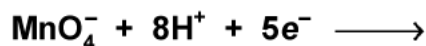
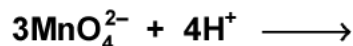


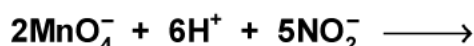
Q1. Complete the following equation:



Q2. Complete the following equation:



Q3. Complete the following equation:



Q4. Why Cd^{2+} salts are white?

Q5. Account for the following: Compounds of transition elements are often coloured.

Q6. Explain giving reasons: Transition metals and their compounds generally exhibit a paramagnetic behaviour.

Q7. Assign reason for the following: Copper (I) ion is not known in aqueous solution.

Q8. Why do transition elements show variable oxidation states?

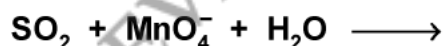
Q9. Zn^{2+} salts are white while Cu^{2+} salts are coloured. Why?

Q10. How would you account for the following: Transition metals form coloured compounds?

Q11. On what ground can you say that scandium ($Z = 21$) is a transition element but zinc ($Z = 30$).

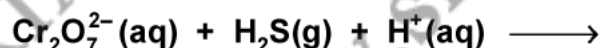
Q12. Account for the following: Zn is not considered as a transition element.

Q13. Complete the following chemical equation:



Q14. Give reason: Orange solution of potassium dichromate turns yellow adding sodium hydroxide to it.

Q15. Complete the following chemical equation:



Q16. Account for the following: Zr and Hf have almost similar atomic radii.

Q17. Name a member of the lanthanoid series which is well known to exhibit +2 oxidation state.

Q18. Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

Q19. Give reason for the following: The second and third transition series elements have almost similar atomic radii.

Q20. Give reason for the following: Among the lanthanoids, Ce (III) is easily oxidised to Ce (IV).

- Q21. Explain the following observations: La^{3+} ($Z = 57$) and Lu^{3+} ($Z = 71$) do not show any colour in solutions.
- Q22. What are different oxidation states exhibited by lanthanoids?
- Q23. What is meant by 'lanthanoid contraction'?
- Q24. Give reason: There is a gradual decrease in the size of atoms with increasing atomic number in the series of lanthanoids.
- Q25. How would you account for the following: Among lanthanoids, Ln (III) compounds are predominant. However, occasionally in solutions or in solid compounds, +2 and +4 ions are also obtained.
- Q26. How would you account for the following: Zr ($Z = 40$) and Hf ($Z = 72$) have almost identical radii.
- Q27. What are the different oxidation states exhibited by the lanthanoids?
- Q28. Explain the following observation: The members of the actinoid series exhibit a larger number of oxidation states than the corresponding members of the lanthanoid series.
- Q29. How would you account for the following: The actinoids exhibit a larger number of oxidation states than the corresponding members in the lanthanoid series.
- Q30. How would you account for the following: Lanthanoids form primarily +3 ions, while the actinoids usually have higher oxidation states in their compounds, +4 or even +6 being typical.
- Q31. Assign reasons for the following: From element to element actinoid contraction is greater than the lanthanoid contraction.
- Q32. Give reasons for the following: Actinoids exhibit a greater range of oxidation states than lanthanoids.
- Q33. How would you account for the following: Actinoid contraction is greater than lanthanoid contraction?
- Q34. Give reasons: Actinoids show irregularities in their electronic configurations.
- Q35. How would you account for the following: There is a greater range of oxidation states among the actinoids than among the lanthanoids.
- Q36. Explain giving reasons: The chemistry of actinoids is not as smooth as that of lanthanoids.
- Q37. Explain the following observation: Actinoids exhibit a much larger number of oxidation states than the lanthanoids.
- Q38. Write down the electronic configuration of:
- (a) Cr^{3+} (b) Cu^+ (c) Co^{2+} (d) Mn^{2+}
- Q39. Give reasons:
- (a) Mn shows the highest oxidation state of +7 with oxygen but with fluorine it shows the highest oxidation state of +4.
- (b) Transition metals show variable oxidation states.
- Q40. Why do transition elements show variable oxidation states? In 3d series (Sc to Zn), which element shows the maximum number of oxidation states and why?

Q41. Account for the following:

- (a) Transition metals show variable oxidation states.
- (b) Cu^+ ion is unstable in aqueous solution.

Q42. How would you account for the following:

- (a) Highest fluoride of Mn is MnF_4 whereas the highest oxide is Mn_2O_7 .
- (b) Transition metals and their compounds show catalytic properties.

Q43. Assign a reason for each of the following observations:

- (a) The transition metals (with the exception of Zn, Cd and Hg) are hard and have high melting and boiling points.
- (b) The ionisation enthalpies (first and second) in the first series of the transition elements are found to vary irregularly.

Q44. (a) Write two characteristic of the transition elements.

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

Q45. Account for the following:

- (a) Mn^{2+} is more stable than Fe^{2+} towards oxidation to +3 state.
- (b) The enthalpy of atomization is lowest for Zn in 3d series of the transition elements.

Q46. What is meant by disproportionation? Give an example of a disproportionation reaction in aqueous solution.

Q47. Give reasons for the following:

- (a) Transition metals exhibit a wide range oxidation states.
- (b) Cobalt(II) is very stable in aqueous solutions but gets easily oxidised in the presence of strong ligands.

Q48. Assign a reason for the following:

- (a) Copper(I) ion is not known to exist in aqueous solutions.
- (b) Both O_2 and F_2 stabilize high oxidation states of transition metals but the ability of oxygen to do so exceeds that of fluorine.

Q49. How would you account for the following:

- (a) The $E_{\text{M}^{2+}/\text{M}}^\circ$ for copper is positive (+ 0.34 V). Copper is the only metal in theirst series of transition elements showing this behaviour.
- (b) The metallic radii of the third (5d) series of transition metals are nearly the same as those of the corresponding members of the second (4d) series.

Q50. How would you account for the following:

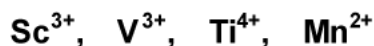
- (a) With the same d-orbital configuration (d^4) Cr^{2+} is a reducing agent while Mn^{3+} is an oxidising agent while Mn^{3+} is an oxidising agent.
- (b) Most of the transition metal ions exhibit characteristic colours in aqueous sloutions.

Q51. How would you account for the following?

- (a) Many of the transition elements are known to form interstitial compounds.
- (b) The metallic radii of the third (5d) series of transition metals are virtually the same as those of the corresponding group member of the second (4d) series.

Q52. (a) Which metal in the first transition series (3d-series) exhibits +1 oxidation state most frequently and why?

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



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

Q53. How would you account for the following?

- (a) Transition metals exhibit variable oxidation states.
- (b) Transition metals and their compounds act as catalyst.

Q54. Assign reasons for the following:

- (a) Transition metals and many of their compounds act as good catalysts.
- (b) Transition metals generally form coloured compounds.

Q55. Assign reasons for the following:

- (a) Cu(I) ion is not known to exist in aqueous solutions.
- (b) Transition metals are much harder than the alkali metals.

Q56. Account for the following:

- (a) Mn^{2+} compounds are more stable than Fe^{2+} compounds towards oxidation to their +3 state.
- (b) Cr^{2+} is reducing and Mn^{3+} oxidizing when both have d^4 configuration.

Q57. How is the variability in oxidation states of transition elements different from that of non-transition elements? Illustrate with examples.

Q58. Give reason:

- (a) Se (21) is a transition element but Ca (20) is not.
- (b) The Fe^{2+} is much more easily oxidised to Fe^{3+} than Mn^{2+} to Mn^{3+} .

Q59. Explain the following:

- (a) The enthalpies of atomization of transition metals are quite high.
- (b) The transition metals and many of their compounds act as good catalysis.

Q60. Explain the following observations:

- (a) With the same d -orbital configuration (d^4), Cr^{2+} is a reducing agent while Mn^{3+} is an oxidising agent.
- (b) There is hardly any increase in atomic size with increasing atomic numbers in a series of transition metals.

Q61. Explain the following observations:

- (a) Many of the transition elements are known to form interstitial compounds.
- (b) There is a general increase in density from titanium ($Z = 22$) to copper ($Z = 29$)

Q62. How would you account for the following:

- (a) Cr^{2+} is reducing in nature while with the same d -orbital configuration (d^4) Mn^{3+} is an oxidising agent.
- (b) In a transition series of metals, the metal which exhibits the greatest number of oxidation states occurs in the middle of the series.

Q63. Assign reasons for each of the following:

- (a) Transition metals generally form coloured compounds.
- (b) Manganese exhibits the highest oxidation state of +7 among the 3rd series of transition elements.

Q64. Explain the following observations:

- (a) Generally there is an increase in density of elements from titanium ($Z = 22$) to copper ($Z = 29$) in the first series of transition elements.
- (b) Transition elements and their compounds are generally found to be good catalysts in chemical reactions.

Q65. Explain giving a suitable reason for each of the following:

- (a) Transition metals and their compounds are generally found to be good catalysts.
- (b) Metal-metal bonding is more frequent for the 4 d and the 5 d series of transition metals than that for the 3 d series.

Q66. State reasons for the following:

- (a) Cu(I) ion is not stable in an aqueous solution.
- (b) Unlike Cr^{3+} , Mn^{2+} , Fe^{3+} and the subsequent other V^{2+} ions of the 3 d series of elements, the 4 d and the 5 d series metals generally do not form stable cationic species.

Q67. How would you account for the following:

- (a) Transition elements have high enthalpies of atomisation.
- (b) The transition metals and their compounds are found to be good catalysts in many processes?

Q68. How would you account for the following:

- (a) Many of the transition elements and their compounds can act as good catalysts.
- (b) The metallic radii of the third (5 d) series of transition elements are virtually the same as those of the corresponding members of the second series.

Q69. Account for the following:

- (a) The lowest oxide of a transition metal is basic, the highest is amphoteric/acidic.
- (b) Cobalt (II) is stable in aqueous solution but in the presence of complexing agents, it is easily oxidised.

Q70. Account for the following:

- (a) In the series Sc to Zn, the enthalpy of atomisation of zinc is the lowest.
- (b) The E° value for the $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is much more positive than that for $\text{Cr}^{3+}/\text{Cu}^{2+}$.

Q71. Account for the following:

- (a) Cu^+ ions are not stable in aqueous solution.
- (b) Most of the transition metal ions exhibit paramagnetic behaviour.

Q72. Explain the following observations:

- (a) Among the divalent cations in the first series of transition elements, manganese exhibits the maximum paramagnetism.
- (b) Cu^+ ion is not known in aqueous solutions.

Q73. When chromite ore FeCr_2O_4 is fused with NaOH in presence of air, a yellow coloured compound (A) is obtained which on acidification with dilute sulphuric acid gives a compound (B). Compound (B) on reaction with KCl forms a orange coloured crystalline compound (C).

- (a) Write the formulae of the compounds (A), (B) and (C).
- (b) Write one use of compound (C).

Q74. What is lanthanoid contraction? List any two consequences of lanthanoid contraction.

Q75. Write reference to structural variability and chemical reactivity, write the difference between lanthanoids and actinoids.

Q76. Why do actinoids show a wide range of oxidation states? Write one similarity between the chemistry of lanthanoids and actinoids.

Q77. Describe the preparation of potassium permanganate. How does the acidified permanganate solution react with oxalic acid? Write the ionic equations for the reaction.

Q78. Complete the following equations:

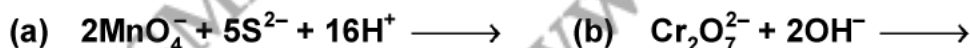


Q79. How do you prepare:



Q80. Describe the oxidising action of potassium dichromate and write the ionic equations for its with (a) an iodide (b) H_2S .

Q81. Complete the following equations:



Q82. Complete the following equations:



Q83. Complete the following chemical equations:



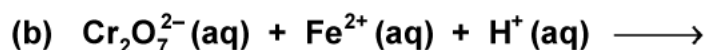
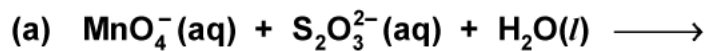
Q84. Complete the following equations:



Q85. Complete the following reactions in an aqueous medium:



Q86. Complete the following chemical equations:

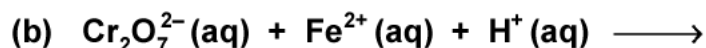
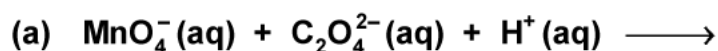


Q87. How does the acidified potassium permanganate solution react with (a) iron, (b) ions and (c) oxalic acid? Write the ionic equations for the reactions.

Q88. Complete the following chemical equations:

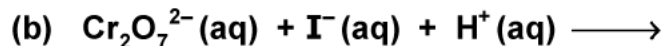
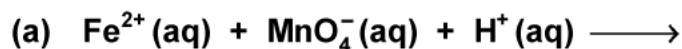


Q89. Complete the following chemical reaction equations:

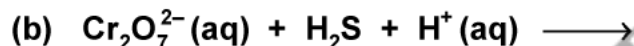
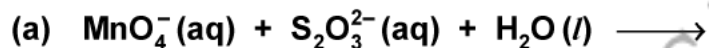


Q90. Describe the reactions involved in the preparation of $\text{K}_2\text{Cr}_2\text{O}_7$ from chromite ore.

Q91. Complete the following chemical reaction equations:



Q92. Complete the following chemical reaction equations:



Q93. Write complete chemical equations for

(a) Oxidation of Fe^{2+} by $\text{Cr}_2\text{O}_7^{2-}$ in acidic medium.

(b) Oxidation of $\text{S}_2\text{O}_3^{2-}$ by MnO_4^- in neutral aqueous medium.

Q94. (a) Describe how potassium dichromate is prepared from sodium chromate.

(b) The colour of potassium dichromate solution changes with the change of pH of the solution. Explain how.

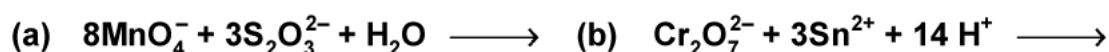
Q95. What is lanthanoid contraction? What are its two consequences?

Q96. Write the steps involved in the preparation of



Q97. What is lanthanoid contraction? Mention its main consequences.

Q98. Complete the following chemical equations:



Q99. What is lanthanoid contraction and what is it due to? Write two consequences of lanthanoid contraction.

Q100 Name an important alloy which contains some of the lanthanoid metals. Mention its two uses.

Q101 Write the electronic configuration of Ce^{3+} ion, and calculate the magnetic moment on the basis of 'spin-only' formula. (Atomic no. of Ce = 58).

Q102 Why is europium (II) more stable than cerium (II)?

Q103 What is meant by the term lanthanoid contraction? What is it due to and what consequences does it have on the chemistry of elements following lanthanoids in the periodic table?

Q104 Account for the following:

- Mn shows the highest oxidation state of +7 with oxygen but with fluorine, it shows the highest oxidation state of +4.
- Cr^{2+} is a strong reducing agent.
- Cu^{2+} salts are coloured, while Zn^{2+} salts are white.

Q105 Give reasons:

- d*-block elements exhibit more oxidation states than *f*-block elements.
- The enthalpies of atomization of the transition metals are high.
- The variation in oxidation states of transition metals is of different type from that of the non-transition metals.

Q106 What is lanthanoid contraction? What is its effect on the chemistry of the elements which follow the lanthanoids?

Q107 What is meant by disproportionation? Give an example of disproportionation reaction in aqueous solutions.

Q108

$E^\circ_{(M^{2+}/M)}$	Cr	Mn	Fe	Co	Ni	Cu
	-0.91	-1.18	-0.44	-0.28	-0.25	+0.34

Form the given data of E° values, answer the following questions:

- Why is $E^\circ_{(\text{Cu}^{2+}/\text{Cu})}$ value exceptionally positive?
- Why is $E^\circ_{(\text{Mn}^{2+}/\text{Mn})}$ value highly negative as compared to other elements?
- Which is a stronger reducing agent Cr^{2+} or Fe^{2+} ? Give reason.

Q109 How would you account for the following:

- Metal-metal bonding is more extensive in the 4*d* and 5*d* series of transition elements than the 3*d* series.
- Mn(III) undergoes disproportionation reaction easily.
- Co(II) is easily oxidised in the presence of strong ligands.

Q110 Explain the following:

- Copper (I) ion is not stable in an aqueous solution.
- With same (*d*⁴) configuration Cr(II) is reducing whereas Mn(III) is oxidising.
- Transition metals in general act as good catalysts.

Q111 How would you account for the following:

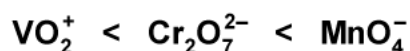
- The atomic radii of the metals of the third (5d) series of transition elements are virtually the same as those of the corresponding members of the second (4d) series.
- The E° value for the $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is much more positive than that for $\text{Cr}^{3+}/\text{Cr}^{2+}$ couple of $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple.
- The highest oxidation state of a metal is exhibited in its oxide or fluoride.

Q112 Account for the following:

- The transition metals and their compounds act as good catalysts.
- The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.
- A transition metal exhibits higher oxidation states in oxides and fluorides.

Q113 How would you account for the following:

- The oxidising power of oxoanions are in the order



- The third ionization enthalpy of manganese ($Z = 25$) is exceptionally high.
- Cr^{2+} is a stronger reducing agent than Fe^{2+} .

Q114 Give reason for the following:

- Transition metals have high enthalpies of atomisation.
- $\text{Fe}^{3+} | \text{Fe}^{2+}$ redox couple has less positive electrode potential than $\text{Mn}^{3+} | \text{Mn}^{2+}$ couple.
- Copper (I) has d^{10} configuration, while copper (II) has d^9 configuration, still copper (II) is more stable in aqueous solution than copper (I).

Q115 Give reasons for the following observations:

- Cu^+ ion is not stable in aqueous solution.
- Mn(II) ion shows maximum paramagnetic character amongst the bivalent ions of first transition series.
- Scandium (At. no. 21) salts are white.

Q116 Explain the following observations:

- In general the atomic radii of transition elements decrease with atomic number in a given series.
- The $E_{M^{2+}/M}^\circ$ for copper is positive (+0.34 V). It is only metal in the first series of transition elements showing this type of behaviour.
- The E° value for $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is much more positive than for $\text{Cr}^{3+}/\text{Cr}^{2+}$ or $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple.

Q117 Assign reasons for the following:

- The enthalpies of atomisation of transition elements are high.
- The transition metals and many of their compounds act as good catalyst.
- The E° value for the $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is much more positive than that for $\text{Cr}^{3+}/\text{Cr}^{2+}$.

Q118 Explain the following observations:

- Cu^+ ion is unstable in aqueous solutions.
- Although Co^{2+} ion appears to be stable, it is easily oxidised to Co^{3+} ion in the presence of a strong ligand.
- The $E_{\text{Mn}^{2+}/\text{Mn}}^\circ$ value for manganese is much more than expected from the trend for other elements in the series.

Q119 Describe the preparation of potassium permanganate from pyrochroite ore. Write balanced chemical equation for one reaction to show the oxidizing nature of potassium permanganate.

Q120 Complete the following chemical equations:

- $\text{Cr}_2\text{O}_7^{2-} + 6\text{Fe}^{2+} + 14\text{H}^+ \longrightarrow$
- $2\text{CrO}_4^{2-} + 2\text{H}^+ \longrightarrow$
- $3\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \longrightarrow$

Q121 Describe the preparation of potassium permanganate from pyrochroite ore. What happens when acidified potassium permanganate solution reacts with ferrous sulphate solution? Write balanced chemical equations.

Q122 Describe the preparation of potassium dichromate from chromite ore. What is the effect of change of pH on dichromate ion?

Q123 Describe the preparation of potassium permanganate from pyrolusite ore. Write the ionic equation for the reaction that takes place between acidified KMnO_4 solution and iron (II) ions.

Q124 Complete the following chemical equations:

- $\text{MnO}_4^- + \text{C}_2\text{O}_4^{2-} + \text{H}^+ \longrightarrow$
- $\text{KMnO}_4 \xrightarrow{\text{Heat}}$
- $\text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{S} + \text{H}^+ \longrightarrow$

Q125(a) Describe the commercial preparation of potassium permanganate from pyrochroite ore.

- Write ionic equation to represent the reaction of acidified KMnO_4 solution with oxalic acid.

Q126 Describe the oxidising actions of potassium dichromate and write the ionic equations for its reaction with (a) iodide, (b) iron (II) solution and (c) H_2S .

Q127 What is lanthanoid contraction? What are the consequences of lanthanoid contraction?

Q128 Compare the chemistry of the actinoids with that of lanthanoids with reference to

- electronic configuration. (b) oxidation states (c) chemical reactivity.

Q129 Give reasons for the following:

- Mn^{3+} is a good oxidising agent.
- $E_{\text{M}^{2+}/\text{M}}^\circ$ values are not regular for first row transition metals (3d-series).
- Although 'F' is more electronegative than 'O', the highest Mn fluoride is MnF_4 , whereas the highest oxide is Mn_2O_7 .

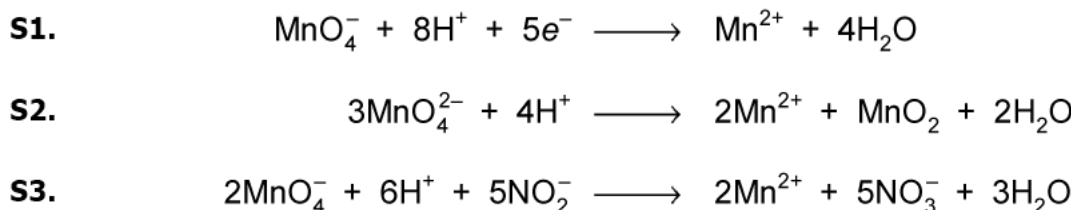
Q130The elements of 3d transition series are given as:

Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn

Answer the following:

- (a) Write the element which shows maximum number of oxidation states. Given reason.
- (b) Which element has the highest melting point?
- (c) Which element shows only +3 oxidation state?
- (d) Which element is a strong oxidising agent in +3 oxidation state and why?

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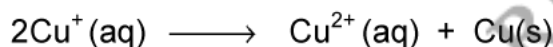
S4. It has completely filled d -orbitals (d^{10}).

S5. Due to presence of vacant d -orbitals and $d-d$ transitions, compounds of the transition metals are generally coloured.

When an electron from a lower energy d -orbital is excited to a higher energy d -orbital, the energy of excitation corresponds to the frequency which generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand.

S6. Transition metals and most of their compounds contain unpaired electrons in the $(n-1)d$ orbitals hence show paramagnetic behaviour.

S7. In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.



Cu^{2+} in aqueous solutions is more stable than Cu^+ ion because hydration enthalpy of Cu^{2+} is higher than that of Cu^+ . It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

S8. Transition elements can use their ns and $(n-1)d$ orbital electrons for bond formation therefore, they show variable oxidation states.

For example – Sc has $ns^2(n-1)d^1$ electronic configuration.

It utilizes two electrons from its ns subshell then its oxidation state = +2. When it utilizes both the electrons then its oxidation state = +3.

S9. Zn^{2+} ion has completely filled d -subshell and no $d-d$ transition is possible. So zinc salts are white.

Configuration of Cu^{2+} is $[\text{Ar}] 3d^9$. It has partly filled d -subshell and hence it is coloured due to $d-d$ transition.

S10. Due to presence of vacant d -orbitals and $d-d$ transitions, compounds of the transition metals are generally coloured.

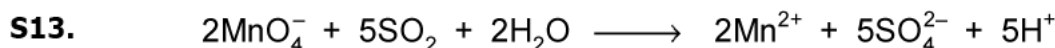
When an electron from a lower energy d -orbital is excited to a higher energy d -orbital, the energy of excitation corresponds to the frequency which generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand.

S11. On the basis of incompletely filled d -orbitals:

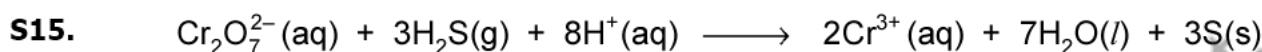
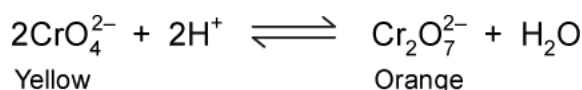
Scandium ($Z = 21$), atom has incompletely filled d -orbitals ($3d^1$) in its ground state, so it is regarded as transition element.

On the other hand zinc ($Z = 30$) atom has completely filled d -orbitals ($3d^{10}$) in its ground state as well as most common oxidation state of +2.

S12. In the electronic configuration of Zn, Cd and Hg the d -orbitals are completely filled in the ground state as well as in their common oxidation state. So, they are not regarded as transition metals.

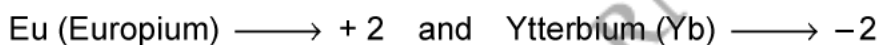


S14. When the pH of the solution of potassium dichromate is decreased, the colour of the solution changes from yellow to orange due to the conversion of CrO_4^{2-} ions into $\text{Cr}_2\text{O}_7^{2-}$ ions.



S16. Due to lanthanoid contraction the elements of $4d$ - and $5d$ -series have similar atomic radii e.g., Zr = 145 pm and Hf = 144 pm.

S17. Europium (Eu) is well known to exhibit +2 oxidation state due to its half-filled f orbital in +2 oxidation state.



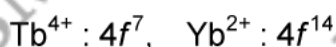
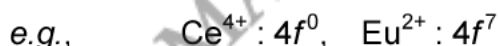
S18. Lanthanoids showing +4 oxidation state are Ce, and Tb.

S19. Due to lanthanoid contraction the elements of $4d$ - and $5d$ -series have similar atomic radii e.g., Zr = 145 pm and Hf = 144 pm.

S20. Ce(III) has outer configuration $4f^1 5d^0 6s^0$. It easily loses an electron to acquire the configuration $4f^0$ and forms Ce(IV). In fact this is the only (+IV) lanthanoid which exists in solution.

S21. Because they have empty $4f$ sub-shell.

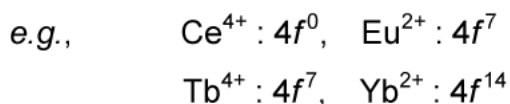
S22. Lanthanum and all the lanthanoids predominantly show +3 oxidation state. However, some of the lanthanoids also show +2 and +4 oxidation states in solution or in solid compounds. This irregularity arises mainly due to attainment of stable empty ($4f^0$), half-filled ($4f^7$) and fully filled ($4f^{14}$) sub shell.



S23. The steady decrease in the atomic and ionic radii (having the same charge) with increase in atomic number across the series from lanthanum to lutetium is known as lanthanoid contraction.

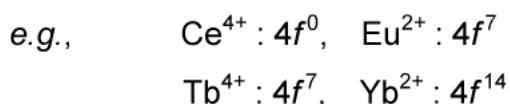
S24. As the atomic number increases, each succeeding element contains one more electron in the $4f$ orbital and one extra proton in the nucleus. The $4f$ electrons are rather ineffective in screening the outer electrons from the nucleus. As a result, there is gradual increase in the nuclear attraction for the outer electrons. Consequently, the atomic size gradually decreases. This is called lanthanoid contraction.

S25. Lanthanum and all the lanthanoids predominantly show +3 oxidation state. However, some of the lanthanoids also show +2 and +4 oxidation states in solution or in solid compounds. This irregularity arises mainly due to attainment of stable empty ($4f^0$), half-filled ($4f^7$) and fully filled ($4f^{14}$) sub shell.



S26. Due to lanthanoid contraction the elements of $4d$ - and $5d$ -series have similar atomic radii e.g., Zr = 145 pm and Hf = 144 pm.

S27. Lanthanum and all the lanthanoids predominantly show +3 oxidation state. However, some of the lanthanoids also show +2 and +4 oxidation states in solution or in solid compounds. This irregularity arises mainly due to attainment of stable empty ($4f^0$), half-filled ($4f^7$) and fully filled ($4f^{14}$) sub shell.



S28. The actinoid contraction is more than lanthanoid contraction because $5f$ -electrons are more poorly shielding than $4f$ -electrons.

S29. The actinoid contraction is more than lanthanoid contraction because $5f$ -electrons are more poorly shielding than $4f$ -electrons.

S30. The actinoid contraction is more than lanthanoid contraction because $5f$ -electrons are more poorly shielding than $4f$ -electrons.

S31. The actinoid contraction is more than lanthanoid contraction because of poor shielding by $5f$ -electrons is more than $4f$ -electrons.

S32. Actinoids exhibit greater range of oxidation states than lanthanoids. This is because there is less energy difference between $5f$ and $6d$ orbitals in actinoids than the energy difference between $4f$ and $5d$ orbitals in case of lanthanoids.

S33. The actinoid contraction is more than lanthanoid contraction because $5f$ -electrons are more poorly shielding than $4f$ -electrons.

S34. The irregularities in the electronic configurations of actinoids are due to extra stabilities of the f^0 , f^7 and f^{14} orbitals.

S35. The actinoid contraction is more than lanthanoid contraction because $5f$ -electrons are more poorly shielding than $4f$ -electrons.

S36. The chemistry of actinoids is not as smooth as lanthanoid because they show greater number of oxidation states due to comparable energies of $5f$, $6d$ and $7s$ orbitals.

S37. The actinoid contraction is more than lanthanoid contraction because $5f$ -electrons are more poorly shielding than $4f$ -electrons.

S38. (a) $\text{Cr}^{3+} = {}_{18}[\text{Ar}]3d^3$ (b) $\text{Cu}^+ = {}_{18}[\text{Ar}]3d^{10}$ (b) $\text{Co}^{2+} = {}_{18}[\text{Ar}]3d^7$ (b) $\text{Mn}^{2+} = {}_{18}[\text{Ar}]3d^5$

S39. (a) Manganese can form $p\pi - d\pi$ bond with oxygen by utilising $2p$ -orbital of oxygen and $3d$ -orbital of manganese due to which it can show highest oxidation state of +7. While with fluorine it cannot form such $p\pi - d\pi$ bond thus, it can show a maximum of +4 oxidation state.

(b) Transition elements can use their ns and $(n - 1) d$ orbital electrons for bond formation therefore, they show variable oxidation states.

For example – Sc has $ns^2(n - 1) d^1$ electronic configuration.

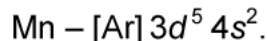
It utilizes two electrons from its ns subshell then its oxidation state = +2. When it utilizes both the electrons then its oxidation state = +3.

S40. Variation in oxidation state: Transition elements can use their ns and $(n - 1) d$ orbital electrons for bond formation. Therefore, they show variable oxidation state.

For example – Sc has $ns^2(n - 1) d^1$ electronic configuration.

It utilizes two electrons from its ns subshell then its oxidation state = +2. When it utilizes both the electrons then its oxidation state = +3.

Among the $3d$ series manganese (Mn) exhibits the largest number of oxidation states from +2 to +7 because it has maximum number of unpaired electrons.

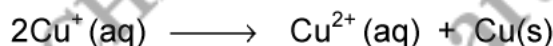


S41. (a) Transition elements can use their ns and $(n - 1) d$ orbital electrons for bond formation therefore, they show variable oxidation states.

For example – Sc has $ns^2(n - 1) d^1$ electronic configuration.

It utilizes two electrons from its ns subshell then its oxidation state = +2. When it utilizes both the electrons then its oxidation state = +3.

(b) In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.



Cu^{2+} in aqueous solutions is more stable than Cu^+ ion because hydration enthalpy of Cu^{2+} is higher than that of Cu^+ . It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

S42. (a) Manganese can form $p\pi - d\pi$ bond with oxygen by utilising $2p$ -orbital of oxygen and $3d$ -orbital of manganese due to which it can show highest oxidation state of +7. While with fluorine it cannot form such $p\pi - d\pi$ bond thus, it can show a maximum of +4 oxidation state.

(b) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysis involves the formation of bonds between reactant molecules and atoms at the surface of the catalyst.

S43. (a) As we move along transition metal series from left to right (*i.e.*, Ti to Cu), the atomic radii decrease due to increase in nuclear charge. Hence the atomic volume decreases. At the same time, atomic mass increases. Hence, the density from titanium (Ti) to copper (Cu) increases.

(b) Irregular variation of ionisation enthalpies is mainly attributed to varying degree of stability of different 3d-configurations (*e.g.*, d^0 , d^5 , d^{10} are exceptionally stable).

S44. (a) Elements which have incompletely filled d -orbitals in their ground state or in any one of their oxidation states are called transition elements.

Characteristics of transition elements:

(a) They show variable oxidation states. (b) They exhibit catalytic properties.

(b) In the electronic configuration of Zn, Cd and Hg the d -orbitals are completely filled in the ground state as well as in their common oxidation state. So, they are not regarded as transition metals.

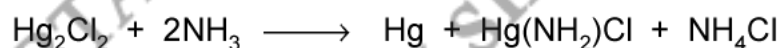
S45. (a) Electronic configuration of Mn^{2+} is $3d^5$ which is half filled and hence stable. Therefore, third ionization enthalpy is very high, *i.e.*, 3rd electron cannot be lost easily. In case of Fe^{2+} , electronic configuration is $3d^6$. Hence, it can lose one electron easily to give the stable configuration $3d^5$.

(b) Zinc ($Z = 30$) has completely filled d -orbital ($3d^{10}$) d -orbitals do not take part in interatomic bonding. Hence, metallic bonding is weak.

This is why it has very low enthalpy of atomisation (126 kJ mol^{-1}).

S46. Disproportionation reaction involves the oxidation and reduction of the same substance. The two examples of disproportionation reaction are:

(a) Aqueous NH_3 when treated with Hg_2Cl_2 (solid) forms mercury aminochloride disproportionatively.



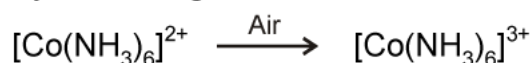
(b) $2Cu^+ \longrightarrow Cu + Cu^{2+}$.

S47. (a) Transition elements can use their ns and $(n - 1) d$ orbital electrons for bond formation therefore, they show variable oxidation states.

For example – Sc has $ns^2(n - 1) d^1$ electronic configuration.

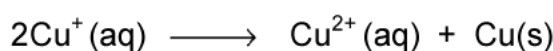
It utilizes two electrons from its ns subshell then its oxidation state = +2. When it utilizes both the electrons then its oxidation state = +3.

- (b) The tendency to form complexes is high for Co(III) as compared to Co(II). Co^{2+} ions are very stable and are difficult to oxidise. Co^{3+} ions are less stable and are reduced by water. In contrast many Co(II) complexes are readily oxidised to Co(III) complexes and Co(III) complexes are very stable, e.g.,



This happens because the crystal field stabilisation energy of Co(III) with a $d^6(t_{2g}^6)$ configuration is higher than for Co(II) with a $d^7(t_{2g}^6 e_g^1)$ arrangement.

- S48.** (a) In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.



Cu^{2+} in aqueous solutions is more stable than Cu^+ ion because hydration enthalpy of Cu^{2+} is higher than that of Cu^+ . It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

- (b) This is due to ability of oxygen to form multiple bonds with metals.

- S49.** (a) Electrode potential (E°) value is the sum of three factors:

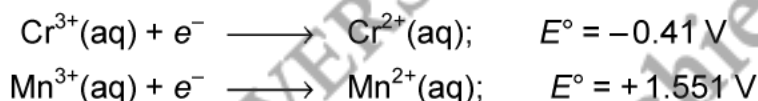
- (i) Enthalpy of atomisation $\Delta_a H$ for $\text{Cu}(\text{s}) \longrightarrow \text{Cu}(\text{g})$
- (ii) Ionisation enthalpy $\Delta_i H$ for $\text{Cu}(\text{g}) \longrightarrow \text{Cu}^{2+}(\text{g})$
- (iii) Hydration enthalpy $\Delta_{\text{hyd}} H$ For $\text{Cu}^{2+}(\text{g}) \longrightarrow \text{Cu}^{2+}(\text{aq})$

In case of copper the sum of enthalpy of atomisation and ionisation enthalpy is greater than enthalpy of hydration.

This is why $E^\circ_{\text{M}^{2+}/\text{M}}$ for Cu is positive.

- (b) This is due to lanthanoid contraction.

- S50.** (a) E° values for the $\text{Cr}^{3+}/\text{Cr}^{2+}$ and $\text{Mn}^{3+}/\text{Mn}^{2+}$ couples are:



These E° values indicate that Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidising.

- (b) Since, transition elements contain partially filled 5-subshells. Therefore, electrons in these subshells go from lower d -subshells to higher d -subshells. This is called $d-d$ transition takes place by absorbing energy from the visible light. The mixture of the wavelength which is not absorbed is transmitted out. This accounts for the colour of transition elements.

- S51.** (a) Transition metals form a large number of interstitial compounds because small atoms of certain non metallic elements (H, B, C, N, etc.) get trapped in voids or vacant spaces of lattices of the transition metals. As a result of filling up of the interstitial spaces such interstitial compounds are hard and rigid.

- (b) This is due to lanthanoid contraction.

- S52.** (a) Copper exhibits +1 oxidation state in its compounds. Electronic configuration of Cu in the ground state is $3d^{10} 4s^1$. So, Cu can easily lose $4s^1$ electron to give a stable $3d^{10}$ configuration. Thus, it shows +1 oxidation state.

- (b) Only those ions will be coloured which have partially filled d -orbitals facilitating $d-d$ transition. Ions with d^0 and d^{10} will be colourless.

From electronic configuration of the ions, $V^{3+}(3d^2)$ and $Mn^{2+}(3d^5)$, are all coloured. $Ti^{4+}(3d^0)$ and $Sc^{3+}(3d^0)$ are colourless.

- S53.** (a) Transition elements can use their ns and $(n - 1) d$ orbital electrons for bond formation therefore, they show variable oxidation states.

For example – Sc has $ns^2(n - 1) d^1$ electronic configuration.

It utilizes two electrons from its ns subshell then its oxidation state = +2. When it utilizes both the electrons then its oxidation state = +3.

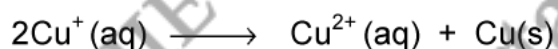
- (b) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysis involves the formation of bonds between reactant molecules and atoms at the surface of the catalyst.

- S54.** (a) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysis involves the formation of bonds between reactant molecules and atoms at the surface of the catalyst.

- (b) Due to presence of vacant d -orbitals and $d-d$ transitions, compounds of the transition metals are generally coloured.

When an electron from a lower energy d -orbital is excited to a higher energy d -orbital, the energy of excitation corresponds to the frequency which generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand.

- S55.** (a) In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.

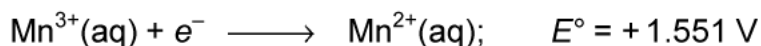
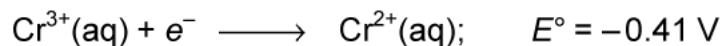


Cu^{2+} in aqueous solutions is more stable than Cu^+ ion because hydration enthalpy of Cu^{2+} is higher than that of Cu^+ . It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

- (b) This is attributed to the involvement of greater number of electrons from $(n - 1) d$ in addition to the ns electrons in the interatomic metallic bonding.

- S56.** (a) Electronic configuration of Mn^{2+} is $3d^5$ which is half filled and hence stable. Therefore, third ionization enthalpy is very high, *i.e.*, 3rd electron cannot be lost easily. In case of Fe^{2+} , electronic configuration is $3d^6$. Hence, it can lose one electron easily to give the stable configuration $3d^5$.

(b) E° values for the $\text{Cr}^{3+}/\text{Cr}^{2+}$ and $\text{Mn}^{3+}/\text{Mn}^{2+}$ couples are:



These E° values indicate that Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidising.

S57. The variability in oxidation states of transition metals is due to the incomplete filling of d -orbitals. Their oxidation states differ from each other by unity.

For example, Fe^{3+} and Fe^{2+} , Cu^{2+} and Cu^+ , etc.

In case of non transition elements the oxidation states normally differ by units of two. For example Pb^{2+} and Pb^{4+} , Sn^{2+} and Sn^{4+} , etc. It arises due to expansion of octet and inert pair effect.

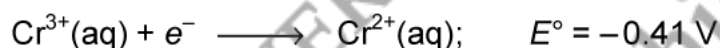
S58. (a) Sc(21) is a transition element but Ca(20) is not because of incompletely filled $3d$ orbitals.

(b) Electronic configuration of Mn^{2+} is $3d^5$ which is half filled and hence stable. Therefore, third ionization enthalpy is very high, *i.e.*, 3rd electron cannot be lost easily. In case of Fe^{2+} , electronic configuration is $3d^6$. Hence, it can lose one electron easily to give the stable configuration $3d^5$.

S59. (a) As transition metals have large number of unpaired electrons in the d -orbitals of their atoms they have strong interatomic attraction or metallic bonds. Hence, they have high enthalpy of atomization.

(b) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysis involves the formation of bonds between reactant molecules and atoms at the surface of the catalyst.

S60. (a) E° values for the $\text{Cr}^{3+}/\text{Cr}^{2+}$ and $\text{Mn}^{3+}/\text{Mn}^{2+}$ couples are:



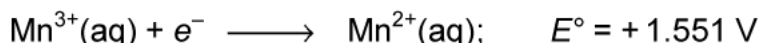
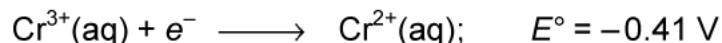
These E° values indicate that Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidising.

(a) As one proceeds along a transition series, the nuclear charge increases which tends to decrease the size but the addition of electrons in the d -subshell increases the screening effect which counter balances the effect of increased nuclear charge.

S61. (a) Transition metals form a large number of interstitial compounds because small atoms of certain non metallic elements (H, B, C, N, etc.) get trapped in voids or vacant spaces of lattices of the transition metals. As a result of filling up of the interstitial spaces such interstitial compounds are hard and rigid.

(b) As we move along transition metal series from left to right (*i.e.*, Ti to Cu), the atomic radii decrease due to increase in nuclear charge. Hence, the atomic volume decreases. At the same time, atomic mass increases. Hence, the density from titanium (Ti) to copper (Cu) increases.

S62. (a) E° values for the $\text{Cr}^{3+}/\text{Cr}^{2+}$ and $\text{Mn}^{3+}/\text{Mn}^{2+}$ couples are:



These E° values indicate that Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidising.

(b) Middle of the transition series contains greater number of unpaired electrons in $(n-1)d$ and ns orbitals.

S63. (a) Due to presence of vacant d -orbitals and $d-d$ transitions, compounds of the transition metals are generally coloured.

When an electron from a lower energy d -orbital is excited to a higher energy d -orbital, the energy of excitation corresponds to the frequency which generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed. The frequency of the light absorbed is determined by the nature of the ligand.

(b) As manganese has maximum number of unpaired electrons (5) in $3d$ subshell in addition to 2 electrons in the $4s$ subshell, it can use the 7 electrons for bonding purpose.

S64. (a) As we move along transition metal series from left to right (*i.e.*, Ti to Cu), the atomic radii decrease due to increase in nuclear charge. Hence, the atomic volume decreases. At the same time, atomic mass increases. Hence, the density from titanium (Ti) to copper (Cu) increases.

(b) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysis involves the formation of bonds between reactant molecules and atoms at the surface of the catalyst.

S65. (a) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysis involves the formation of bonds between reactant molecules and atoms at the surface of the catalyst.

(b) The metals of $4d$ and $5d$ -series have more frequent metal bonding in their compounds than the $3d$ -metals because $4d$ and $5d$ -orbitals are more exposed in space than the $3d$ -orbitals. So the valence electrons are less tightly held and form metal-metal bonding more frequently.

S66. (a) In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.



Cu^{2+} in aqueous solutions is more stable than Cu^+ ion because hydration enthalpy of Cu^{2+} is higher than that of Cu^+ . It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

(b) This is because due to lanthanoid contraction the expected increase in size does not occur hence they have very high value of ionisation enthalpies.

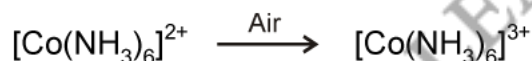
- S67.** (a) As transition metals have large number of unpaired electrons in the d -orbitals of their atoms they have strong interatomic attraction or metallic bonds. Hence, they have high enthalpy of atomization.
- (b) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysis involves the formation of bonds between reactant molecules and atoms at the surface of the catalyst.

- S68.** (a) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysis involves the formation of bonds between reactant molecules and atoms at the surface of the catalyst.
- (b) This is due to lanthanoid contraction.

- S69.** (a) Lowest oxidation compounds of transition metals are basic due to their ability to get oxidised to higher oxidation states. Whereas the higher oxidation state of metal and compounds gets reduced to lower ones and hence acts as acidic in nature.

e.g., MnO is basic whereas Mn_2O_7 is acidic.

- (b) The tendency to form complexes is high for Co(III) as compared to Co(II) . Co^{2+} ions are very stable and are difficult to oxidise. Co^{3+} ions are less stable and are reduced by water. In contrast many Co(II) complexes are readily oxidised to Co(III) complexes and Co(III) complexes are very stable, *e.g.*,



This happens because the crystal field stabilisation energy of Co(III) with a $d^6(t_{2g}^6)$ configuration is higher than for Co(II) with a $d^7(t_{2g}^6 e_g^1)$ arrangement.

- S70.** (a) Zinc ($Z = 30$) has completely filled d -orbital ($3d^{10}$) d -orbitals do not take part in interatomic bonding. Hence, metallic bonding is weak.

This is why it has very low enthalpy of atomisation (126 kJ mol^{-1}).

- (b) Much larger third ionisation energy of Mn (where change is d^5 to d^4) is mainly responsible for this. This also explains that +3 state of Mn is of little importance.

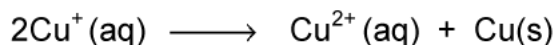
- S71.** (a) In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.



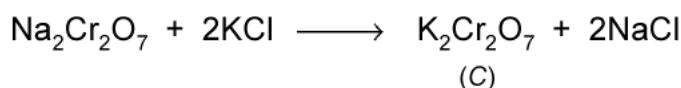
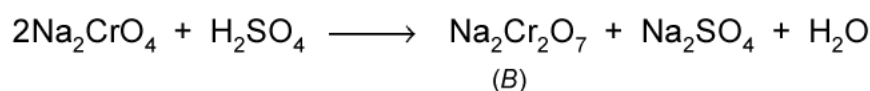
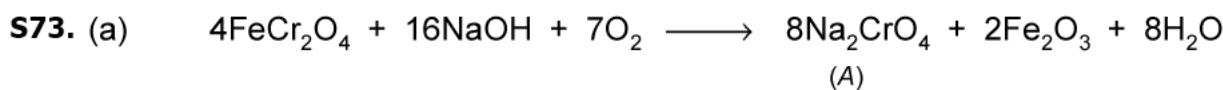
Cu^{2+} in aqueous solutions is more stable than Cu^+ ion because hydration enthalpy of Cu^{2+} is higher than that of Cu^+ . It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

- (b) Transition metals and most of their compounds contain unpaired electrons in the $(n-1)d$ orbitals hence show paramagnetic behaviour.

- S72.** (a) This is due to presence of maximum number of unpaired electrons in Mn^{2+} in ($3d^5$).
- (b) In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.



Cu^{2+} in aqueous solutions is more stable than Cu^+ ion because hydration enthalpy of Cu^{2+} is higher than that of Cu^+ . It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.



- (b) Potassium dichromate is used as a powerful oxidising agent in industries and for staining and tanning of leather.

S74. Lanthanoid contraction: The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number is called lanthanoid contraction. It is caused due to imperfect shielding of nuclear charge by $4f$ -electrons.

Consequences of lanthanoid contraction:

- (a) The basic strength of oxides and hydroxides of lanthanoids decrease with increasing atomic number.
- (b) Atomic and ionic sizes of $4d$ transition series elements and $5d$ series elements are similar. e.g., atomic radii of zirconium (Zr) is same as that of hafnium (Hf).

S75. Structure: All the lanthanoids are silvery white soft metals. Hardness of Lanthanoids increases with increasing atomic number.

The actinoid metals are all silvery in appearance but display a variety of structures. The structural variability is due to irregularities in metallic radii which are greater than that of lanthanoids.

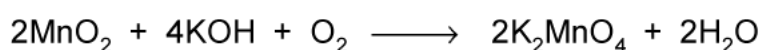
Chemical reactivity: Earlier members of lanthanoid series are quite reactive similar to calcium but with increasing atomic number they behave more like aluminium.

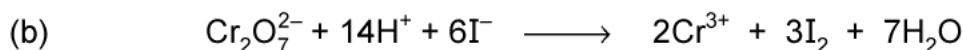
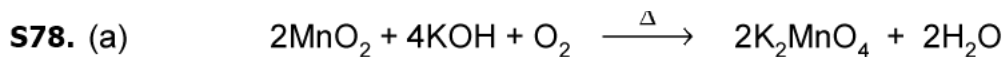
The actinoids are highly reactive in finely divided state.

S76. The actinoid contraction is more than lanthanoid contraction because $5f$ -electrons are more poorly shielding than $4f$ -electrons.

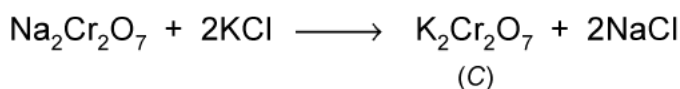
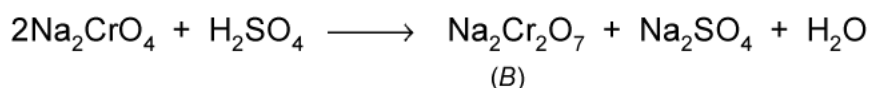
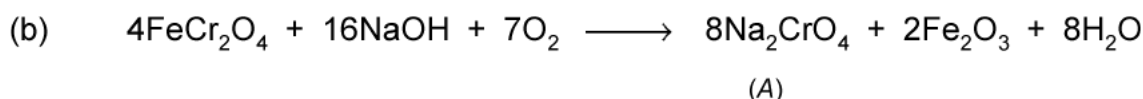
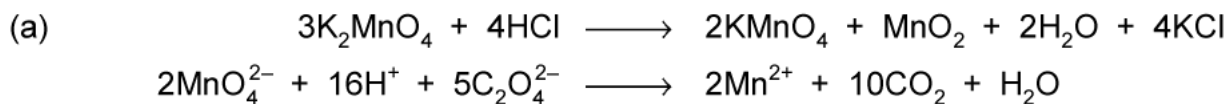
Only trends of magnetic properties and colour of lanthanoids are similar to actinoids.

S77. Preparation of potassium permanganate: Potassium permanganate is prepared by the fusion of MnO_2 (pyrolusite) with potassium hydroxide and an oxidising agent like KNO_3 to form potassium manganate which disproportionates in a neutral or acidic solution to form permanganate.



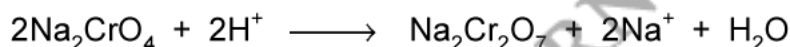


S79. Potassium dichromates are strong oxidising agents.

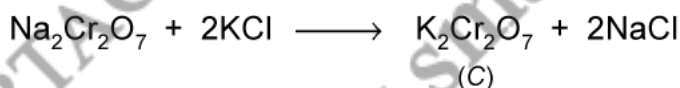
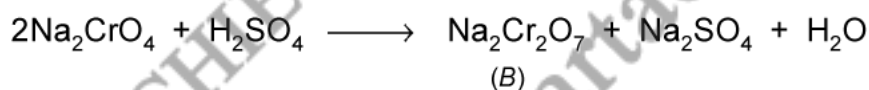
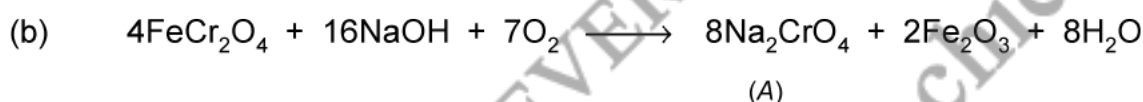
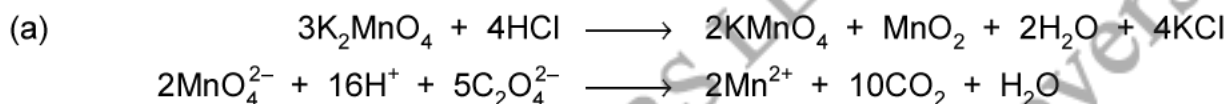


Potassium dichromate is used as a powerful oxidising agent in industries and for staining and tanning of leather.

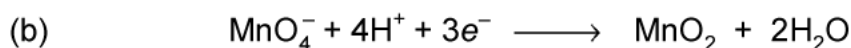
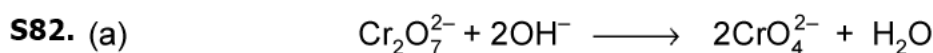
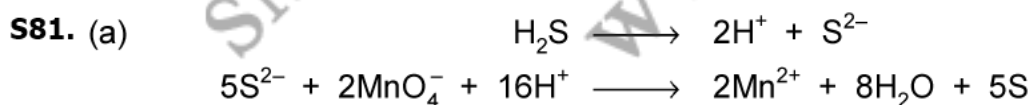
(b) Sodium dichromate can be crystallised out from sodium chromate solution by acidifying it with sulphuric acid.



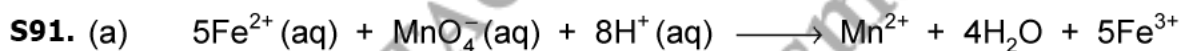
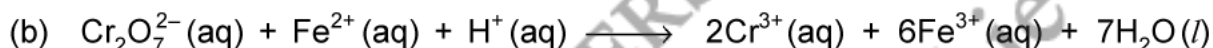
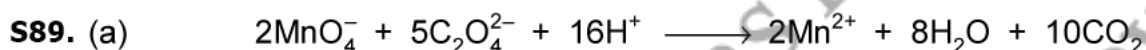
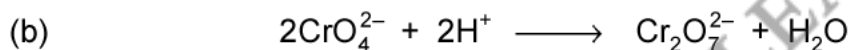
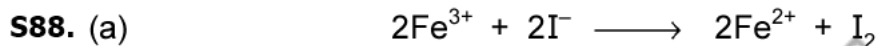
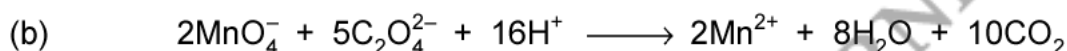
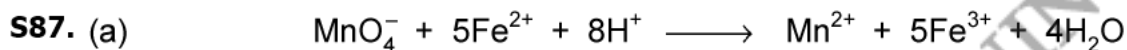
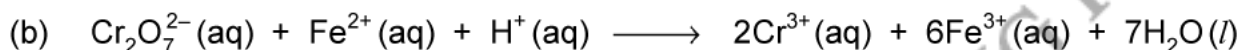
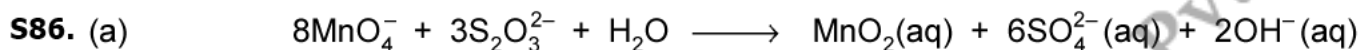
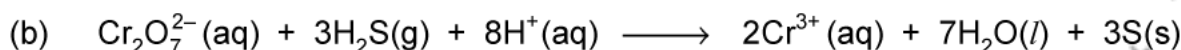
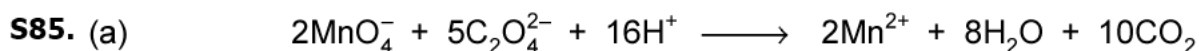
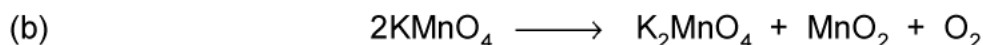
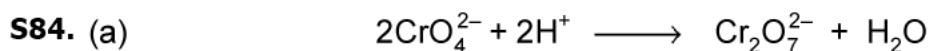
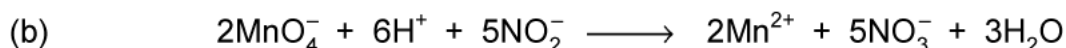
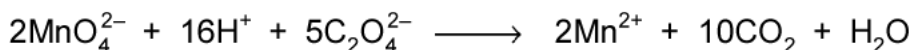
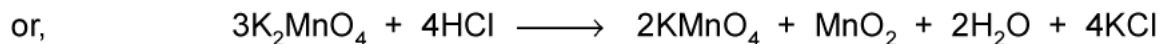
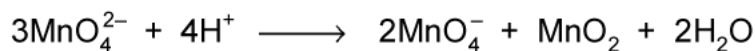
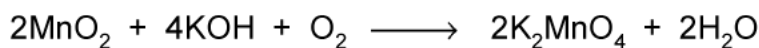
S80. Potassium dichromates are strong oxidising agents.



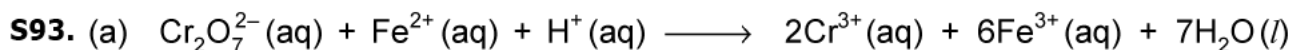
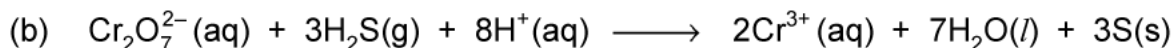
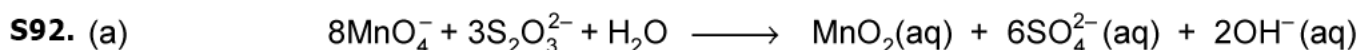
Potassium dichromate is used as a powerful oxidising agent in industries and for staining and tanning of leather.



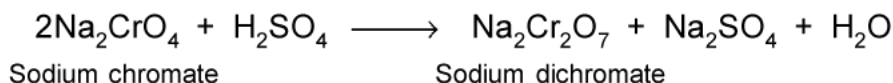
S83. (a) Preparation of potassium permanganate: Potassium permanganate is prepared by the fusion of MnO_2 (pyrolusite) with potassium hydroxide and an oxidising agent like KNO_3 to form potassium manganate which disproportionates in a neutral or acidic solution to form permanganate.



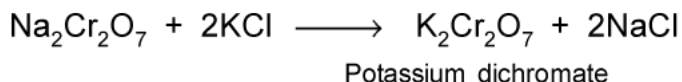
(b) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysis involves the formation of bonds between reactant molecules and atoms at the surface of the catalyst.



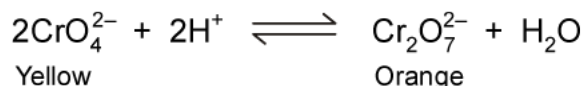
- S94.** (a) The yellow solution of sodium chromate is acidified with sulphuric acid to give a orange solution of sodium dichromate $\text{Na}_2\text{Cr}_2\text{O}_7$ which is crystallised.



The solution of sodium dichromate is treated with potassium chloride to obtain potassium dichromate.



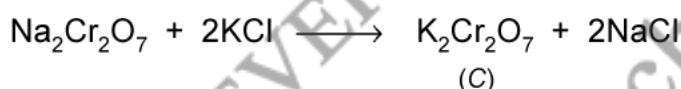
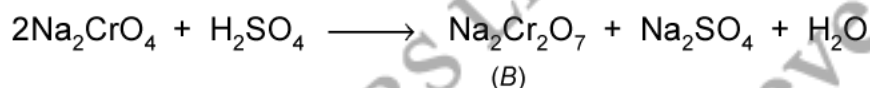
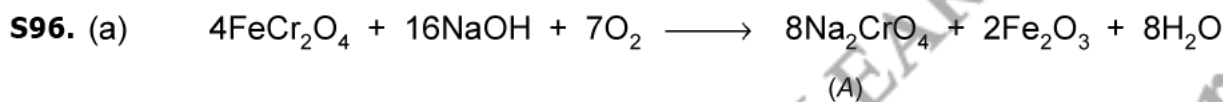
- (b) When the pH of the solution of potassium dichromate is decreased, the colour of the solution changes from yellow to orange due to the conversion of CrO_4^{2-} ions into $\text{Cr}_2\text{O}_7^{2-}$ ions.



- S95. Lanthanoid contraction:** The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number is called lanthanoid contraction. It is caused due to imperfect shielding of nuclear charge by $4f$ -electrons.

Consequences of lanthanoid contraction:

- (a) The basic strength of oxides and hydroxides of lanthanoids decrease with increasing atomic number.
- (b) Atomic and ionic sizes of $4d$ transition series elements and $5d$ series elements are similar. e.g., atomic radii of zirconium (Zr) is same as that of hafnium (Hf).

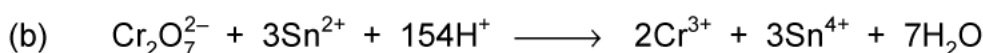


- (b) The potassium manganate is oxidised to potassium permanganate by oxidation with chlorine.

- S97. Lanthanoid contraction:** The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number is called lanthanoid contraction. It is caused due to imperfect shielding of nuclear charge by $4f$ -electrons.

Consequences of lanthanoid contraction:

- (a) The basic strength of oxides and hydroxides of lanthanoids decrease with increasing atomic number.
- (b) Atomic and ionic sizes of $4d$ transition series elements and $5d$ series elements are similar. e.g., atomic radii of zirconium (Zr) is same as that of hafnium (Hf).



S99. Lanthanoid contraction: The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number is called lanthanoid contraction. It is caused due to imperfect shielding of nuclear charge by 4*f*-electrons.

Consequences of lanthanoid contraction:

- (a) The basic strength of oxides and hydroxides of lanthanoids decrease with increasing atomic number.
- (b) Atomic and ionic sizes of 4*d* transition series elements and 5*d* series elements are similar. e.g., atomic radii of zirconium (Zr) is same as that of hafnium (Hf).

S100. Mischmetal is well known alloy which consists of a lanthanoid metal (about 95%), iron (about 5%) and traces of S, C, Ca, Al etc.

Mischmetal is used in Mg based alloy to produce bullets shells and lighter flint.

S101.
$$\text{Ce (Z = 58)} = [\text{Xe}]^{54} 4f^1 5d^1 6s^2$$
$$\therefore \text{Ce}^{3+} = [\text{Xe}]^{54} 4f^1 5d^0 6s^0$$

Therefore, it has only one unpaired electron. *i.e.*, $n = 1$

$$\therefore \mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.73 \text{ BM}$$

S102. Europium (II) has electronic configuration $[\text{Xe}]4f^7 5f^0$ while cerium (II) has electronic configuration $[\text{Xe}]4f^1 5d^1$. In Eu^{2+} , 4*f* subshell is half filled and 5*d*-subshell is empty. Since half filled and completely filled electronic configurations are more stable, Eu^{2+} ions is more stable than Ce^{2+} in which neither 4*f* subshell nor 5*d*-subshell is half filled or completely filled.

S103. Lanthanoid contraction: The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number is called lanthanoid contraction. It is caused due to imperfect shielding of nuclear charge by 4*f*-electrons.

Consequences of lanthanoid contraction:

- (a) The basic strength of oxides and hydroxides of lanthanoids decrease with increasing atomic number.
- (b) Atomic and ionic sizes of 4*d* transition series elements and 5*d* series elements are similar. e.g., atomic radii of zirconium (Zr) is same as that of hafnium (Hf).

S104. (a) Manganese can form $p\pi - d\pi$ bond with oxygen by utilising 2*p*-orbital of oxygen and 3*d*-orbital of manganese due to which it can show highest oxidation state of +7. While with fluorine it cannot form such $p\pi - d\pi$ bond thus, it can show a maximum of +4 oxidation state.

(b) Cr^{2+} is reducing since its configuration is converted to d^3 from d^4 . d^3 has half filled t_{2g} configuration with higher stability.

(c) Zn^{2+} ion has completely filled *d*-subshell and no *d-d* transition is possible. So zinc salts are white.

Configuration of Cu^{2+} is $[\text{Ar}] 3d^9$. It has partly filled *d*-subshell and hence it is coloured due to *d-d* transition.

- S105(a)** All transition elements except the first and the last member in each series show a large number of variable oxidation states. This is because difference of energy in the $(n - 1)d$ and ns orbitals is very little.

Hence, electrons from both the energy levels can be used for bond formation.

- (b) As transition metals have large number of unpaired electrons in the d -orbitals of their atoms they have strong interatomic attraction or metallic bonds. Hence, they have high enthalpy of atomization.
- (c) The variability in oxidation states of transition metals is due to the incomplete filling of d -orbitals. Their oxidation states differ from each other by unity.

For example, Fe^{3+} and Fe^{2+} , Cu^{2+} and Cu^+ , etc.

In case of non transition elements the oxidation states normally differ by units of two. For example Pb^{2+} and Pb^{4+} , Sn^{2+} and Sn^{4+} , etc. It arises due to expansion of octet and inert pair effect.

S106 Lanthanoid contraction: The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number is called lanthanoid contraction. It is caused due to imperfect shielding of nuclear charge by $4f$ -electrons.

Consequences of lanthanoid contraction:

- (a) The basic strength of oxides and hydroxides of lanthanoids decrease with increasing atomic number.
- (b) Atomic and ionic sizes of $4d$ transition series elements and $5d$ series elements are similar. e.g., atomic radii of zirconium (Zr) is same as that of hafnium (Hf).

S107 Disproportionation reaction involves the oxidation and reduction of the same substance. The two examples of disproportionation reaction are:

- (a) Aqueous NH_3 when treated with Hg_2Cl_2 (solid) forms mercury aminochloride disproportionatively.



- (b) $2\text{Cu}^+ \longrightarrow \text{Cu} + \text{Cu}^{2+}$.

S108(a) Electrode potential (E°) value is the sum of three factors:

- (i) Enthalpy of atomisation $\Delta_a H$ for $\text{Cu}(\text{s}) \longrightarrow \text{Cu}(\text{g})$
- (ii) Ionisation enthalpy $\Delta_i H$ for $\text{Cu}(\text{g}) \longrightarrow \text{Cu}^{2+}(\text{g})$
- (iii) Hydration enthalpy $\Delta_{\text{hyd}} H$ For $\text{Cu}^{2+}(\text{g}) \longrightarrow \text{Cu}^{2+}(\text{aq})$

In case of copper the sum of enthalpy of atomisation and ionisation enthalpy is greater than enthalpy of hydration.

This is why $E^\circ_{\text{M}^{2+}/\text{M}}$ for Cu is positive.

- (b) Mn^{2+} ion has stable half-filled ($2d^5$) electronic configuration. Its ionisation enthalpy value is lower in comparison to hydration enthalpy. Hence, $E^\circ_{\text{Mn}^{2+}/\text{Mn}}$ is more negative.

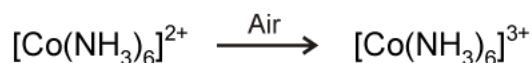
- (c) Cr^{2+} is stronger reducing agent than Fe^{2+} .

Reason is negative (-0.41 V) whereas $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}}$ is positive ($+0.77\text{ V}$). Thus, Cr^{2+} is easily oxidized to Cr^{3+} but Fe^{2+} cannot be easily oxidized to Fe^{3+} . Hence, Cr^{2+} is stronger reducing agent than Fe^{2+} .

S109(a) The metals of $4d$ and $4d$ -series have more frequent metal bonding in their compounds than the $3d$ -metals because $4d$ and $5d$ -orbitals are more exposed in space than the $3d$ -orbitals. So the valence electrons are less tightly held and form metal-metal bonding more frequently.

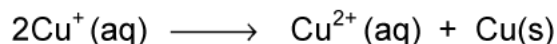
- (b) Mn^{3+} is less stable and changes to Mn^{2+} which is more stable due to half-filled d -orbital configuration. That is why, Mn^{3+} undergoes disproportionation reaction.

- (c) The tendency to form complexes is high for Co(III) as compared to Co(II) . Co^{2+} ions are very stable and are difficult to oxidise. Co^{3+} ions are less stable and are reduced by water. In contrast many Co(II) complexes are readily oxidised to Co(III) complexes and Co(III) complexes are very stable, e.g.,



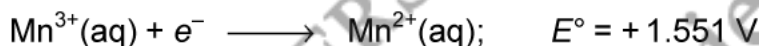
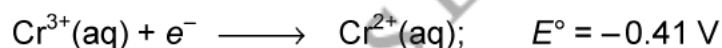
This happens because the crystal field stabilisation energy of Co(III) with a $d^6(t_{2g}^6)$ configuration is higher than for Co(II) with a $d^7(t_{2g}^6 e^1_g)$ arrangement.

S110(a) In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.



Cu^{2+} in aqueous solutions is more stable than Cu^+ ion because hydration enthalpy of Cu^{2+} is higher than that of Cu^+ . It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

- (b) E° values for the $\text{Cr}^{3+}/\text{Cr}^{2+}$ and $\text{Mn}^{3+}/\text{Mn}^{2+}$ couples are:



These E° values indicate that Cr^{2+} is strongly reducing while Mn^{3+} is strongly oxidising.

- (c) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysis involves the formation of bonds between reactant molecules and atoms at the surface of the catalyst.

S111(a) This is due to lanthanoid contraction.

- (b) Much larger third ionisation energy of Mn (where change is d^5 to d^4) is mainly responsible for this. This also explains that $+3$ state of Mn is of little importance.

- (c) Mn^{2+} is more stable due to half-filled d^5 configuration and Mn^{3+} easily changes to Mn^{2+} hence, it is oxidising.

S112(a) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysis involves the formation of bonds between reactant molecules and atoms at the surface of the catalyst.

(b) Zinc ($Z = 30$) has completely filled d -orbital ($3d^{10}$) d -orbitals do not take part in interatomic bonding. Hence, metallic bonding is weak.

This is why it has very low enthalpy of atomisation (126 kJ mol^{-1}).

(c) Manganese can form $p\pi - d\pi$ bond with oxygen by utilising $2p$ -orbital of oxygen and $3d$ -orbital of manganese due to which it can show highest oxidation state of +7. While with fluorine it cannot form such $p\pi - d\pi$ bond thus, it can show a maximum of +4 oxidation state.

S113(a) Change in $\text{Cr}_2\text{O}_7^{2-}$ to Cr(III) is 3 and in MnO_4^- to Mn(II) is 5.

Change in oxidation state is large and the stability of reduced products in $\text{V(III)} < \text{Cr(III)} < \text{Mn(II)}$. This is why oxidising power of $\text{VO}_2^+ < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$.

(b) Third ionization enthalpy of Mn is very high because the third electron has to be removed from the stable half-filled $3d$ -orbitals [$\text{Mn}^{2+} (Z = 25) = 3d^5$].

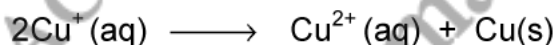
(c) Zn^{2+} ion has completely filled d -subshell and no $d-d$ transition is possible. So zinc salts are white.

Configuration of Cu^{2+} is $[\text{Ar}] 3d^9$. It has partly filled d -subshell and hence it is coloured due to $d-d$ transition.

S114(a) As transition metals have large number of unpaired electrons in the d -orbitals of their atoms they have strong interatomic attraction or metallic bonds. Hence, they have high enthalpy of atomization.

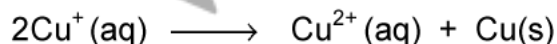
(b) Electronic configuration of Mn^{2+} is $3d^5$ which is half filled and hence stable. Therefore, third ionization enthalpy is very high, i.e., 3rd electron cannot be lost easily. In case of Fe^{2+} , electronic configuration is $3d^6$. Hence, it can lose one electron easily to give the stable configuration $3d^5$.

(c) In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.



Cu^{2+} in aqueous solutions is more stable than Cu^+ ion because hydration enthalpy of Cu^{2+} is higher than that of Cu^+ . It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

S115(a) In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.



Cu^{2+} in aqueous solutions is more stable than Cu^+ ion because hydration enthalpy of Cu^{2+} is higher than that of Cu^+ . It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

- (b) This is due to presence of maximum number of unpaired electrons in Mn^{2+} in ($3d^5$).
- (c) Only these ions are coloured which have partially filled d -orbitals facilitating $d-d$ transitions. Sc^{3+} with $3d^0$ configuration is colourless while Ti^{3+} ($3d^1$) is coloured.

S116(a) The atomic radii of transition elements decrease with the increase in atomic number as the effective nuclear charge increases because shielding effect of d -electron is small.

(b) Electrode potential (E°) value is the sum of three factors:

- (i) Enthalpy of atomisation $\Delta_a H$ for $Cu(s) \longrightarrow Cu(g)$
- (ii) Ionisation enthalpy $\Delta_i H$ for $Cu(g) \longrightarrow Cu^{2+}(g)$
- (iii) Hydration enthalpy $\Delta_{hyd} H$ For $Cu^{2+}(g) \longrightarrow Cu^{2+}(aq)$

In case of copper the sum of enthalpy of atomisation and ionisation enthalpy is greater than enthalpy of hydration.

This is why $E_{M^{2+}/M}^\circ$ for Cu is positive.

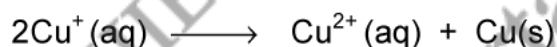
(c) Much larger third ionisation energy of Mn (where change is d^5 to d^4) is mainly responsible for this. This also explains that +3 state of Mn is of little importance.

S117(a) As transition metals have large number of unpaired electrons in the d -orbitals of their atoms they have strong interatomic attraction or metallic bonds. Hence, they have high enthalpy of atomization.

(b) The transition metals and their compounds, are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states, ability to adsorb the reactant(s) and ability to form complexes. Vanadium (V) oxide (in Contact Process), finely divided iron (in Haber's Process), and nickel (in catalytic hydrogenation) are some of the examples. Catalysis involves the formation of bonds between reactant molecules and atoms at the surface of the catalyst.

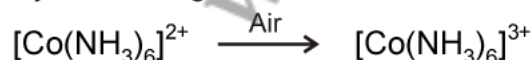
(c) Much larger third ionisation energy of Mn (where change is d^5 to d^4) is mainly responsible for this. This also explains that +3 state of Mn is of little importance.

S118(a) In aqueous solutions, Cu^+ undergoes disproportionation to form a more stable Cu^{2+} ion.



Cu^{2+} in aqueous solutions is more stable than Cu^+ ion because hydration enthalpy of Cu^{2+} is higher than that of Cu^+ . It compensates the second ionisation enthalpy of Cu involved in the formation of Cu^{2+} ions.

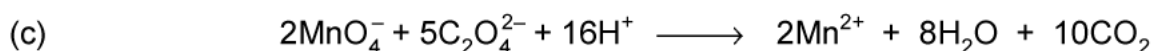
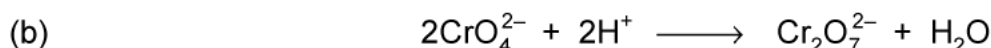
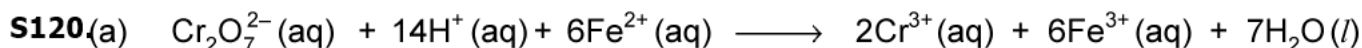
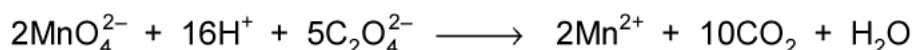
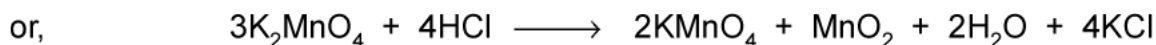
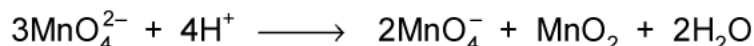
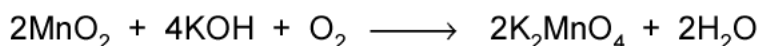
(b) The tendency to form complexes is high for Co(III) as compared to Co(II). Co^{2+} ions are very stable and are difficult to oxidise. Co^{3+} ions are less stable and are reduced by water. In contrast many Co(II) complexes are readily oxidised to Co(III) complexes and Co(III) complexes are very stable, e.g.,



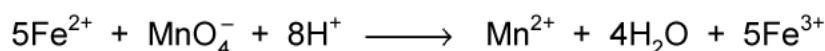
This happens because the crystal field stabilisation energy of Co(III) with a $d^6(t_{2g}^6)$ configuration is higher than for Co(II) with a $d^7(t_{2g}^6 e_g^1)$ arrangement.

(c) Much larger third ionisation energy of Mn (where change is d^5 to d^4) is mainly responsible for this. This also explains that +3 state of Mn is of little importance.

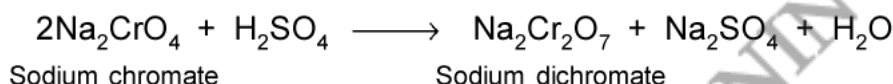
S119 Preparation of potassium permanganate: Potassium permanganate is prepared by the fusion of MnO_2 (pyrolusite) with potassium hydroxide and an oxidising agent like KNO_3 to form potassium manganate which disproportionates in a neutral or acidic solution to form permanganate.



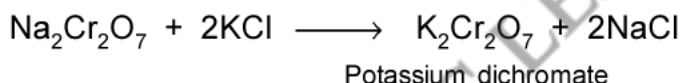
S121 Preparation of potassium permanganate: Potassium permanganate is prepared by the fusion of MnO_2 (pyrolusite) with potassium hydroxide and an oxidising agent like KNO_3 to form potassium manganate which disproportionates in a neutral or acidic solution to form permanganate.



S122(a) The yellow solution of sodium chromate is acidified with sulphuric acid to give a orange solution of sodium dichromate $\text{Na}_2\text{Cr}_2\text{O}_7$ which is crystallised.



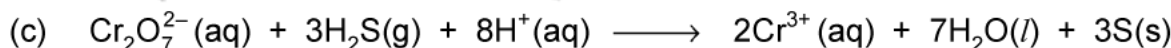
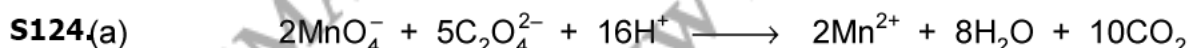
The solution of sodium dichromate is treated with potassium chloride to obtain potassium dichromate.



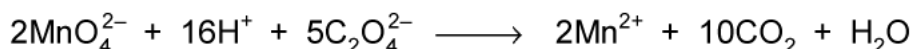
(b) When the pH of the solution of potassium dichromate is decreased, the colour of the solution changes from yellow to orange due to the conversion of CrO_4^{2-} ions into $\text{Cr}_2\text{O}_7^{2-}$ ions.

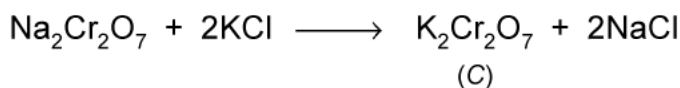
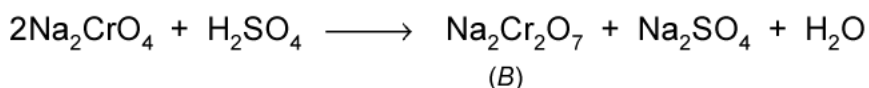
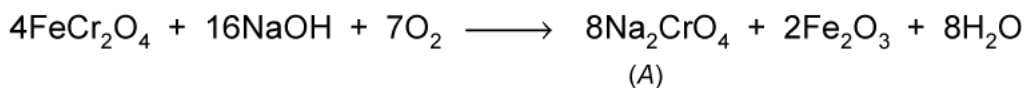


S123 Preparation of potassium permanganate: Potassium permanganate is prepared by the fusion of MnO_2 (pyrolusite) with potassium hydroxide and an oxidising agent like KNO_3 to form potassium manganate which disproportionates in a neutral or acidic solution to form permanganate.



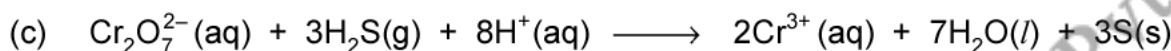
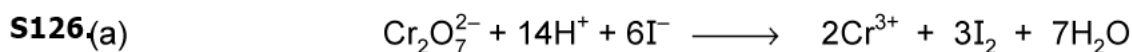
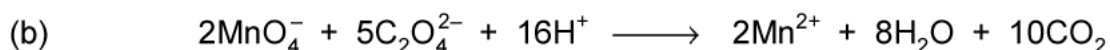
S125(a) Potassium dichromates are strong oxidising agents.





Potassium dichromate is used as a powerful oxidising agent in industries and for staining and tanning of leather.

- (ii) Sodium dichromate can be crystallised out from sodium chromate solution by acidifying it with sulphuric acid.



S127 Lanthanoid contraction: The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number is called lanthanoid contraction. It is caused due to imperfect shielding of nuclear charge by 4f-electrons.

Consequences of lanthanoid contraction:

- (a) The basic strength of oxides and hydroxides of lanthanoids decrease with increasing atomic number.
- (b) Atomic and ionic sizes of 4d transition series elements and 5d series elements are similar. e.g., atomic radii of zirconium (Zr) is same as that of hafnium (Hf).

S128(a) **Electronic configuration:** The general electronic configuration of lanthanoids is $[\text{Xe}]4f^{1-14}5d^{0-1}6s^2$ whereas that of actinoids is $[\text{Rn}]5f^{1-14}6d^{0-1}7s^2$. Thus, lanthanoids involve the filling of 4f-orbitals whereas actinoids involve the filling of 5f-orbitals.

- (b) **Oxidation states:** Lanthanoids have principal oxidation state of +3. In addition, the lanthanoids show limited oxidation states such as +2, +3 and +4 because of large energy gap between 4f and 5d subshells. On the other hand, actinoids show a large number of oxidation states because of small energy gap between 5f and 6d subshells.

(c) **Chemical reactivity:**

- (i) First few members of lanthanoids are quite reactive almost like calcium, whereas actinoids are highly reactive metals especially in the finely divided state.
- (ii) Lanthanoids react with dilute acids to liberate H_2 gas whereas actinoids react with boiling water to give a mixture of oxide and hydride.

S129(a) Mn^{2+} is more stable due to half-filled d^5 configuration and Mn^{3+} easily changes to Mn^{2+} hence, it is oxidising.

- (b) The $E_{M^{2+}/M}^\circ$ values are not regular which can be explained from the irregular variation of ionisation enthalpies *i.e.*, $IE_1 + E_2$ and also the sublimation enthalpies which are relatively much less for manganese and vanadium.
- (c) Manganese can form $p\pi - d\pi$ bond with oxygen by utilising $2p$ -orbital of oxygen and $3d$ -orbital of manganese due to which it can show highest oxidation state of +7. While with fluorine it cannot form such $p\pi - d\pi$ bond thus, it can show a maximum of +4 oxidation state.

- S130**(a) Mn shows maximum no. of oxidation states from +2 to +7 because Mn has maximum number of unpaired electrons in $3d$ -subshell.
- (b) Cr has maximum melting point, because it has 6 unpaired electrons in the valence shell, hence it has strong interatomic interaction.
- (c) Sc shows only +3 oxidation state because after losing 3 electrons, it has noble gas electronic configuration.
- (d) Mn is strong oxidising agent in +3 oxidation state because change of Mn^{3+} to Mn^{2+} give stable half-filled (d^5) electronic configuration, $E_{(Mn^{3+}/Mn^{2+})}^\circ = 1.5V$.

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