Exercise-1

✍ **Marked questions are recommended for Revision.**

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Electronic configuration, atomic size and ionic size, density, melting and boiling points, Ionization enthalpy and oxidation state.

A-1. What is the general electronic configuration of transition elements.

A-2. Write the electronic configurations of the following ions.
(i) Mn^{2+} (ii) Fe^{3+} (iii) Ni^{2+} (iv) Cr^{3+}

A-3. Name the d-block elements which do not have partially filled d-orbitals in their atoms or in their simple ions.

A-4. What is meant by the ‘lanthanide contraction’? Mention one important fact that can be considered as a consequence of the lanthanide contraction.

A-5. Name the (i) lightest and the (ii) heaviest elements (in terms of density) among the transition elements.

A-6. Which element among d-block elements has (i) the lowest melting point and (ii) the highest melting point

A-7. Why zinc has lowest melting point in 3d series ?

A-8. Why are ionization energies of 5d-elements greater then those of 3d-elements ?

A-9. Why do transition elements show variable oxidation state ?

A-10. What is the most common oxidation state of first transition series?

Section (B) : Electrode potential and chemical reactivity, Magnetic properties, formation of coloured ions, Catalytic properties, formation of interstitial compounds, alloy formation.

B-1. Name the three factors which determine the stability of a particular oxidation state in solution.

B-2. Explain as to why the $E^{\ominus}$ value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+}.

B-3.

Element	**Cr**	**Mn**	**Fe**
$E^o(M^{2+}/M)$	– 0.90 V	– 1.18 V	– 0.4 V
$E^o(M^{3+}/M^{2+})$	– 0.41 V	+ 1.57 V	+ 0.8 V

Use this data to comment upon
(i) The stability of Fe^{3+} and Mn^{2+} in acid solutions.
(ii) The ease with which iron can be oxidised as compared to the similar process for either Cr or Mn metals.

B-4. Which of the following ions would form (i) coloured and (ii) colourless complexes in water ?
Cu^{2+}, Zn^{2+}, Ti^{3+}, Ti^{+4}, Cd^{2+}, Mn^{2+}

B-5. Why Ti^{+4} complexes are diamagnetic ?

B-6. A substance is found to have a magnetic moment of 3.9 BM. How many unpaired electrons does it contain?

B-7. Explain giving reason.
(a) Transition metals and many of their compounds show paramagnetic behaviour.
(b) The enthalpies of atomisation of the transition metals are high.
(c) The transition metals generally form coloured compounds.

B-8. Describe the general characteristics of transition elements with special reference to the following :
(i) catalytic behaviour. (ii) complex formation. (iii) interstitial compounds.

Section (C) : Important d-block metal compounds.

C-1. Which type of reaction MnO_4^{2-} shows with acid, dilute-alkali or water.

C-2. Why $KMnO_4$ is stored in dark bottle and what happens to it's acidic solution ?

C-3. Why does $AgNO_3$ produce a black stain on the skin ?

C-4. Why is AgBr used in photography ?

C-5. Why it is not advisable to dissolve $KMnO_4$ in cold and concentrated H_2SO_4 ?

C-6. What happens when :
(a) Green vitriol is strongly heated.
(b) Malachite is made to react with dilute H_2SO_4.
(c) Copper sulphate is exposed to air for longer period.
(d) Lunar caustic is made to react with sodium hydroxide and then product is dried.
(e) Silver nitrate reacts with excess iodine.
(f) Potassium dichromate reacts with cold and concentrated H_2SO_4.

C-7. State true or false : Reaction of $K_2Cr_2O_7$ with cold and concentrated H_2SO_4 yields bright orange/red precipitate of CrO_3. Write reactions involved.

C-8. Write balanced chemical equations for :
(i) Mixture of $K_2Cr_2O_7$ and NaCl is heated with concentrated H_2SO_4.
(ii) Potassium permanganate is added to a hot solution of manganous sulphate.
(iii) Potassium dichromate and concentrated HCl are heated together.

Section (D) : Lanthanoids and actinoids

D-1. What are inner-transition elements ? Decide which of the following atomic numbers are the numbers of the inner transition elements : 29, 59, 74, 95, 102, 104.

D-2. Actinoid contraction is greater from element to element than lanthanoid contraction. Why ?

D-3. The chemistry of the actinoid elements is not so smooth as that of the lanthanoid. Justify this statement by giving some examples from the oxidation state of these elements.

D-4. Why Sm^{2+}, Eu^{2+} and Yb^{2+} ions in solutions are good reducing agents but an aqueous solution of Ce^{4+} is a good oxidizing agent ?

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Electronic configuration, atomic size and ionic size, density, melting and boiling points, Ionization enthalpy and oxidation state.

A-1. The transition elements have a general electronic configuration :
(A) $ns^2np^6nd^{1-10}$
(B) $(n-1)d^{1-10}ns^{0-2}np^{0-6}$
(C) $(n-1)d^{1-10}ns^{1-2}$
(D) none

A-2. The atomic volumes of the transition elements are low compared with elements in neighboring group 1 and 2 because :
(A) the nuclear charge is poorly screened and so attracts all the electrons more strongly.
(B) the extra electrons added occupy inner orbitals.
(C) (A) and (B) both.
(D) none.

A-3. The wrong statement regarding transition metals among the following is :
(A) 4s electrons penetrate towards the nucleus more than 3d electrons
(B) atomic radii of transition metals increase rapidly with increase in atomic number because of poor shielding of nuclear attraction by (n – 1)d electrons
(C) second and third transition series elements have nearly the same size
(D) their densities are higher and densities of the 5d series elements are higher than those of 4d series elements.

A-4. First IE of 5d series elements are higher than those of 3d and 4d series elements. This is due to :
(A) bigger size of atoms of 5d-series elements than 3d-series elements.
(B) greater effective nuclear charge is experienced by valence electrons because of the weak shielding of the nucleus by 4*f*-electrons in 5d series.
(C) (A) and (B) both.
(D) None of these.

A-5. Ionisation energies of Ni and Pt in kJ mol^{-1} are given below.

	$(IE)_1 + (IE)_2$	$(IE)_3 + (IE)_4$
Ni	2.49	8.80
Pt	2.60	6.70

So, (select the correct statement)
(A) nickel (II) compounds tend to be thermodynamically more stable than platinum (II)
(B) platinum (IV) compounds tend to be more stable than nickel (IV)
(C) (A) & (B) both
(D) none is correct

A-6. Maximum oxidation sate is shown by :
(A) Os (B) Mn (C) Cr (D) Co

Section (B) : Electrode potential and chemical reactivity, Magnetic properties, formation of coloured ions, Catalytic properties, formation of interstitial compounds, alloy formation.

B-1. Which of the following statement is false ?
(A) Of the d^4 species, manganese (III) is strongly reducing while Cr^{2+} is strongly oxidising.
(B) Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidised.
(C) The d^1 configuration is very unstable in ions.
(D) None of these

B-2. Which of the following has the maximum number of unpaired d-electron?
(A) Zn^{2+} (B) Fe^{2+} (C) Ni^{2+} (D) Cu^{2+}

B-3. The highest magnetic moment is shown by the transition metal ion with the outermost electronic configuration is :
(A) 3d^5 (B) 3d^2 (C) 3d^7 (D) 3d^9

B-4. Magnetic moment of Cr^{+2} (Z =24), Mn^{+2} (Z = 25) and Fe^{2+}(Z = 26) are x,y,z. They are in order :
(A) $x < y < z$ (B) $x > y > z$ (C) $z < x = y$ (D) $x = z < y$

B-5. The magnetic moment of $_{25}$Mn in ionic state is $\sqrt{15}$ B.M, then Mn is in :
(A) +2 state (B) +3 state (C) +4 state (D) +5 state

B-6. The colour of transition metal ions is attributed to :
(A) exceptionally small size of cations (B) absorption of ultraviolet rays
(C) incomplete (n – 1) d-subshell (D) absorption of infrared radiations

B-7. MnO_4^- is of intense pink colour, though Mn is in (+7) oxidation state. It is due to :
(A) oxygen gives colour to it
(B) charge transfer when Mn gives its electron to oxygen
(C) charge transfer when oxygen gives its electron to Mn making it Mn(+VI) hence coloured
(D) none is correct

B-8. The yellow colour of chromates changes to orange on acidification due to formation of :
(A) Cr^{3+} (B) Cr_2O_3 (C) $Cr_2O_7^{2-}$ (D) CrO_4^-

B-9. The catalytic activity of the transition metals and their compounds is ascribed to :
(A) their chemical reactivity.
(B) their magnetic behaviour.
(C) their filled d-orbitals.
(D) their ability to adopt multiple oxidation state and their complexing ability.

Section (C) : Important d-block metal compounds.

C-1. $KMnO_4$ is the oxo salt of :
(A) MnO_2 (B) Mn_2O_7 (C) MnO_3 (D) Mn_2O_3

C-2. The solubility of silver bromide in hypo solution (excess) is due to the formation of :
(A) Ag_2SO_3 (B) $Ag_2S_2O_3$ (C) $[Ag(S_2O_3)]^-$ (D) $[Ag(S_2O_3)_2]^{3-}$

C-3. In dilute alkaline solution, MnO_4^- changes to :
(A) MnO_4^{2-} (B) MnO_2 (C) Mn_2O_3 (D) MnO

C-4. Cl_2 gas is obtained by various reactions but not by :
(A) $KMnO_4(s) + \text{conc. } HCl \xrightarrow{\Delta}$ (B) $KCl(s) + K_2Cr_2O_7(s) + \text{conc. } H_2SO_4 \xrightarrow{\Delta}$
(C) $MnO_2(s) + \text{conc. } HCl \xrightarrow{\Delta}$ (D) $KCl(s) + F_2(g) \longrightarrow$

C-5. The developer used in photography is an alkaline solution of :
(A) hydroquinol (B) glycerol (C) phenol (D) picric acid

C-6. When acidified solution of $K_2Cr_2O_7$ is shaken with aqueous solution of $FeSO_4$, then :
(A) $Cr_2O_7^{2-}$ ion is reduced to Cr^{3+} ions (B) $Cr_2O_7^{2-}$ ion is converted to CrO_4^{2-} ions
(C) $Cr_2O_7^{2-}$ ion is reduced to Cr (D) $Cr_2O_7^{2-}$ ion is converted to CrO_3

C-7. Which of the following compounds is used as the starting material for the preparation of potassium dichromate?
(A) $K_2SO_4.Cr_2(SO_4)_3.24H_2O$ (chrome alum) (B) $PbCrO_4$ (chrome yellow)
(C) $FeCr_2O_4$ (chromite) (D) $PbCrO_4.PbO$ (chrome red)

C-8. CrO_3 dissolves in aqueous NaOH to give :
(A) CrO_4^{2-} (B) $Cr(OH)_3$ (C) $Cr_2O_7^{2-}$ (D) $Cr(OH)_2$

C-9. The final products obtained for the following reaction is :

$$KMnO_4 \text{ (excess)} + H_2SO_4 \text{ (concentrated and cold)} \longrightarrow$$

(A) Mn_2O_7 (B) MnO (C) Mn_3O_4 (D) MnO_3^+

Section (D) : Lanthanoids and actinoids

D-1. The f-block of the periodic table contains those elements in which :
(A) only 4f orbitals are progressively filled in 6th period.
(B) only 5f orbitals are progressively filled in 7th period.
(C) 4f and 5f orbitals are progressively filled in 6th and 7th periods respectively.
(D) none

D-2. Among the lanthanoides the one obtained by synthetic method is :
(A) Lu (B) Pm (C) Pr (D) Gd

D-3. The most common lanthanoide is :
(A) lanthanum (B) cerium (C) samarium (D) plutonium

D-4. Across the lanthanide series, the basicity of the lanthanoide hydroxides :
(A) increases (B) decreases
(C) first increases and then decreases (D) does not change

D-5. Actinides :
(A) are all synthetic elements (B) includes element 104
(C) have only short lived isotopes (D) have variable valency

D-6. The lanthonoide contraction is reponsible for the fact that
(A) Zr and Y have about the same radius (B) Zr and Nb have similar oxidation state
(C) Zr and Hf have about the same radius (D) Zr and Ce have the same oxidation state

D-7. Lanthanoid and actinides resemble in :
(A) electronic configuration (B) oxidation state
(C) ionization energy (D) formation of complexes

D-8. The separation of lanthanoids by ion exchange method is based on
(A) sizes of the ions (B) oxidation state of the ions
(C) the solubility of their nitrates (D) basicity of hydroxides of lanthanides

PART - III : MATCH THE COLUMN

1. Match the salts/mixtures listed in column(I) with their respective name listed in column(II).

	Column - I		**Column - II**
(A)	$ZnS + BaSO_4$ mixture	(p)	Lunar caustic
(B)	$FeSO_4(NH_4)_2SO_4. 6H_2O$	(q)	Schwitzer`s regent.
(C)	$AgNO_3$	(r)	Lithopone
(D)	$[Cu(NH_3)_4]SO_4$	(s)	Mohr's salt

2. Match the reactions listed in column(I) with the characteristic(s) of the products/type of reactions listed in column(II).

	Column-I		**Column-II**
(A)	$MnO_4^{2-} + CO_2 \longrightarrow$	(p)	a pungent smelling gas is liberated.
(B)	$CrO_4^{2-} + H^+ \longrightarrow$	(q)	Show disproportionation reaction.
(C)	$FeSO_4 \xrightarrow{\Delta}$	(r)	Dimeric bridged tetrahedral metal ion.
(D)	$K_2CrO_4 + Cr_2O_3 + O_2 \longrightarrow$	(s)	One of the products has central metal in its highest stable oxidation state.

3. Match the pairs of complexes/compounds listed in column(I) with the characteristic(s) of the reaction products listed in column(II).

	Column - I		**Column - II**
(A)	Cu(I) and Zn(II) complexes	(p)	Pair of compounds having similar colour and some magnetic moment but equal.
(B)	$KMnO_4$ and $K_2Cr_2O_7$	(q)	Pair of compounds which are diamagnetic but coloured.
(C)	Cu_2O and HgI_2	(r)	Pair of compounds having metals in the highest stable oxidation states.
(D)	$VOCl_2$ and $CuCl_2$	(s)	Pair of compounds which show diamagnetism and are colourless.

Exercise-2

✍ **Marked questions are recommended for Revision.**

PART - I : ONLY ONE OPTION CORRECT TYPE

1.✍ Match the compounds of column X with oxidation state of central atom in column Y.

	Column X	**Column Y**
I	$[Cr(H_2O)_6]Cl_3$	5
II	CrO_5	8
III	HNO_3	6
IV	OsO_4	3

	I	II	III	IV		I	II	III	IV
(A)	3	6	5	8	(B)	3	8	5	6
(C)	8	5	6	3	(D)	6	5	8	3

2.✍ Standard reduction electrode potential of Zn^{2+} / Zn is –0.76 V. This means :
(A) ZnO can’t be reduced to Zn by H_2 under standard conditions.
(B) Zn can't liberates H_2 with concentrated acids
(C) Zn is generally the anode in an electrochemical cell
(D) Zn is generally the cathode in an electrochemical cell

3. Of the ions Zn^{2+}, Ni^{2+} and Cr^{3+} (atomic number Zn = 30, Ni = 28, Cr = 24) :
(A) only Zn^{2+} is colourless and Ni^{2+} and Cr^{3+} are coloured.
(B) all three are colourless.
(C) all three are coloured.
(D) only Ni^{2+} is coloured and Zn^{2+} and Cr^{3+} are colourless.

4. Which of the following group of ions is paramagnetic in nature :
(A) Cu^+, Zn^{2+}, Sc^{3+} (B) $Mn^{2+}, Fe^{3+}, Ni^{2+}$ (C) $Cr^{2+}, Mn^{3+}, Sc^{3+}$ (D) $Cu^{2+}, Ni^{2+}, Ti^{4+}$

5. Which forms interstitial compounds?
(A) Fe (B) Co (C) Ni (D) All

6. When H_2O_2 is added to an acidified solution of $K_2Cr_2O_7$:
(A) solution turns green due to formation of Cr_2O_3
(B) solution turns yellow due to formation of K_2CrO_4
(C) a blue coloured compound $CrO(O_2)_2$ is formed
(D) solution gives green ppt of $Cr(OH)_3$

7. Sodium thiosulphate is used in photography because of its :
(A) oxidising behaviour (B) reducing behaviour
(C) complexing behaviour (D) photochemical behaviour

8.✍ Lanthanide contraction is due to increase in :
(A) shielding by 4f electrons (B) atomic number
(C) effective nuclear charge (D) size of 4f orbitals

9. Which of the following is not an actinide ?
(A) Curium (B) Californium (C) Uranium (D) Terbium

10. The correct statement(s) from among the following is/are ?
(i) all the d and f-block elements are metals
(ii) all the d and f-block elements form coloured ions
(iii) all the d- and f-block elements form paramagnetic ions
(A) (i) only (B) (i) and (ii) (C) (ii) and (iii) (D) All

11.✍ Which of the following statements is not correct ?
(A) $La(OH)_3$ is less basic than $Lu(OH)_3$.
(B) In lanthanide series ionic radius of Ln^{3+} ions decreases.
(C) La is actually an element of transition series rather than lanthanide series.
(D) Atomic radii of Zr and Hf are same because of lanthanide contraction.

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1.✍ Total number of 3d-series transition elements contain either $3d^1$ or $4s^1$ orbital in their ground state electronic configuration.

2.✍ How many of the following show variable oxidation states in their compounds ?
Sc, Cr, Cu, Zn, Fe, Hg, La

3. Magnetic moment value for a d-block ion is 4.90 BM determine value of total spin for it (consider clock wise spin)

4. Determine total number of unpaired electrons in following ions
$Ti^{3+}, V^{3+}, Cr^{3+}, Cr^{2+}, Mn^{3+}, Mn^{2+}, Fe^{3+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}$

5. An element of Ist transition series X^{+3} have highest magnetic moment in series and X^{+2} have non magnetic nature as low spin complex. If Atomic number of X is ‘a’ and number of unpaired e^- in free state X^{+2} and X^{+3} is ‘b’ and ‘c’ then calculate a + b + 2c.

6.✍ Chromite ore is processed through the following sequence :

$$\begin{tikzcd}
FeCr_2O_4 \arrow[r, "Na_2O_2", "Fuse"'] & \{(A) + (B)\} \arrow[r, "Boil", "H_2O"'] & (B)aq. \arrow[rr, "excess\ H^+"] & & (C) \arrow[d, "H_2O_2"] \\
(H) & (G) \arrow[l, "H_2O_2"'] & (F) \arrow[l, "NaOH"', "excess"] & (E) \arrow[l, "NH_3\ little"'] & (D) \arrow[l, "warm\ H^+"', "-O_2"]
\end{tikzcd}$$

In this sequence how many species (from A to H) show green colour ?

7. $KMnO_4 \xrightarrow[R.A.]{H^+} Mn^x$

$KMnO_4 \xrightarrow[R.A.]{OH^-} Mn^y$

$K_2Cr_2O_7 \xrightarrow{OH^-} Cr^z$
$x + y + z$ is :

8. The no. of electrons satisfying $n+l = 7$ for Lu (Atomic number : 71)

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1.✍ Correct statements about transition metals are that they :
(A) form complex
(B) show variable oxidation states
(C) show magnetic properties
(D) do not form coloured compounds

2. Transition elements have greater tendency to form complexes because they have :
(A) vacant d–orbitals
(B) small size
(C) higher nuclear charge
(D) variable oxidation states

3. Which of the following statements are correct ?
(A) Transition elements exhibit higher enthalpies of atomization as they have stronger interatomic interaction.
(B) IE_2 of ${}_{23}V < {}_{24}Cr > {}_{25}Mn$ and ${}_{28}Ni < {}_{29}Cu > {}_{30}Zn$
(C) Ni(II) compounds are more stable than Pt(II) where as Pt(IV) compounds are more stable than nickel (IV).
(D) The elements which gives the greatest number of oxidation states does not occur in or near the middle of the series.

4. The melting point of Zn is lower as compared to those of the other elements of 3d series because :
(A) the d-orbitals are completely filled.
(B) the d-orbitals are partially filled.
(C) d-electrons do not participate in metallic bonding.
(D) size of Zn atom is smaller

5. The less stable oxidation states of Cr are :
(A) Cr^{2+}
(B) Cr^{3+}
(C) Cr^{4+}
(D) Cr^{6+}

6. Which of the following statement is/are correct ?
(A) Transition metals and their many compounds act as good catalyst.
(B) The enthalpies of atomistation of the transition metals are high.
(C) The transition metals generally form interstitial compounds with small atoms like C, B, H etc.
(D) All transition metal compounds are not paramagnetic.

7. Select correct statement (s).
(A) PH_3 reduces $AgNO_3$ to metallic Ag.
(B) Organic tissues turn $AgNO_3$ black by reducing it to Ag.
(C) AgCN is soluble in KCN.
(D) Zr and Ta have almost similar size due to lanthanide contraction.

8. The colour of the transition metal ions is/are due to :
(A) d-d transition of electrons in presence of ligands
(B) charge transfer from ligand to metal ion.
(C) change in the geometry
(D) polarisation of anion by cation

9. Which of the following chemical reaction(s) is/are involved in developing of photographic plate ?
(A) $C_6H_4(OH)_2 + 2AgBr \longrightarrow 2Ag + C_6H_4O_2 + 2HBr$
(B) $AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr$
(C) $2AgNO_3 + Na_2S_2O_3 \longrightarrow Ag_2S_2O_3 + 2NaNO_3$
(D) $AgNO_3 + KCN \longrightarrow AgCN + KNO_3$

10. Which of the following statements are correct when a mixture of NaCl and $K_2Cr_2O_7$ is gently warmed with conc. H_2SO_4 ?
(A) Deep red vapours are liberated
(B) Deep red vapours dissolve in NaOH (aq.) forming a yellow solution.
(C) Greenish yellow gas is liberated
(D) Deep red vapours dissolve in water forming yellow solution

11. Which of the following statement (s) is/are correct ?
(A) $S_2O_8^{2-}$ oxidises Mn^{2+} to give pink colour.
(B) MnO_4^{2-} disproportionates to yield MnO_4^- and MnO_2 in presence of H^+ ions.
(C) In $Cr_2O_7^{2-}$ each Cr is linked to four oxygen atoms.
(D) Ti^{3+} is purple while Ti^{4+} is colourless.

12. Pyrolusite is MnO_2 used to prepare $KMnO_4$. Steps are :

$$MnO_2 \xrightarrow{I} MnO_4^{2-} \xrightarrow{II} MnO_4^-$$

Steps I and II are respectively :
(A) fuse with KOH / air, electrolytic oxidation
(B) fuse with KOH / KNO_3, electrolytic oxidation
(C) fuse with concentrated HNO_3 / air, electrolytic reduction
(D) dissolve in H_2O, oxidation

13. Which of the following statements are correct
(A) Tendency to form complex: $Sc^{+3} > Y^{+3} > La^{+3}$
(B) Most of Ln^{3+} are coloured.
(C) Ln(II) hydroxides are mainly basic in character
(D) Lanthanoids release H_2 on reaction with strong acids

PART - IV : COMPREHENSION

Read the following passage carefully and answer the questions.

Comprehension # 1

Transition metals usually form coloured complexes and d–d transitions ($t_{2g} \rightleftharpoons e_g$) are responsible for colour as the energy difference between t_{2g} and e_g lies in visible region. But all the coloured ions are not due to d–d transition but charge transfer bands also play important roles. Charge transfer bands may be of two types. (i) ligand to metal (CTLM) (ii) metal to ligand (CTML).
Charge transfer transition always produces intense colour as compared to d-d transition.

1. Select the incorrect statement :
(A) d-block metal ions are usually coloured.
(B) Colour of the most of d-block metal ions is generally due to d-d transition.
(C) All the complexes of Cu^+ are colourless on account of diamagnetic nature i.e. d^{10} configuration.
(D) CrO_3 is bright orange due to CTLM.

2. MnO_4^- is dark purple coloured although Mn is in (+ VII) oxidation state with $3d^0$ configuration :
(A) due to d-d transition. (B) due to CTML spectra.
(C) due to CTLM spectra (D) none of these.

Comprehension # 2

Pyrolusite ore on oxidation with $KClO_3/KNO_3$ in basic medium produces dark green coloured compound (A), which on electrolysis produces a purple coloured compound (B). The purple coloured compound can be crystallised to deep purple rhombic prisms. It shows different reactions in different mediums.
Excess of compound (B) on heating with concentrated H_2SO_4 gives an explosive oil (C), which on heating decomposes to gives another compound (D) along with oxygen.

3. On passing CO_2 in the solution of (A), a purple coloured solution along with brown precipitate is observed. Select the correct statement.
(A) This is a disproportionation reaction where oxidation number changes from +6 to +7, +4.
(B) This is a comproportionation reaction where oxidation number changes from +3 to +2.
(C) both (A) and (B).
(D) none

4. The nature of compound (C) is :
(A) basic (B) acidic (C) neutral (D) amphoteric

5. Identify (D).
(A) Mn_2O_7 (B) MnO_2 (C) $MnSO_4$ (D) Mn_2O_3

Comprehension # 3

Answer Q.6, Q.7 and Q.8 by appropriately matching the information given in the three columns of the following table.

Observe the three columns in which column-1 Elements, Column-2 Property (Compare in given elements), while column-3 Aqueous solution of element salts show colours.

Column-1 (Element)		**Column-2 (Property compare in given element)**		**Column-3 (Aqueous solution of element salts show colour)**	
(I)	Fe	(i)	Highest IInd I.E.	(P)	Light pink
(II)	Ni	(ii)	M in $M(CO)_4$ is sp^3 hybridization	(Q)	Green
(III)	Cu	(iii)	(+3) oxidation state is more paramagnetic than (+2)	(R)	Colour less
(IV)	Mn	(iv)	Shows +7 oxidation state (highest)	(S)	Green Pale

6. Which combination is correct :
(A) (I) (i) (P) (B) (II) (ii) (Q) (C) (III) (iii) (S) (D) (IV) (iv) (R)

7. Which combination is/are not correct
(A) (I) (ii) (Q) (B) (III) (i) (R) (C) (I) (iii) (S) (D) (IV) (iv) (P)

8. Which combination is correct for Ni.
(A) (II) (i) (R) (B) (II) (ii) (Q) (C) (II) (iii) (S) (D) (II) (iv) (P)

Exercise-3

*** Marked Questions may have more than one correct option.**

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. Amongst the following identify the species with an atom in +6 oxidation state. **[JEE 2000(S), 3/35]**
(A) MnO_4^- (B) $Cr(CN)_6^{3-}$ (C) NiF_6^{2-} (D) CrO_2Cl_2

2. Write the balanced chemical equations for developing photographic films. **[JEE 2000(M), 2/100]**

3. In the standardization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent weight of $K_2Cr_2O_7$ is :
(A) (molecular weight)/2, (molar mass)/2 (B) (molecular weight)/6
(C) (molecular weight)/3 (D) same as molecular weight **[JEE 2001(S), 3/35]**

4. When MnO_2 is fused with KOH, a coloured compound is formed. The product and its colour is : **[JEE 2003(S), 3/144]**
(A) K_2MnO_4, green (B) Mn_2O_3, brown (C) Mn_2O_4, black (D) $KMnO_4$, purple

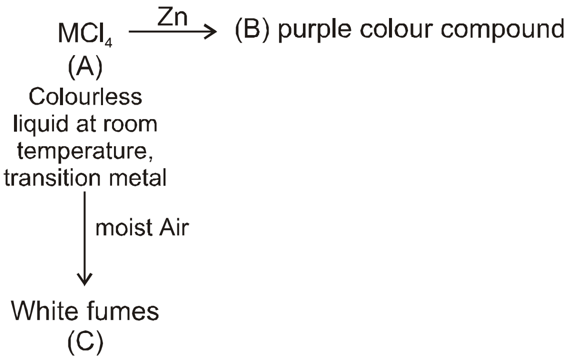
5. The product of oxidation of I^- with MnO_4^- in alkaline medium is : **[JEE 2004(S), 3/144]**
(A) IO_3^- (B) I_2 (C) IO^- (D) IO_4^-

6. The pair of compounds having metals in their highest oxidation state is : **[JEE 2004(S), 3/144]**
(A) MnO_2, $FeCl_3$ (B) $[MnO_4]^-$, CrO_2Cl_2
(C) $[Fe(CN)_6]^{2-}$, $[Co(CN)_6]^{3-}$ (D) $[NiCl_4]^{2-}$, $[Ni(CO)_4]$.

7. Which of the following pair of compounds is expected to exhibit same colour in aqueous solution ? **[JEE 2005(S), 3/84]**
(A) $FeCl_3$, $CuCl_2$ (B) $VOCl_2$, $CuCl_2$ (C) $VOCl_2$, $FeCl_2$ (D) $FeCl_2$, $MnCl_2$

8. Give equations and describe the process for the developing of black and white photographic film. When sodium thiosulphate solution is treated with acidic solution turns milky white. Give the half reaction of the above described process. **[JEE 2005(M), 4/60]**

9.



Identify (A), (B) and (C). Also explain colour difference between MCl_4 and (B). **[JEE 2005(M), 4/60]**

10. Match the reactions in Column I with nature of the reactions/type of the products in Column II. **[JEE 2007, 6/162]**

	Column I		**Column II**
(A)	$O_2^- \rightarrow O_2 + O_2^{2-}$	(p)	Redox reaction
(B)	$CrO_4^{2-} + H^+ \rightarrow$	(q)	One of the products has trigonal planar structure
(C)	$MnO_4^- + NO_2^- + H^+ \rightarrow$	(r)	Dimeric bridged tetrahedral metal ion
(D)	$NO_3^- + H_2SO_4 + Fe^{2+} \rightarrow$	(s)	Disproportionation

11. Among the following, the coloured compound is : **[JEE 2008, 3/163]**
(A) CuCl (B) $K_3[Cu(CN)_4]$ (C) CuF_2 (D) $[Cu(CH_3CN)_4]BF_4$

12. The oxidation number of Mn in the product of alkaline oxidative fusion of MnO_2 is. **[JEE 2009, 4/160]**

13.* Reduction of the metal centre in aqueous permanganate ion involves : **[JEE 2011, 4/180]**
(A) 3 electrons in neutral medium (B) 5 electrons in neutral medium
(C) 3 electrons in alkaline medium (D) 5 electrons in acidic medium

14. The colour of light absorbed by an aqueous solution of $CuSO_4$ is : **[JEE 2012, 3/136]**
(A) organge-red (B) blue-green (C) yellow (D) violet

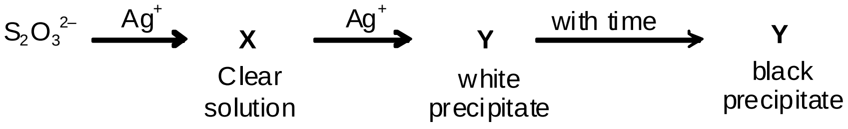
15.* Which of the following halides react(s) with $AgNO_3(aq)$ to give a precipitate that dissolves in $Na_2S_2O_3(aq)$? **[JEE 2012, 4/136]**
(A) HCl (B) HF (C) HBr (D) HI

16. Consider the following list of reagents :
Acidified $K_2Cr_2O_7$, alkaline $KMnO_4$, $CuSO_4$, H_2O_2, Cl_2, O_3, $FeCl_3$, HNO_3 and $Na_2S_2O_3$. The total number of reagents that can oxidise aqueous iodide to iodine is : **[JEE(Advanced) 2014, 3/120]**

17.* The correct statement(s) about Cr^{2+} and Mn^{3+} is (are) : **[JEE(Advanced) 2015, 4/168]**
[Atomic numbers of Cr = 24 and Mn = 25]
(A) Cr^{2+} is a reducing agent
(B) Mn^{3+} is an oxidizing agent
(C) Both Cr^{2+} and Mn^{3+} exhibit d^4 electronic configuration
(D) When Cr^{2+} is used as a reducing agent, the chromium ion attains d^5 electronic configuration.

18.* Fe^{3+} is reduced to Fe^{2+} by using **[JEE(Advanced) 2015, 4/168]**
(A) H_2O_2 in presence of NaOH (B) Na_2O_2 in water
(C) H_2O_2 in presence of H_2SO_4 (D) Na_2O_2 in presence of H_2SO_4

19. In the following reaction sequence in aqueous solution, the species **X**, **Y** and **Z**, respectively, are **[JEE(Advanced) 2016, 3/124]**



(A) $[Ag(SO_2O_3)_2]^{3-}$, $Ag_2S_2O_3$, Ag_2S (B) $[Ag(S_2O_3)_3]^{5-}$, Ag_2SO_3,Ag_2S
(C) $[Ag(SO_3)_2]^{3-}$, $Ag_2S_2O_3$, Ag (D) $[Ag(SO_3)_3]^{3-}$, Ag_2SO_4,Ags

20. Which of the following combination will produce H_2 gas ? **[JEE(Advanced) 2017, 3/122]**
(A) Fe metal and conc. HNO_3
(B) Cu metal and conc. HNO_3
(C) Au metal and NaCN(aq) in the presence of air
(D) Zn metal and NaOH(aq)

PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

JEE(MAIN) OFFLINE PROBLEMS

1. Number of electrons transferred in each case when $KMnO_4$ acts as an oxidising agent to give MnO_2, Mn^{2+}, $Mn(OH)_3$ and MnO_4^{2-} are respectively : **[AIEEE 2002, 3/225]**
(1) 3, 5, 4 and 1 (2) 4, 3, 1 and 5 (3) 1, 3, 4 and 5 (4) 5, 4, 3 and 1

2. Which of the following ions has the maximum magnetic moment? **[AIEEE 2002, 3/225]**
(1) Mn^{2+} (2) Fe^{2+} (3) Ti^{2+} (4) Cr^{2+}.

3. Most common oxidation state fo Ce (Cerium) are : **[AIEEE 2002, 3/225]**
(1) +3, +4 (2) +2, +3 (3) +2, +4 (4) +3, +5

4. What would happen when a solution of potassium chromate is treated with an excess of dilute HNO_3 ? **[AIEEE 2003, 3/225]**
(1) $Cr_2O_7^{2-}$ and H_2O are formed (2) CrO_4^{2-} is reduced to +3 state of Cr
(3) CrO_4^{2-} is oxidised to +7 state of Cr (4) Cr^{3+} and $Cr_2O_7^{2-}$ are formed

5. Which one of the following nitrates will leaves behind a metal on strong heating ? **[AIEEE 2003, 3/225]**
(1) Copper nitrate (2) Manganese nitrate (3) Silver nitrate (4) Ferric nitrate

6. The atomic numbers of V, Cr, Mn and Fe are respectively 23, 24, 25 and 26. Which one of these may be expected to have the highest second ionization enthalpy ? **[AIEEE 2003, 3/225]**
(1) Cr (2) Mn (3) Fe (4) V

7. Which of the following group of transition metals is called coinage metals ? **[AIEEE 2003, 3/225]**
(1) Cu, Ag, Au (2) Ru, Rh, Pb (3) Fe, Co, Ni (4) Os. Ir, Pt

8. The number of d-electrons retained in Fe^{2+} (At. no. Fe = 26) ions are : **[AIEEE 2003, 3/225]**
(1) 3 (2) 4 (3) 5 (4) 6

9. Ammonia forms the complex ion $[Cu(NH_3)_4]^{2+}$ with copper ions in the alkaline solutions but not in acidic solutions. What is the Statement-2 for it ? **[AIEEE 2003, 3/225]**
(1) In acidic solutions hydration protects copper ions
(2) In acidic solutions protons co-ordinate with ammonia molecules forming NH_4^+ ions and NH_3 molecules are not available.
(3) In alkaline solutions insoluble $Cu(OH)_2$ is precipitated which is soluble in excess of any alkali
(4) Copper hydroxide is an amphoteric substance.

10. The radius of La^{3+} (Atomic number of La = 57) is 1.06Å. Which one of the following given values will be closest to the radius of Lu^{3+} (Atomic number of Lu = 71) ? **[AIEEE 2003, 3/225]**
(1) 1.60Å (2) 1.40Å (3) 1.06Å (4) 0.85Å

11. Cerium (Z = 58) is an important member of the lanthanoide. Which of the following statement about cerium is incorrect? **[AIEEE 2004, 3/225]**
(1) The common oxidation state of cerium are +3 and +4.
(2) The +3 oxidation state of cerium is more stable than +4 oxidation state.
(3) The +4 oxidation state of cerium is not known in solution.
(4) Cerium (IV) acts as an oxidizing agent.

12. The lanthanide contraction is responsible for the fact that **[AIEEE 2005, 3/225]**
(1) Zr and Y have about the same radius
(2) Zr and Nb have similar oxidation state
(3) Zr and Hf have about the same radius
(4) Zr and Zn have same oxidation state.

13. Which of the following factors may be regarded as the main cause of lanthanide contraction ?

(1) Greater shielding of 5d electrons by 4f electrons **[AIEEE 2005, 4½/225]**
(2) Poorer shielding of 5d electron by 4f electrons
(3) Effective shielding of one of 4f electrons by another in the sub-shell
(4) Poor shielding of one of 4f electron by another in the sub-shell.

14. The ''spin-only'' magnetic moment [in units of Bohr magneton, (μ_B) of Ni^{2+} in aqueous solution would be (atomic number of Ni = 28) **[AIEEE 2006, 3/165]**

(1) 2.84 (2) 4.90 (3) 0 (4) 1.73

15. Lanthanoid contraction is caused due to : **[AIEEE 2006, 3/165]**

(1) the appreciable shielding on outer electrons by $4f$ electrons from the nuclear charge
(2) the appreciable shielding on outer electrons by $5f$ electrons from the nuclear charge
(3) the same effective nuclear charge from Ce to Lu
(4) the imperfect shielding on outer electrons by 4f electrons from the nuclear charge

16. Identify the incorrect statement among the following. **[AIEEE 2007, 3/120]**

(1) The chemistry of various lanthanoids is very similar.
(2) 4f and 5f orbitals are equally shielded.
(3) d-block elements show irregular and erratic chemical properties among themselves.
(4) La and Lu have partially filled d orbitals and no other partially filled orbitals.

17. The actinoids exhibit more number of oxidation states in general than the lanthanoids. This is because

(1) The actinoids are more reactive than the lanthanoids. **[AIEEE 2007, 3/120]**
(2) The 5f orbitals extend farther from the nucleus than the 4f orbitals.
(3) The 5f orbitals are more buried than the 4f orbitals
(4) There is a similarity between 4f and 5f orbitals in their angular part of the wave function

18. Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being. **[AIEEE 2008, 3/105]**

(1) lesser energy difference between 5f and 6d than between 4f and 5d orbitals
(2) more energy difference between 5f and 6d than between 4f and 5d orbitals
(3) more reactive nature of the actinoids than the lanthanoids
(4) 4f orbitals more diffused than the 5f orbitals

19. In context with the transition elements, which of the following statements is incorrect?

[AIEEE 2009, 4/144]

(1) In the highest oxidation states, the transition metal show basic character and form cationic complexes.
(2) In the highest oxidation states of the first five transition elements (Sc to Mn), all the 4s and 3d electrons are used for bonding.
(3) Once the d^5 configuration is exceeded, the tendency to involve all the 3d electrons in bonding decreases.
(4) In addition to the normal oxidation states, the zero oxidation state is also shown by these elements in complexes.

20. Knowing that the Chemistry of lanthanoids (Ln) is dominated by its +3 oxidation state, which of the following statement is incorrect ? **[AIEEE 2009, 4/144]**

(1) The ionic sizes of Ln (III) decrease in general with increasing atomic number.
(2) Ln (III) compounds are generally colourless.
(3) Ln (III) hydroxides are mainly basic in character
(4) Because of the large size of the Ln (III) ions the bonding in its compounds is predominently ionic in character.

21. The correct order of $E^0_{M^{2+}/M}$ values with negative sign for the four successive elements Cr, Mn, Fe and Co is : **[AIEEE 2010, 4/144]**

(1) Mn > Cr > Fe > Co (2) Cr > Fe > Mn > Co
(3) Fe > Mn > Cr > Co (4) Cr > Mn > Fe > Co

22. In context of the lanthanoids, which of the following statement is not correct ? **[AIEEE 2011, 4/120]**
(1) There is a gradual decrease in the radii of the members with increasing atomic number in the series.
(2) All the member exhibit +3 oxidation state.
(3) Because of similar properties the separation of lanthanoids is not easy.
(4) Availability of 4f electrons results in the formation of compounds in +4 state for all the members of the series.

23. The outer electron configuration of Lu (Atomic No : 71) is : **[AIEEE 2011, 4/120]**
(1) $4f^3\ 5d^5\ 6s^2$ (2) $4f^8\ 5d^0\ 6s^2$ (3) $4f^4\ 5d^4\ 6s^2$ (4) $4f^{14}\ 5d^1\ 6s^2$

24. Iron exhibits +2 and + 3 oxidation states. Which of the following statements about iron is incorrect ?
(1) Ferrous oxide is more basic in nature than the ferric oxide. **[AIEEE 2012, 4/120]**
(2) Ferrous compounds are relatively more ionic than the corresponding ferric compounds
(3) Ferrous compounds are less volatile than the corresponding ferric compounds
(4) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds.

25. Which of the following arrangements does not represent the correct order of the property stated against it? **[JEE(Main) 2013, 4/120]**
(1) $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: paramagnetic behaviour
(2) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: ionic size
(3) $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: stability in aqueous solution
(4) Sc < Ti < Cr < Mn : number of oxidation states

26. Four successive members of the first row transition elements are listed below with atomic numbers. Which one of them is expected to have the highest $E^{\circ}_{M^{3+}/M^{2+}}$ value ? **[JEE(Main) 2013, 4/120]**
(1) Cr(Z = 24) (2) Mn(Z = 25) (3) Fe(Z = 26) (4) Co(Z = 27)

27. Which series of reactions correctly represents chemical relations related to iron and its compound ?
(1) $Fe \xrightarrow{\text{dil. } H_2SO_4} FeSO_4 \xrightarrow{H_2SO_4,\ O_2} Fe_2(SO_4)_3 \xrightarrow{\text{heat}} Fe$
(2) $Fe \xrightarrow{O_2,\ \text{heat}} FeO \xrightarrow{\text{dil. } H_2SO_4} FeSO_4 \xrightarrow{\text{heat}} Fe$
(3) $Fe \xrightarrow{Cl_2,\ \text{heat}} FeCl_3 \xrightarrow{\text{heat, air}} FeCl_2 \xrightarrow{Zn} Fe$
(4) $Fe \xrightarrow{O_2,\ \text{heat}} Fe_3O_4 \xrightarrow{CO,\ 600^{o}C} FeO \xrightarrow{CO,\ 700^{o}C} Fe$ **[JEE(Main) 2014, 4/120]**

28. The equation which is balanced and represents the correct product(s) is : **[JEE(Main) 2014, 4/120]**
(1) $Li_2O + 2KCl \longrightarrow 2LiCl + K_2O$
(2) $[CoCl(NH_3)_5]^+ + 5H^+ \longrightarrow Co^{2+} + 5NH_4^+ + Cl^-$
(3) $[Mg(H_2O)_6]^{2+} + (EDTA)^{4-} \xrightarrow{\text{excess NaOH}} [Mg(EDTA)]^{2+} + 6H_2O$
(4) $CuSO_4 + 4KCN \longrightarrow K_2[Cu(CN)_4] + K_2SO_4$

29. Match the catalysts to the correct processes : **[JEE(Main)-2015, 4/120]**

	Catalyst		**Process**
(A)	$TiCl_3$	(i)	Wacker process
(B)	$PdCl_2$	(ii)	Ziegler-Natta polymerization
(C)	$CuCl_2$	(iii)	Contact process
(D)	V_2O_5	(iv)	Deacon's process

(1) (A) - (iii), (B) - (ii), (C) - (iv), (D) - (i) (2) (A) - (ii), (B) - (i), (C) - (iv), (D) - (iii)
(3) (A) - (ii), (B) - (iii), (C) - (iv), (D) - (i) (4) (A) - (iii), (B) - (i), (C) - (ii), (D) - (iv)

30. The colour of $KMnO_4$ is due to : **[JEE(Main) 2015, 4/120]**
(1) M → L charge transfer transition (2) d – d transition
(3) L → M charge transfer transition (4) $\sigma - \sigma^*$ transition

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JEE(MAIN) ONLINE PROBLEMS

1. Chloro compound of Vanadium has only spin magnetic moment of 1.73 BM. This Vanadium chloride has the formula : (at. no. of V = 23) **[JEE(Main) 2014 Online (09-04-14), 4/120]**
(1) VCl_2 (2) VCl_4 (3) VCl_3 (4) VCl_5

2. Which one of the following exhibits the largest number of oxidation states?
[JEE(Main) 2014 Online (12-04-14), 4/120]
(1) Ti (22) (2) V(23) (3) Cr (24) (4) Mn (25)

3. Copper becomes green when exposed to moist air for a long period. This is due to :
[JEE(Main) 2014 Online (12-04-14), 4/120]
(1) the formation of a layer of cupric oxide on the surface of copper.
(2) the formation of a layer of basic carbonate of copper on the surface of copper.
(3) the formation of a layer of cupric hydroxide on the surface of copper.
(4) the formation of basic copper sulphate layer on the surface of the metal.

4. Which of the following statements is false ? **[JEE(Main) 2015 Online (11-04-15), 4/120]**
(1) $Na_2Cr_2O_7$ is less soluble than $K_2Cr_2O_7$
(2) $Na_2Cr_2O_7$ is primary standard in volumetry
(3) CrO_4^{2-} is tetrahedral in shape
(4) CrO_7^{2-} has a Cr–O–Cr bond

5. Which one of the following species is stable in aqueous solution?
[JEE(Main) 2016 Online (09-04-16), 4/120]
(1) MnO_4^{2-}
(2) MnO_4^{3-}
(3) Cu^{+}
(4) Cr^{2+}

6. The transition metal ions responsible for color in ruby and emerald are, respectively :
[JEE(Main) 2016 Online (10-04-16), 4/120]
(1) Cr^{3+} and Cr^{3+}
(2) Co^{3+} and Co^{3+}
(3) Co^{3+} and Cr^{3+}
(4) Cr^{3+} and Co^{3+}

7. The pair of compounds having metals in their highest oxidation state is :
[JEE(Main) 2017 Online (08-04-17), 4/120]
(1) MnO_2 and CrO_2Cl_2
(2) $[FeCl_4]^-$ and Co_2O_3
(3) $[Fe(CN)_6]^{3-}$ and $[Cu(CN)_4]^{2-}$
(4) $[NiCl_4]^{2-}$ and $[CoCl_4]^{2-}$

8. When XO_2 is fused with an alkali metal hydroxide in presence of an oxidizing agent such as KNO_3 ; a dark green product is formed which disproportioates in acidic solution to afford a dark purple solution. X is : **[JEE(Main) 2018 Online (16-04-18), 4/120]**
(1) Mn
(2) Cr
(3) V
(4) Ti

9. The highest value of the calculated spin–only magnetic moment (in BM) among all the transition metal complexes is : **[JEE(Main) 2019 Online (09-01-19), 4/120]**
(1) 4.90
(2) 6.93
(3) 3.87
(4) 5.92

10. The transition element that has lowest enthalpy of atomisation, is :
[JEE(Main) 2019 Online (09-01-19), 4/120]
(1) V
(2) Fe
(3) Zn
(4) Cu

11. The 71st electron of an element X with an atomic number of 71 enters into the orbital:
[JEE(Main) 2019 Online (10-01-19), 4/120]
(1) 6s
(2) 5d
(3) 4f
(4) 6p

12. The element that usually does NOT show variable oxidation states is :
[JEE(Main) 2019 Online (11-01-19), 4/120]
(1) Cu
(2) Ti
(3) Sc
(4) V

13. $\underline{A} \xrightarrow{4KOH, O_2} 2\underline{B} + 2H_2O$
(Green)
$3\,\underline{B} \xrightarrow{4HCl} 2\underline{C} + MnO_2 + 2H_2O$
(Purple)
$2\,\underline{C} \xrightarrow{H_2O, KI} 2\underline{A} + 2\,KOH + \underline{D}$
In the above sequenec of reactions,
$\underline{A}$ and $\underline{D}$, respectively, are : **[JEE(Main) 2019 Online (11-01-19), 4/120]**
(1) KIO_3 and MnO_2
(2) MnO_2 and KIO_3
(3) KI and K_2MnO_4
(4) KI and $KMnO_4$

14. The pair of metal ions that can give a spin-only magnetic moment of 3.9 BM for the complex $[M(H_2O)_6]Cl_2$ is : **[JEE(Main) 2019 Online (12-01-19), 4/120]**
(1) Cr^{2+} and Mn^{2+}
(2) V^{2+} and Co^{2+}
(3) V^{2+} and Fe^{2+}
(4) Co^{2+} and Fe^{2+}

15. The correct order of atomic radii is : **[JEE(Main) 2019 Online (12-01-19), 4/120]**
(1) Eu > Ce > Ho > N
(2) N > Ce > Eu > Ho
(3) Ce > Eu > Ho > N
(4) Ho > N > Eu > Ce

Answers

EXERCISE - 1

PART - I

A-1. $(n-1)\ d^{1-10}\ ns^{1-2}$ (palladium is exception); $[Kr]^{36}\ 4d^{10}\ 5s^0$.

A-2. (i) $[Ar]\ 3d^5\ 4s^0$ (ii) $[Ar]\ 3d^5\ 4s^0$ (iii) $[Ar]\ 3d^8\ 4s^0$ (iv) $[Ar]\ 3d^3\ 4s^0$

A-3. Zn, Cd and Hg have $(n-1)d^{10}ns^2$ electron configuration in their atoms and $(n-1)d^{10}ns^0$ electron configuration in their most stable simple ions i.e. M^{2+}. So they do not have partially filled d-orbitals in their atoms or in their simple ions.

A-4. Lanthanide contraction phenomenon is associated with the intervention of the 4f orbitals which must be filled before the 5d series of elements begin. The filling of 4f before 5d orbital results in a regular decrease in atomic radii called **Lanthanoid contraction.** This essentially compensates for the expected increase in atomic size with increasing atomic number. The net result of the lanthanoid contraction is that the second and the third d-series exhibit similar radii and have very similar physical and chemical properties.

A-5. (i) Sc (ii) Os or Ir

A-6. (i) As Hg has weakest interatomic interaction on account of no unpaired electrons, $(n-1)d^{10}ns^2$ available for bonding.
(ii) As W has highest interatomic interaction on account of more number of unpaired electrons, $(n-1)d^5\ ns^1$ available for bonding.

A-7. In case of zinc, no electrons from 3d-orbitals are involved in the formation of metallic bonds.

A-8. In the 5d series, after lanthanum (Z = 57), there is lanthanide contraction. As a result, in each group the atomic size of 5d element is small and its nuclear charge is large. Hence the ionisation energies of 5d elements are large than 3d elements.

A-9. The energies of (n – 1)d orbitals and ns orbitals are very close. Hence, electrons from both can participate in bonding.

A-10. +2

B-1. (i) enthalpy of sublimation (ii) ionisation energy (iii) enthalpy of hydration

B-2. Much larger third ionisation energy of Mn (change from $3d^5$ to $3d^4$) is responsible for this. This also explains why the +3 state of Mn is of little importance.

B-3. (i) Mn^{2+} is more stable than Fe^{3+}.
(ii) The order of getting oxidised is Mn > Cr > Fe.

B-4. (i) Ti^{3+} ($3d^1$), Cu^{2+} ($3d^9$) and Mn^{2+} ($3d^5$) have unpaired electron(s). Thus they are coloured due to d-d transition of electron according to CFT.
(ii) Zn^{2+}($3d^{10}$), Ti^{+4} ($3d^0$) and Cd^{2+} ($4d^{10}$) do not have unpaired electron(s). Thus they do not under go d-d transition of electron according to CFT and, therefore, are colourless.

B-5. Electronic configuration of $_{22}Ti^{+4}$ is $[Ar]^{18}\ 3d^04s^0$. So all electrons are paired and thus its all complexes are diamagnetic.

B-6. μ_B = 3.9 BM, n = 3

B-7. (a) As metal ions generally contain one or more unpaired electrons in them & hence their complexes are generally paramagnetic.
(b) Because of having larger number of unpaired electrons in their atoms, they have stronger interatomic interaction and hence stronger bonding between the atoms.
(c) May be attributed to the presence of unpaired electrons (d-d transition in most of the compounds)

B-8. (i) The transition metals form reaction intermediates due to the presence of vacant orbitals or their tendency to form variable oxidation states. These intermediates give reaction paths of lower activation

energy and, therefore, increase the rate of the reaction. These reaction intermediates readily decompose yielding the products and regenerating the original substance.
(ii) The transition elements form a large number of coordination complexes. The transition metal ions bind to a number of anions or neutral molecules in these complexes. The great tendency of transition metal ions to form complexes is due to (i) small size of the atoms and ions, (ii) high nuclear charge and (iii) availability of vacant d-orbitals of suitable energy to accept lone pairs of electrons donated by ligands.
(iii) Transition metals form interstitial compounds with elements such as hydrogen, boron, carbon and nitrogen. The small atoms of these non-metallic elements (H, B, C, N etc.) get trapped in vacant spaces of the lattices of the transition metal atoms.
As a result of the filling up of the interstitial spaces, the transition metals become rigid and hard. These interstitial compounds have similar chemical properties as the parent metals but differ significantly in their physical properties particularly, density, hardness and conductivity.

C-1. It is unstable in acidic medium and disproportionates.
$3MnO_4^{2-} + 4H^+ \longrightarrow MnO_2 + 2MnO_4^- + 2H_2O$
$3MnO_4^{2-} + 2H_2O \longrightarrow 2MnO_4^- + MnO_2 + 4OH^-$

C-2. MnO_4^- solutions are intrinsically unstable in acidic solutions and decompose slowly. This decomposition is catalysed by sun light. This is the Statement-2 for which $KMnO_4$ solution is kept in dark bottles.

$$4MnO_4^- + 4H^+ \xrightarrow{h\nu} 4MnO_2 + 3O_2 + 2H_2O$$

C-3. In presence of organic matter (skin) and light, $AgNO_3$ decomposes to produce a black stain of metallic silver.

$$2AgNO_3 \longrightarrow 2Ag + 2NO_2 + O_2$$

C-4. Out of all silver halides, AgBr is most sensitive to light and under goes photo reduction to metallic silver instantaneously on exposure to light.

$$2AgBr \longrightarrow 2Ag + Br_2$$

Unexposed AgBr can be dissolved out in hypo ($Na_2S_2O_3$) solution.

$$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr.$$

C-5. Because explosive Mn_2O_7 is formed.

$$2KMnO_4 + 2H_2SO_4 \longrightarrow Mn_2O_7 + 2KHSO_4 + H_2O$$
$$2Mn_2O_7 \longrightarrow 4MnO_2 + 3O_2$$

C-6. (a) $FeSO_4.7H_2O \xrightarrow[H_2O]{300°C} FeSO_4 \xrightarrow[tempt]{high} Fe_2O_3 + SO_2 + SO_3$
(b) $CuCO_3.Cu(OH)_2 + 2H_2SO_4 \longrightarrow 2CuSO_4 + 3H_2O + CO_2\uparrow$
(c) $CuSO_4.5H_2O \xrightarrow[effloresces]{air} CuSO_4 .3H_2O$
(d) $2AgNO_3 + 2NaOH \longrightarrow Ag_2O\downarrow$ (black) $+ 2NaNO_3 + H_2O$
(e) $5AgNO_3 + 3I_2$ (excess) $+ H_2O \longrightarrow HIO_3 + 5AgI\downarrow$ (yellow) $+ 5HNO_3$
(f) $K_2Cr_2O_7 + 2H_2SO_4$ (conc. & cold) $\longrightarrow 2CrO_3$ (red) $+ 2KHSO_4 + H_2O$

C-7. True

C-8. (i) $K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow \underset{Orange}{2CrO_2Cl_2}\uparrow + 4NaHSO_4 + 2KHSO_4 + 3H_2O$
(ii) $2KMnO_4 + 3MnSO_4 + 2H_2O \longrightarrow 5MnO_2 + K_2SO_4 + 2H_2SO_4$
(iii) $K_2Cr_2O_7 + 14HCl \xrightarrow[\Delta]{} 2KCl + 2CrCl_3 + 7H_2O + 3Cl_2$

D-1. The f-block elements, in which the last electron enters into f-subshell are called inner transition elements. These include lanthanoids (58-71) and actinoids (90-103). Thus elements with atomic numbers 59, 95 and 102 are inner transition elements.

D-2. The 5f electrons are more effectively shielded from nuclear charge. In other words the 5f electrons themselves provide poor shielding from element to element in the series.

D-3. Lanthanoids show limited number of oxidation state, viz, +2, +3 and +4 (out of which +3 is most common). This is because of large energy gap between 4f, 5d and 6s subshells, the dominant oxidation state of actinoids is also + 3 but they show a number of other oxidation states also, e.g. uranium (Z = 92) and plutonium (Z = 94), show +3 +4 +5 and +6 neptunium (Z = 94) shows +3 +4 +5 and +7 etc. This is due to small energy difference between 5f, 6d and 7s subshell of the actinoids

D-4. The most stable oxidation state of lanthanoides is +3. Hence, ions in +2 state tend to change to +3 state by loss of electron and those in +4 state tend to change to +3 state by gain of electron.

PART - II

A-1.	(C)	**A-2.**	(C)	**A-3.**	(B)	**A-4.**	(B)	**A-5.**	(C)
A-6.	(A)	**B-1.**	(A)	**B-2.**	(B)	**B-3.**	(A)	**B-4.**	(D)
B-5.	(C)	**B-6.**	(C)	**B-7.**	(C)	**B-8.**	(C)	**B-9.**	(D)
C-1.	(B)	**C-2.**	(D)	**C-3.**	(B)	**C-4.**	(B)	**C-5.**	(A)
C-6.	(A)	**C-7.**	(C)	**C-8.**	(A)	**C-9.**	(A)	**D-1.**	(C)
D-2.	(B)	**D-3.**	(B)	**D-4.**	(B)	**D-5.**	(D)	**D-6.**	(C)
D-7.	(A)	**D-8.**	(A)						

PART - III

1. (A) - r ; (B) - s ; (C) - p ; (D) - q.

2. (A) - q, s ; (B) - r, s ; (C) - p, s ; (D) - s

3. (A) - s ; (B) - q, r ; (C) - q ; (D) – p

EXERCISE - 2

PART - I

1.	(A)	**2.**	(A)	**3.**	(A)	**4.**	(B)	**5.**	(D)
6.	(C)	**7.**	(C)	**8.**	(C)	**9.**	(D)	**10.**	(A)
11.	(A)								

PART - II

1.	3	**2.**	4	**3.**	2	**4.**	34		
5.	(26 + 4 + (2 × 5)) = 40			**6.**	3	**7.**	12	**8.**	15

PART - III

1.	(ABC)	**2.**	(ABC)	**3.**	(ABC)	**4.**	(AC)	**5.**	(ACD)
6.	(ABCD)	**7.**	(ABC)	**8.**	(ABD)	**9.**	(AB)	**10.**	(ABD)
11.	(ABCD)	**12.**	(AB)	**13.**	(ABCD)				

PART - IV

1.	(C)	**2.**	(C)	**3.**	(A)	**4.**	(B)	**5.**	(B)
6.	(B)	**7.**	(B)	**8.**	(B)				

EXERCISE - 3

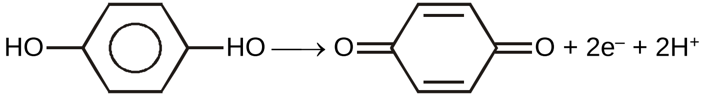
PART - I

1. (D)

2. $C_6H_4(OH)_2 + 2AgBr \longrightarrow 2Ag + C_6H_4O_2 + 2HBr.$
$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr.$

3. (B) **4.** (A) **5.** (A) **6.** (B) **7.** (B)

8. Developer is usually a weak reducing agent like potassium ferrous oxalate, an alkaline solution of pyrogallol or an alkaline solution of quinol.
In the process of development of the photographic film, the exposed/activated AgBr grains are preferentially reduced by one of the reducing agent described above.



Hydroquinone Quinone

$AgBr + e^- \longrightarrow Ag(s) + Br^-$

The photographic film is then fixed by washing with hypo solution to remove the unreduced AgBr grains from the film.

$AgBr + 2Na_2S_2O_3 \longrightarrow Na_3[Ag(S_2O_3)_2] + NaBr.$
$S_2O_3^{2-} + H_2O \longrightarrow 2SO_2 + 2H^+ + 4e^-.$
$S_2O_3^{2-} + 6H^+ \longrightarrow 2S \downarrow \text{(white milky)} + 3H_2O.$

9. (A) is $TiCl_4$ as it has no unpaired electron and is liquid at room temperature on account of covalent character because of high polarising power of Ti^{+4}. $TiCl_4$ being covalent gets hydrolysed forming $TiO_2(H_2O)_2$ and HCl (B) which fumes in air.
In $[Ti(H_2O)_6]Cl_3$ complex Ti(III) has one unpaired electron($3d^1$) which gives violet / purple colour due to d-d transition.

$$\begin{tikzcd} \underset{\text{Colour less}}{\underset{(A)}{TiCl_4}} \arrow[r, "Zn"] \arrow[d, "\text{moist air}"] & TiCl_3 \arrow[r, "\text{Hydrolysis}", "H_2O"'] & \underset{(B)}{\underset{\text{purple or violet}}{[Ti(H_2O)_6]Cl_3}} \\ TiO_2.(H_2O)_2 + HCl \ \text{(white fumes)} & & \end{tikzcd}$$

10. (A – p, s); (B – r); (C – p, q); (D – p). **11.** (C) **12.** 6

13.* (ACD)/(AD) **14.** (A) **15.*** (ACD) **16.** 7

17.* (ABC) **18.*** (CD) **19.** (A) **20.** (D)

PART - II

JEE(MAIN) OFFLINE PROBLEMS

1.	(1)	**2.**	(1)	**3.**	(1)	**4.**	(1)	**5.**	(3)
6.	(1)	**7.**	(1)	**8.**	(4)	**9.**	(2)	**10.**	(4)
11.	(3)	**12.**	(3)	**13.**	(4)	**14.**	(1)	**15.**	(4)
16.	(2)	**17.**	(2)	**18.**	(1)	**19.**	(1)	**20.**	(2)
21.	(1)	**22.**	(4)	**23.**	(4)	**24.**	(4)	**25.**	(1)
26.	(4)	**27.**	(4)	**28.**	(2)	**29.**	(2)	**30.**	(3)

JEE(MAIN) ONLINE PROBLEMS

1.	(2)	**2.**	(4)	**3.**	(2)	**4.**	(1)	**5.**	(1)
6.	(1)	**7.**	(3)	**8.**	(1)	**9.**	(4)	**10.**	(3)
11.	(2)	**12.**	(3)	**13.**	(2)	**14.**	(2)	**15.**	(1)