



Name :

Time : 6 hr

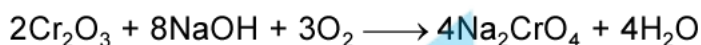
Total Marks = 66

Date: 23/10/2017

S1. (a) (i) Reactivity decreases with increase in atomic number of due to decrease in size and increase in ionisation energy.

(ii) In *d*-block elements, electrons *s*-orbital and *d*-orbital both take part in bond formation. In *f*-block elements due to poor shielding effect of *f*-electrons effective nuclear charge increases. Therefore, fewer number of oxidation states are shown.

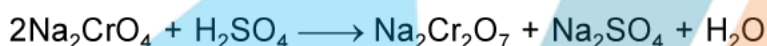
(b) Compounds A, B, C and D are identified with the help of the following equations



'A'

(yellow)

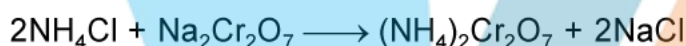
'B'



'B'

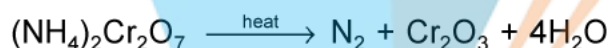
(orange)

'C'



(orange)

'D'

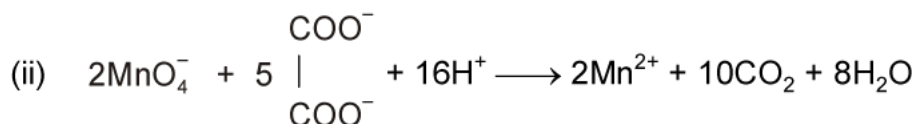
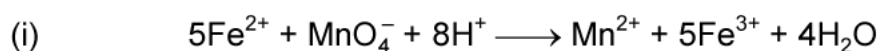


Ammonium
dichromate

(green)

'A'

S2. (a) Oxidation of Fe^{2+} into Fe^{3+} and decomposition of oxalate in the presence of KMnO_4 in acidic medium is explained with the help of following equations.



(b) (i) Cr^{2+} (d^4) is less stable than Cr^{3+} (d^5), therefore, it is good reducing agent whereas Mn^{2+} is stable due to half filled *d*-orbitals. It does not change into Mn^{3+} easily therefore, it is not reducing agent.

(ii) Cu^+ , Ag^+ and Sc^{3+} are colourless because they do not have unpaired electrons.

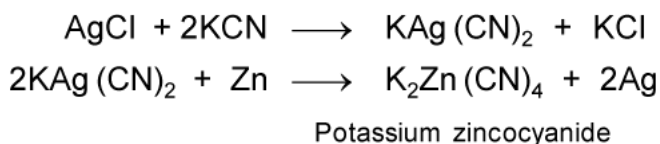
(iii) In actinoids, energies of $5f$, $6d$ and $7s$ orbitals are comparable and, therefore, they show large number of oxidation states compared to lanthanoids. That is why their chemistry is more complicated. Secondly, all of them are radioactive and their study becomes difficult. Also there is possibility of frequent electronic transition among $5f$, $6d$ and $7s$ orbitals.

- S3.** (a) **Electronic configurations:** 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, actinoids show a large number of oxidation states because of small energy gap between $5f$ and $6d$ subshells.
- (c) **Atomic and ionic sizes:** Both lanthanoids and actinoids show decrease in size of their atoms or ions in +3 oxidation state. In lanthanoids, the decrease is called lanthanoid contraction and in actinoids, it is called actinoid contraction.

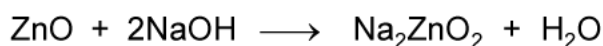
- S4.** (a) **Metallic character:** Since the number of electrons in the outermost shell are two or one and can be removed easily. Therefore, all the transition elements are metals. All three of structures: fcc, hcp and bcc are shown by them. The electrons present in the outermost orbitals form metallic bonds. Due to these metallic bonds they have high melting and boiling points and high thermal and electrical conductivities. All transition metals except Hg, are malleable and ductile.
- (b) **Ionisation energies:** The first ionization energies of transition element lie between the value of ionization energies of s -block and p -block elements. In transition elements last electron goes to $(n - 1) d$ sub-shell which shields the outer ns electrons from the inward pull due to the attraction by the nuclear.

The nuclear charge and shielding effect of $(n - 1)d$ electrons will increase with the increase in atomic number. The ionization energies gradually increase in a particular series of d -block elements. This is due to decrease in size with the increase in atomic numbers which will make the removal of electron difficult. However, shielding effect will also increase with the increase in atomic number which will oppose the decrease in size. Due to these two opposite effects (increased nuclear charge and shielding effect), ionization energies will increase rather slowly in the $3d$ -series.

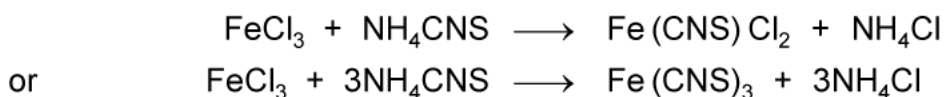
- S5.** (a) AgCl dissolves in KCN forming a complex, potassium argentocyanide. The addition of zinc precipitates silver.



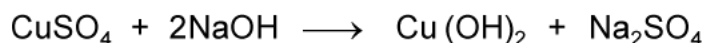
- (b) ZnO dissolves in NaOH forming sodium zincate.



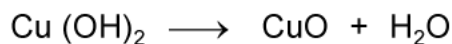
- (c) Deep red coloration due to the formation of a complex is developed.



- 56.** (a) NaOH reacts with CuSO₄ when dark blue precipitate of Cu(OH)₂ is formed. This precipitate on heating forms CuO which is black in colour. Hence, the colour darkens on heating.

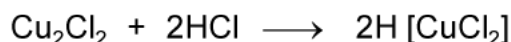


Blue

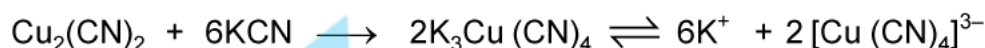
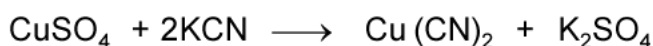


Black

- (b) Cu₂Cl₂ dissolves in conc. HCl due to the formation of a copper complex.



- (c) CuSO₄ forms a complex with KCN.



K₃Cu(CN)₄ complex does not furnish Cu²⁺ ions. Hence, no precipitate of CuS is formed when H₂S is passed through solution.

- (d) AgNO₃ is photosensitive. It decomposes in presence of light. To prevent its decomposition, it is kept in coloured bottles as these do not permit light to pass through.

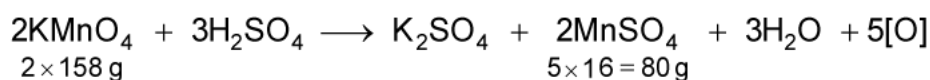
- 57.** (a) The most stable oxidation state of lanthanides is +3. Hence, ions in +2 state tend to change to +3 oxidation state by loss of electron and act as reducing agents.

- (b) La³⁺ has a stable configuration of an inert gas [(Xe)5d⁰6s⁰], i.e., xenon (54–2, 8, 18, 18, 8). To obtain +4 oxidation state, the stable configuration is to be disturbed which is not possible under ordinary conditions and hence La⁴⁺ does not exist.

- (c) This is because gadolinium in +3 state has half filled 4f-subshell (4f⁷) and lutetium in +3 state has completely filled 4f-subshell which are very stable configurations.

- (d) Due to lanthanide contraction, the atomic radii of both Zr and Hf are same. Hence, their properties are similar.

- 58.** Oxidising action of KMnO₄ acidic medium is represented as:



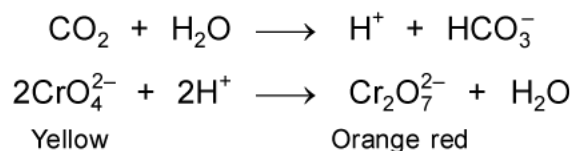
$$\text{Eq. mass of KMnO}_4 = \frac{2 \times 158}{80} \times 8 = 31.6$$

or
$$\text{Eq. mass of KMnO}_4 = \frac{\text{Molecular mass}}{\text{Number of electrons gained per molecule}} = \frac{158}{5} = 31.6$$

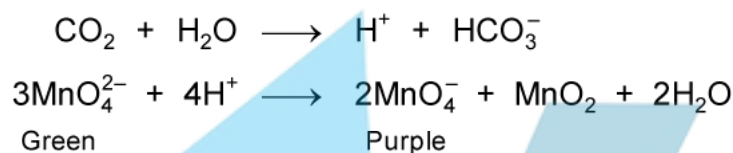


$$\text{Eq. mass of KMnO}_4 = \frac{\text{Molecular mass}}{\text{Change in oxidation state per molecule}} = \frac{158}{5} = 31.6$$

- S9.** (a) Yellow coloured aqueous solution of sodium chromate changes to orange red on passing CO_2 as H^+ ions are formed which are responsible for conversion of chlorate into dichromate.



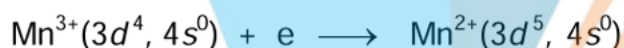
- (b) CO_2 gives H^+ ions which are responsible for conversion of manganate (green) to permanganate (purple).



- S10.** (a) Ce^{3+} has the configuration $4f^1 5d^0 6s^0$. It can easily lose an electron to acquire more stable configuration ($4f^0 5d^0 6s^0$), i.e., configuration of an inert gas, xenon (2, 8, 18, 18, 8), i.e., Ce^{3+} can be easily oxidised to Ce^{4+} .



- (b) E° for $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is more positive than for $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple because Mn^{2+} state is more stable than Mn^{3+} state. Thus, the reduction is spontaneous.



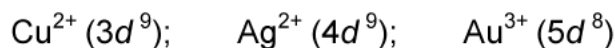
For $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple, $\text{Fe}^{3+}(3d^5, 4s^0)$ is more stable than $\text{Fe}^{2+}(3d^6, 4s^0)$

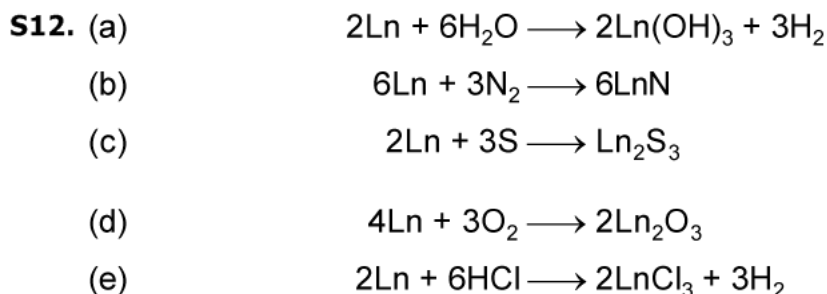
- (c) In the lanthanide series, the size of the M^{3+} ion decreases from La^{3+} to Lu^{3+} . Thus, the covalent nature of $\text{Lu}(\text{OH})_3$ increases (Fajan's rule). Hence, $\text{Lu}(\text{OH})_3$ is weaker than $\text{La}(\text{OH})_3$.

- S11.** (a) In chromium, the interatomic bonding is very strong due to presence of five unpaired electrons in $3d$ -subshell ($3d^5 4s^1$). Therefore, it is a hard metal. In mercury, on the contrary, the $3d$ -subshell is filled to maximum capacity ($5d^{10} 6s^2$), i.e., these electrons are not available for interatomic bonding and thus, bonding is very weak in mercury. Therefore, mercury is a liquid at room temperature.

- (b) In Zn, Cd and Hg the $(n-1)$ d -orbitals are filled to their maximum capacity. These d -electrons do not take part in metallic bonding. Thus, metallic bonding is weak in Zn, Cd and Hg. That is why, they have low melting and boiling points.

- (c) Copper, silver and gold in their common oxidation states have partially filled $(n-1)$ d -orbitals.





S13. (a) Fe^{3+} is more paramagnetic than Fe^{2+} as Fe^{3+} consists five unpaired electrons while Fe^{2+} possesses four unpaired electrons.

(b) Any ion of transition elements which possesses unpaired d electrons, *i.e.*, *d-d* transition is possible shows a characteristic colour. $(n-1)d^0$ or $(n-1)d^{10}$ configuration does not involve *d-d* transition and hence, is colourless.

Fe^{2+} , Mn^{2+} and Cr^{3+} are coloured, while Cu^+ , Sc^{3+} and Ti^{4+} are colourless.

Ion	Configuration	Ion	Configuration
Cu^+	$3d^{10}$ (colourless);	Cr^{3+}	$3d^3$ (coloured)
Fe^{2+}	$3d^6$ (coloured);	Sc^{3+}	$3d^0$ (colourless)
Mn^{2+}	$3d^5$ (coloured);	Ti^{4+}	$3d^0$ (colourless)

(c) Chromium and copper.

Chromium attains $3d^5, 4s^1$ configuration in which all the *d*-orbitals are unpaired in order to get extra stability.

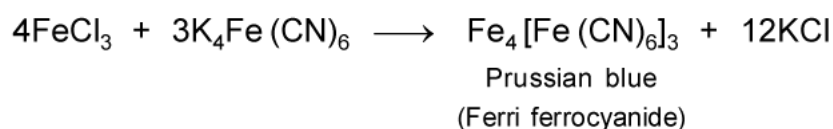
Copper attains $3d^{10}, 4s^1$ configuration in which all the *d*-orbitals are paired in order to get extra stability.

(d) Lightest element – Scandium;
 Heaviest element – Osmium

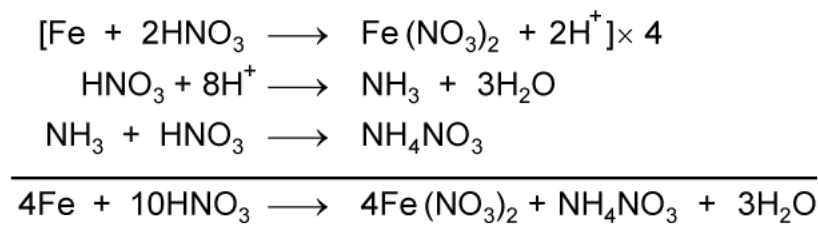
(e) Each transition series consists ten elements. This number cannot be 9 or 11 as the maximum capacity of *d*-orbitals is of 10 electrons which are gradually filled up.

1 st	Tr. series	$3d^{1-10}$	Ten elements
2 nd	Tr. series	$4d^{1-10}$	Ten elements
3 rd	Tr. series	$5d^{1-10}$	Ten elements

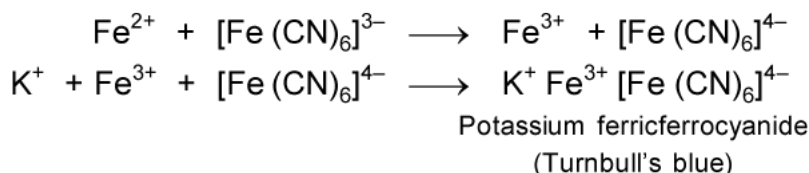
S14. (a) Prussian blue is formed.



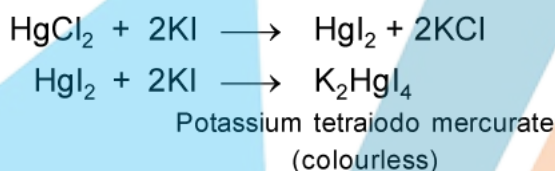
(b) Ammonium nitrate is formed.



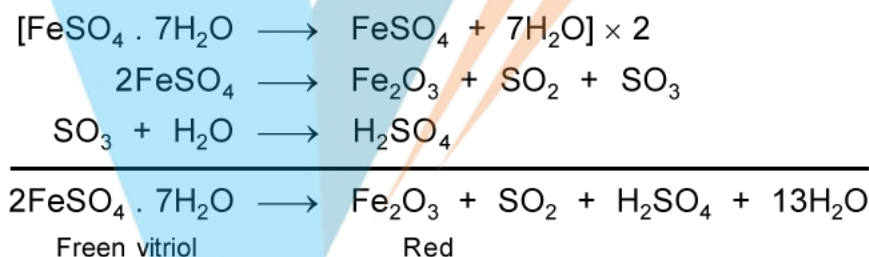
(c) Ferrous ion is first oxidised to ferric ion while ferricyanide ion is reduced to ferrocyanide ion. Then, ferric ions react with ferrocyanide ions to form potassium ferric ferrocyanide (Turnbull's blue).



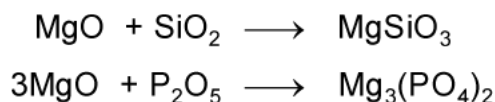
(d) First scarlet precipitate is formed which then dissolves in excess of potassium iodide forming a complex.



(e) When heated strongly, a mixture of gases consisting SO_2 and SO_3 evolved and a red residue, Fe_2O_3 is formed.



S15. (a) MgO is basic in nature. It removes acidic impurities present in cast iron used for making steels.



MgO is also a refractory material as it can tolerate very high temperature of the furnace.

(b) Cast iron consists carbon 2.5 to 5% which is responsible for its hardness.

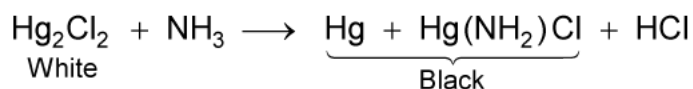
(c) Fe^{3+} has the configuration $[\text{Ar}] 3d^5$, i.e., all the five d -orbitals are singly occupied which is a stable configuration in accordance to Hund's rule of maximum multiplicity while the configuration of Fe^{2+} is $[\text{Ar}] 3d^6$ in which one orbital is doubly occupied and rest of the four orbitals are singly occupied. It is not so stable configuration as it is unsymmetrical in nature.

(d) On heating hydrated ferric chloride, anhydrous ferric chloride is not formed as water of crystallisation reacts to form Fe_2O_3 and HCl.

- (e) Iron compounds either has Fe^{2+} or Fe^{3+} ions and each contains unpaired orbitals which show paramagnetic character. $d-d$ transition is possible. Hence, the compounds are coloured.

S16. (a) HgCl_2 is poisonous (corrosive) in nature. It undergoes sublimation. Due to these properties, it is called corrosive sublimate.

- (b) HgCl_2 reacts with NH_3 to form a mixture of mercury and mercuric amino chloride which is a black substance.



- (c) Carbon has to play a double role,

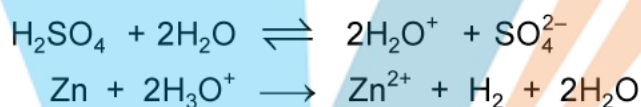
- (i) It reduces zinc oxide to zinc.



- (ii) It reduces CO_2 into CO which is used as a fuel



- (d) H_2SO_4 is a covalent compound. Conc. H_2SO_4 does not contain H_3O^+ ions while dilute H_2SO_4 consists H_3O^+ ions which react with zinc to liberate hydrogen.



- (e) In the compounds of zinc metals, M^{2+} ions possess the penultimate d -orbitals doubly occupied, *i.e.*, $(n-1)d^{10}$ configuration. There is no $d-d$ transition. Hence, the compounds of zinc metals are colourless.

S17. (a) Cu (I) salts undergo disproportionation in aqueous solution



- (b) I^- ion is a stronger reducing agent in comparison to Cl^- ion. Fe^{3+} is easily reduced by iodide ion.



- (c) AgBr is sensitive to light. It is converted into metallic silver grains when light is incident on it.

- (d) Silver and gold are less basic than copper. These are not ionised under the applied voltage and get deposited in the anodic mud.

- (e) The hydration energy of AgF is higher than its lattice energy. Hence, it is soluble in water. The hydration energy values of other halides are smaller than their lattice energy values. Hence, these halides are insoluble in water.

S18. (a) Although copper has $3d^{10}$ configuration yet it can lose one electron from this arrangement. Thus, Cu^{2+} ion has $3d^9$ configuration. So, according to the definition that transition metal cations have partially filled $(n-1)$ d -subshell, copper is regarded as a transition metal.

- (b) Of cobalt and zinc salts, the cobalt salts are attracted in a magnetic field, because cobalt ion containing unpaired electrons is characterised by a permanent magnetic moment. Zn^{2+} ion contains $3d^{10}$ configuration, *i.e.*, no unpaired electrons, so zinc salts are not attracted in magnetic field.
- (c) I^- ion is a stronger reducing agent than Cl^- ion. It reduces Cu^{2+} ion. Hence, cupric iodide is converted into cuprous iodide. Thus, the species $[\text{CuI}_4]^{2-}$ does not exist.
- (d) Copper is a very good conductor of electricity. Moreover, it is not easily affected by the atmosphere.
- (e) On being acidified, the chromate ions dimerise to form dichromate ions which are orange coloured. Thus,

