{IV}}{\text{MnO}}_2 + 2\text{H}_2\text{O}$$
- (b) Eu (II) = $[\text{Xe}] 4f^7 5d^0$ (4f subshell is half filled)
 Ce (II) = $[\text{Xe}] 4f^1 5d^0$ (5d Subshell is empty and 4f subshell has only one electron which can be easily lost.)]
10. (a) For M^{2+}/M and $\text{M}^{3+}/\text{M}^{2+}$ systems, the E^\ominus values for some metals are as follows :
- $\text{Cr}^{2+}/\text{Cr} = -0.9\text{V}$ and $\text{Cr}^{3+}/\text{Cr}^{2+} = -0.4\text{V}$
 $\text{Mn}^{2+}/\text{Mn} = -1.2\text{V}$ and $\text{Mn}^{3+}/\text{Mn}^{2+} = +1.5\text{V}$
 $\text{Fe}^{2+}/\text{Fe} = -0.4\text{V}$ and $\text{Fe}^{3+}/\text{Fe}^{2+} = +0.8\text{V}$
- Use this data to comment upon :
- the stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} and Mn^{3+}
 - the ease with which iron can be oxidised as compared to a similar process for either chromium or manganese.
- (b) How is the variability in oxidation states of transition metals different from that of the non-transition metals? Illustrate with examples.