### **CBSE Test Paper-01**

## Class - 12 Chemistry (The d- & f- Block Elements)

- 1. Oxidation state of Mn in  $MnO_4^-$  is +7 indicating all electrons paired in Mn but  $MnO_4^-$  is coloured. This is due to:
  - a. none of these
  - b. both presence of unpaired electron in d-orbital in oxygen and charge transfer
  - c. presence of unpaired electron in d-orbital in oxygen
  - d. charge transfer
- 2. In dilute alkaline solution,  $MnO_4^-$  changes to
  - a.  $MnO_4^{2-}$
  - b.  $MnO_2$
  - c.  $Mn_2O_3$
  - d. MnO
- 3. Zr and Hf have almost equal atomic and ionic radii because
  - a. Both belong to same transition series
  - b. Of lanthanoid contraction
  - c. Of diagonal relationship
  - d. Of actinoid contraction
- 4. Silver is refined by cupellation process. The process removes the impurity of
  - a. Au
  - b. Pb
  - c. Cu
  - d. Pt
- 5. The compound which is widely used as a white pigment is
  - a. ZnO
  - b.  $Al_2O_3$
  - c.  $PbCO_3$
  - d. CaCO<sub>3</sub>
- 6. Write the outer electronic configuration of Cr atom(Z= 24).

- 7. Name the lanthanoid element which exhibits a + 4 oxidation state besides +3 oxidation state?
- 8. Why is KMnO<sub>4</sub> kept in dark bottles?
- 9. Calculate the 'spin only' magnetic moment of  $M^{2+}$  (aq) ion (Z= 27).
- 10. Give some of the uses of  $KMnO_4$ .
- 11. In what way is the electronic configuration of the transition elements different from that of the non-transition elements?
- 12. What is the lanthanoid contraction? What are its causes and consequences?
- 13. Calculate the 'spin only' magnetic moment of  $M^{2+}_{(ag)}$  ion (Z = 27).
- 14. Explain the following facts:
  - a. Transition metals act as catalysts.
  - b. Chromium group elements have the higher melting points in their respective series.
  - c. Transition metals form coloured complexes.
- 15. a. Give balanced chemical equations of two reactions in which  $KMnO_4$  acts as an oxidizing agent in acidic medium.
  - b. Give reason:
    - i.  $Cr^{2+}$  is a strong reducing agent whereas  $Mn^{2+}$  is not (Cr = 24, Mn = 25)
    - ii. The transition metal ions such as  $Cu^+$ ,  $Ag^+$  and  $Sc^{3+}$  are colourless
    - iii. Chemistry of the actinoids is much more complicated than that of the lanthanoids.

# CBSE Test Paper-01 Class - 12 Chemistry (The d- & f- Block Elements) Solutions

1. d. charge transfer

**Explanation:** The oxidation state of Mn in  $MnO_4^-$  is +7. Which means that Mn does not have any unpaired d-electrons left. However,  $MnO_4^-$  is deep purple in colour because of charge transfer from the ligand ( $O_2^-$ ) to the metal center. This is called a ligand-to-metal charge transfer.

2. b. MnO<sub>2</sub>

**Explanation:** In alkaline medium, reduction of  $MnO_4^-$  take place to form  $MnO_2$ . The chemical equation for this change is given below as:

 $MnO_4^{-}(aq) + 2H_2O(l) + 3e^{-} \rightarrow MnO_2(s) + 4OH^{-}(aq)$ 

3. b. Of lanthanoid contraction

**Explanation:** As after lanthanum, electron filling take place in f-subshell. Electrons present in f-subshell didn't do good shielding due to which with the increasing atomic number or increasing effective nuclear charge size gets constricted and size of Hf and Zr becomes almost equal.

4. b. Pb

**Explanation:** Cupellation is a refining process in metallurgy, where ores or alloyed metals are treated under very high temperatures and have controlled operations to separate noble metals, like gold and silver, from base metals like lead, copper, zinc or bismuth, present in the ore. Cupellation removes the impurity of Pb from silver. The reaction is given as below: Ag(s) + 2Pb(s) + O<sub>2</sub>(g)  $\rightarrow$  2PbO(absorbed) + Ag(l)

5. a. ZnO

**Explanation:** ZnO is white in color. This is because Zn is in +2 oxidation state with d<sup>10</sup> system having no unpaired electrons and hence absence of d-d transition.

- 6. Cr (Z=24) :  $[Ar]3d^{5}4s^{1}$
- 7. Cerium shows +3 as well as +4 oxidation states.
- 8. KMnO<sub>4</sub> is kept in dark bottles because KMnO<sub>4</sub> gets decomposed to  $K_2MnO_4$  in presence of sun light.
- 9. M<sup>2+</sup> (aq) (Z= 27) will have electronic configuration as [Ar]3d<sup>7</sup>4s<sup>0</sup>. It has 3 unpaired electron i.e.(n=3).

Magnetic moment is calculated using spin only formula.

$$egin{aligned} \mu &= \sqrt{n(n+2)} \ \mu &= \sqrt{3 imes 5} = \sqrt{15} \ = 3.87 \ \mathrm{B.M} \end{aligned}$$

- 10. Potassium permanganate is used
  - a. As an oxidizing agent in analytical chemistry and organic chemistry.
  - b. For bleaching of wool, cotton, silk and other textile fibres.
  - c. For decolourisation of oils.
- 11. Transition metals have a partially filled d-orbital of pen-ultimate shell in their ground state or most stable oxidation state. Therefore, the electronic configuration of transition elements is (n 1)d<sup>1-10</sup>ns<sup>1-2</sup> The non-transition elements either do not have a d-orbital in pen ultimate shell or have a fully filled d-orbital. Therefore, the electronic configuration of non-transition elements is ns<sup>1-2</sup> or ns<sup>2</sup>np<sup>1-6</sup>
- 12. Lanthanoid contractions is the cumulative effect of the regular decrease in size or radii of Lanthanoid with increase in atomic number is called Lanthanoid contraction. The main causes of Lanthanoid contraction is the diffused shape of f -orbitals. They have poor shielding effect due to which the effective nuclear charge increase with increase in atomic number. This causes a decrease in atomic radii. Due to Lanthanoid contraction
  - i. Radii of the members of the third transition series is similar to those of second transition series.
  - ii. It becomes difficult to separate Lanthanoids.
- 13. Element M having atomic number(Z) = 27 will have electronic configuration as

[Ar]3d<sup>7</sup>4s<sup>2</sup>. Therefore, the dipositive ion of M will have electronic configuration as [Ar]3d<sup>7</sup>.

3d<sup>7</sup> can be represented as follows:

$\uparrow\downarrow\qquad \uparrow\downarrow$	<b>†</b>	↑	1
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It has 3 unpaired electrons Therefore, n = 3

Magnetic moment can be calculated as

$$egin{aligned} &= \sqrt{n\,(n+2)} = \mu \ &= \sqrt{3\,(3+2)} = \mu \ &= \sqrt{15} = \mu \ &\mu pprox 4BM \end{aligned}$$

- a. Transition metals act as a catalyst due to their abilities to show multiple oxidation state and form unstable complexes with the substrates which decomposes to product.
  - b. Chromium group elements have high melting point in their respective series due to the presence of maximum number of unpaired electrons in d-orbitals because of which they form strong metallic bonding. Because of strong metallic bonding, they have high melting point.
  - c. Transition metal ions have incompletely filled d orbitals. 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 of light absorbed. This frequency generally lies in the visible region. The colour observed corresponds to the complementary colour of the light absorbed.
- 15. a. Acidified permanganate solution act as a strong oxidising agent.  $KMnO_4$  oxidises

oxalates to carbon dioxide, sulphides to sulphur etc and itself get reduced to  ${\rm Mn^{+2}}$ .  $5C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 10CO_2$  $5S^{2-} + 2MnO_4^- + 16H^+ \rightarrow 2Mn^{2+} + 8H_2O + 5S$ 

b. i.  $Cr^{2+}$  is less stable than  $Cr^{3+}$  therefore it is good reducing agent.  $Cr^{3+}$  is stable because outer most electronic configuration of  $Cr^{3+}$  is  $3d^3$ , which makes a stable half filled  $t_{2g}$  configuration. Whereas  $Mn^{2+}$  has outermost electronic configuration as 3d<sup>5</sup> which is stable due to half filled d-orbitals therefore it is not reducing agent.

- ii. Cu<sup>+</sup>, Ag<sup>+</sup>, Sc<sup>3+</sup> are colourless because they do not have unpaired electrons. Due to absence of unpaired electrons in them, no d-d transition occurs.
- iii. Actinoids show large number of oxidation states, that is why their chemistry is more complicated. Secondly all of them are radioactive and the earlier members have relatively long half-lives, the latter ones have half-life values ranging from a day to some minutes. The latter members could be prepared only in nanogram quantities. These facts render their study more difficult.

### **CBSE Test Paper-02**

## Class - 12 Chemistry (The d- & f- Block Elements)

- 1. Silver ornaments turn black by atmospheric
  - a. H<sub>2</sub>S
  - b. O<sub>2</sub>
  - c.  $Cl_2$
  - $d. \ N_2$
- 2.  $Ni^{2+}$  in traces can be tested using
  - a. Dimethylglyoxime
  - b. Potassium ferrocyanide
  - c. Ammonium sulphocyanide
  - d. Sodium nitroprusside
- 3. Which one of the following combines with  $Fe^{2+}$  ion to form a brown complex?
  - a.  $N_2O_3$
  - b.  $N_2O_5$
  - c. N<sub>2</sub>O
  - d. NO
- 4. Which of the following sulphides is soluble in aqua regia?
  - a. ZnS
  - b. HgS
  - c. CdS
  - d. HgS, ZnS
- 5. Among the following, which bivalent ion of the first transition series shows maximum magnetic moment?
  - a. Co<sup>2+</sup>
  - b. Ni<sup>2+</sup>
  - c. Mn<sup>2+</sup>
  - d. Fe<sup>2+</sup>

- 6. What is the general valence shell configuration of f-block elements?
- 7. What is the composition of mischmetall? Give its one use.
- 8. Out of Al, Zn, Mg and Fe which is the maximum density element?
- 9. Complete the following reactions:  $CrO_4^{2-} + \_\_ \rightleftharpoons \_\_ + H_2O$
- 10. Why do transition elements show similarities along the horizontal period?
- 11. Why is any transition series, melting points first increase and then decrease and also they show a dip in the middle?
- 12. Which is a stronger reducing agent  $Cr^{2+}$  or  $Fe^{2+}$  and why?
- 13. Compare the chemistry of actinoids with that of lanthanoids with reference to:
  - i. Electronic configuration
  - ii. Oxidation states
  - iii. Chemical reactivity
- 14. Write down the electronic configuration of all 3d transition metal atoms. Also show the electronic configuration using electron box diagram.
- 15. A violet compound of manganese (A) decomposes on heating to liberate oxygen and compounds (B) and (C) of manganese are formed. Compound (C) reacts with KOH in the presence of oxygen to give compound (B). On heating compound (C) with concentrated  $H_2SO_4$  and NaCl, chlorine gas is liberated and a compound (D) of manganese along with other products is formed. Identify A to D and also explain the reactions involved.

## CBSE Test Paper-02 Class - 12 Chemistry (The d- & f- Block Elements) Solutions

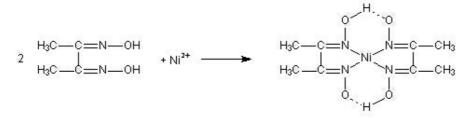
1. a. H<sub>2</sub>S

**Explanation:** Silver ornaments turns black coming in contact with  $H_2S$  due to formation of  $Ag_2S$ . The chemical equation for this change can be represented as given below:

 $2\mathrm{Ag}(\mathrm{s}) + \mathrm{H}_2\mathrm{S}(\mathrm{g}) \to \mathrm{Ag}_2\mathrm{S}(\mathrm{s}) + \mathrm{H}_2(\mathrm{g})$ 

2. a. Dimethylglyoxime

**Explanation:** Ni<sup>2+</sup> forms complex with DMG which is red in colour.



3. d. NO

**Explanation:** The brown ring test is usually carried out by adding dilute ferrous sulphate solution to an aqueous solution containing nitrate ion, and then carefully adding concentrated sulphuric acid along the sides of the test tube. A brown ring at the interface between the solution and sulphuric acid layers indicates the presence of nitrate ion in solution.  $[Fe(H_2O)_5NO]^{2+}$  is brown colour complex formed?  $NO_3 + 3Fe^{2+} + 4H^+ \rightarrow NO + Fe^{3+} + 2H_2O$  $[Fe(H_2O)]^{2+} + NO \rightarrow [Fe(H_2O)_5(NO)]^{2+} + H_2O$ 

4. b. HgS

**Explanation:** HgS is only soluble in aqua regia. Aqua regia is a mixture of concentrated HCl and concentrated HNO<sub>3</sub> in ratio 3:1. The solubilization turns Hg in  $HgCl_4^{2-}$ , a complex called chloromercurate which is stable in water.

 $3HgS + 2NO_3^- + 12Cl^- + 8H_3O^+ \Leftrightarrow 3HgCl_4^{2-} + 2NO + 12H_2O + 3S$ 

5. c. Mn<sup>2+</sup>

**Explanation:**  $Mn^{2+}$  has d<sup>5</sup> configuration so maximum number of unpaired electrons and hence maxium magnetic moment. This magnetic moment can be calculated by using the spin only formula:  $\mu_{so} = \angle n(n+2)$ , where n= number of unpaired electrons.

6. F-block elements are those in which the last electron enters the f orbital. F- orbital can accommodate maximum of 14 electrons.

The general electronic configuration of f-block elements is  $(n-2) \ f^{1-14}(n-1) \ d^{0-1}ns^2$ 

- 7. Mischmetall is an alloy which consists of a Lanthanoid metal (95%) and iron(5%) and traces of S, C, Ca & Al. A good amount of this alloy is used in magnesium based alloy to produce bullets, shell and lighter Flint.
- 8. Fe
- 9.  $2CrO_4^{2-} + 2H^+ \rightleftharpoons 2HCrO_4^- \rightleftharpoons Cr_2O_7^{2-} + H_2O$
- 10. There are greater horizontal similarities in the properties of then transition elements in contrast to the main group elements. This is because all of them contain incompletely filled d-subshell in ground state or in stable oxidation state.
- 11. Melting points first increase because the number of unpaired electrons increases. Due to increase in the number of unpaired electron, strength of metallic bonding increases and hence melting point increases. After reaching the maximum, the melting points decrease because the pairing of electrons starts in the d-subshell and number of unpaired electrons decreases and so the strength of metallic bond decreases. The dip in the middle is due to exactly half filled configuration of d-subshell ( d<sup>5</sup> )which has higher stability. Hence, electrons are held tightly by the nucleus. As a result, metallic bond is weaker. And thus melting point graph shows dip at this point.
- 12. Reducing agents are those which itself get oxidised and make the other substance get reduced. The following reactions are involved when  $Cr^{2+}$  and  $Fe^{2+}$  act as reducing agents.

 $Cr^{2+} \rightarrow Cr^{3+} + e^-$  and  $Fe^{2+} \rightarrow Fe^{3+} + e^-$ . The  $E^{\circ}_{Cr^{3+}/Cr^{2+}}$  value is - 0.41 V and  $E^{\circ}_{Fe^{3+}/Fe^{2+}}$  is +0.77 V. This means that  $Cr^{2+}$  can be easily oxidized to  $Cr^{3+}$ , but  $Fe^{2+}$  does not get oxidized to  $Fe^{3+}$  easily. Therefore,  $Cr^{2+}$  is a better reducing agent than  $Fe^{3+}$ .

13. i. Electronic configuration : In lanthanoids 4f - orbitals are progressively filled so

their electronic configuration is  $4f^{1-14} 5d^{0-1} 6s^2$  whereas in actinoids 5f-orbitals are progressively filled so their electronic configuration is  $5f^{1-14}6d^{0-1} 7s^2$ 

- ii. Oxidation states: Lanthanoid show +3 oxidation state. Some elements show +2 and +4 oxidation states also. Actinoids show +2 ,+4, +5, +6, + 7 oxidation states. Although +3 and +4 are most common.
- iii. **Chemical reactivity:** Actinoids are more reactive than lanthanoids due to bigger atomic size and lower ionization energy.
- 14. Electronic configuration of 3d metal atoms is as follows:

Sc(Z=21) : [Ar]3d<sup>1</sup>4s<sup>2</sup>, Ti(Z=22) : [Ar]3d<sup>2</sup>4s<sup>2</sup>, V(Z=23) : [Ar]3d<sup>3</sup>4s<sup>2</sup>, Cr(Z=24) : [Ar]3d<sup>5</sup>4s<sup>1</sup>, Mn(Z=25) : [Ar]3d<sup>5</sup>4s<sup>2</sup>

Fe(Z=26) : [Ar] $3d^{6}4s^{2}$ , Co(Z=27) : [Ar] $3d^{7}4s^{2}$ , Ni(Z=28) : [Ar] $3d^{8}4s^{2}$ , Cu(Z=29) : [Ar] $3d^{10}4s^{1}$ ,

 $Zn(Z=30): [Ar]3d^{10}4s^2$ 

Electron box diagram is shown below:

From the above set of reaction we can deduce that:

(A) =  $KMnO_4$ (B) =  $K_2MnO_4$ (C) =  $MnO_2$ (D) =  $MnCl_2$ 

### **CBSE Test Paper-03**

## Class - 12 Chemistry (The d- & f- Block Elements)

- 1. Transition metals with highest melting point is
  - a. Hg
  - b. Sc
  - c. Cr
  - d. W

### 2. Which of the following is not considered a transition metal?

- a. Zn
- b. Ac
- **c.** Y
- d. La
- 3. Which is the most stable oxidation state of iron?
  - a. +1
  - b. +3
  - c. 0
  - d. +2
- 4. In the reaction,  $SnCl_2 + HgCl_2 
  ightarrow A + SnCl_4$  , A is
  - a.  $HgCl_2$
  - b. Hg
  - c. HgCl
  - d.  $HgCl_3$
- 5. Maximum magnetic moment is shown by
  - a. d<sup>6</sup>
  - b. d<sup>8</sup>
  - c. d<sup>7</sup>
  - $d. \ d^5$
- 6. Write the outer electronic configuration of Lanthanoids.
- 7. Name the lanthanoid element which exhibit +4 oxidation state besides +3 oxidation

state.

- 8. Name the transition element which does not exhibit variable oxidation states.
- 9. Why do actinoids, in general, exhibit a greater range of oxidation states than the lanthanoids?
- 10. Why are  $Fe^{2+}$  compounds easily oxidises to  $Fe^{3+}$  as compared to  $Mn^{+2}$  compounds.
- 11. Explain why
  - i.  $E^{0}$  for  $Mn^{3+}/Mn^{2+}$  couple is more positive than that for  $Fe^{3+}/Fe^{2+}$  (At. No. of Mn= 25, Fe = 26)
  - ii.  $Ce^{3+}$  can be easily oxidized to  $Ce^{4+}$  (At. No. of Ce = 58)
- 12. Uses Hund's rule to derive the electronic configuration of Ce<sup>3+</sup> ion, and calculate its magnetic moment on the basis of 'spin only' formula.
- 13. What are alloys? Name an important alloy which contains some of the Lanthanoid metals. Mention its uses.
- 14. The chemistry of the actinoid elements is not so smooth as that of the lanthanoids. Justify this statements by giving some examples from the oxidation state of these elements.
- 15. Indicate the steps in the preparation of:
  - i.  $K_2Cr_2O_7$  from chromite ore.
  - ii. KMnO<sub>4</sub> from pyrolusite ore.

# CBSE Test Paper-03 Class - 12 Chemistry (The d- & f- Block Elements) Solutions

1. d. W

**Explanation:** The high melting points of these metals are attributed to the involvement of greater number of electrons from (n-1)d in addition to the ns electrons in the interatomic metallic bonding. W belongs to 5d series and it has lot of unpaired electrons ( $5d^46s^2$ ).

2. a. Zn

**Explanation:** Zinc, cadmium and mercury of group 12 have full d<sup>10</sup> configuration in their ground state as well as in their common oxidation states and hence, are not regarded as transition metals. However, being the end members of the three transition series, their chemistry is studied along with the chemistry of the transition metals.

3. b. +3

**Explanation:** Fe has d<sup>5</sup> configuration in +3 oxidation state.

4. b. Hg

**Explanation:** Tin(II) chloride react with mercury(II) chloride in acidic medium to produce mercury and tin(IV) chloride as given below:  $SnCl_2 + HgCl_2 \rightarrow Hg + SnCl_4$ 

5. d. d<sup>5</sup>

**Explanation:** Magnetic moment is directly proportional to the total number of unpaired electrons. So it will be maximum for the element having maximum unpaired electrons i.e. d<sup>5</sup> system.

- 6.  $4f^{1-14}5d^{0-1}6s^2$  is outer electronic configuration of Lanthanoids.
- Generally, Lanthanide elements shows +3 oxidation state but cerium apart from +3 shows +4 oxidation state. The formation of Ce(IV) is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state. The E<sup>0</sup>

value for  $Ce^{4+}/Ce^{3+}$  is + 1.74 V.

- 8. Scandium ( Z= 21) does not exhibit variable oxidation states. It shows only +3 oxidation state.
- 9. They have lower ionization energy and less effective nuclear charge therefore more number of valence electrons can take part in bond formation. Also there is very less difference between the enegry of 5f ,6d,7s orbitals.
- 10. Mn<sup>2+</sup> compounds are less readily converted to its +3 oxidation state (Mn<sup>3+</sup>) as compared to Fe<sup>2+</sup> because Mn<sup>2+</sup> (3d<sup>5</sup>) is more stable than Mn<sup>3+</sup> (3d<sup>4</sup>) due to stable half filled d-orbital electronic configuration. Whereas Fe<sup>3+</sup> (3d<sup>5</sup>) is more stable than Fe<sup>2+</sup> (3d<sup>6</sup>) due to half filled d-orbitals therefore Fe<sup>2+</sup> gets easily converted to Fe<sup>3+</sup>
- 11. i. Mn<sup>2+</sup> is more stable(3d<sup>5</sup>4s<sup>0</sup>) because of half filled d-orbitals than Mn<sup>3+</sup>(3d<sup>4</sup>4s<sup>0</sup>) whereas Fe<sup>3+</sup>(3d<sup>5</sup> 4s<sup>0</sup>) is more stable than Fe<sup>2+</sup>( 3d<sup>6</sup>4s<sup>0</sup>), therefore Mn<sup>3+</sup> can be easily reduced to Mn<sup>2+</sup> whereas Fe<sup>3+</sup> is not easily reduced to Fe<sup>2+</sup> rather Fe<sup>2+</sup> is more easily oxidized to Fe<sup>3+</sup>.
  - ii. Ce<sup>4+</sup> is more stable than Ce<sup>3+</sup> because of stable inert gas configuration and higher hydration energy hence Ce<sup>3+</sup> is easily oxidized to Ce<sup>4+</sup>.
- 12.  $_{58}$ Ce has electronic configuration as  $[Xe]^{54} 4f^1 5d^1 6s^2$  while  $Ce^{3+}$  will have electronic configuration as  $[Xe]^{54} 4f^1$ . Thus, number of unpaired electron in  $Ce^{3+}$  is 1.  $\mu = \sqrt{n(n+2)}$

Thus, number of unpaired electron in Ce<sup>3</sup> is 1.  $\mu = \sqrt{n(n+2)}$ =  $\sqrt{1(1+2)} = \sqrt{3}BM$ = 1.73 BM

13. Alloys are homogenous mixture of two or more metals. One of them can be non metal also. Mischmetal is an alloy which contains some of the Lanthanoid metals, it contains 45% Lanthanoid metals and iron ~ 5% and traces of S, C, Ca and Al. Mischmetal is used in Mg-based alloy to produce bullets, shell and lighter flint. Addition of 3% mischmetal to magnesium increases its strength and used in making jet engine parts.

- 14. Chemistry of actinoids is not as smooth as lanthanoids because actinoids are radioactive elements and they show a large number of oxidation state compared to lanthanoids. Lanthanoids shows limited number of oxidation state like + 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 state 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 subshells of the actinoids.
- 15. i. Potassium dichromate  $(K_2 C r_2 O_7)$  is prepared from chromite ore  $(Fe C r_2 O_4)$  in the following steps.

**Step (1):** Preparation of sodium chromate- Dichromates are generally prepared from chromate, which in turn are obtained by the fusion of chromite ore  $(FeCr_2O_4)$  with sodium or

potassium carbonate in free access of air.

 $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \rightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8CO_2$  **Step (2):** Conversion of sodium chromate into sodium dichromate- The yellow solution of sodium chromate is filtered and acidified with sulphuric acid to give a solution from which orange sodium dichromate, Na<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>. 2H<sub>2</sub>O can be

crystallised.  $2Na_2CrO_4 + conc. H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$ Step(3): Conversion of sodium dichromate to potassium dichromate- Sodium dichromate is more soluble than potassium dichromate, therefore it is prepared by treating the solution of sodium dichromate with potassium chloride.  $Na_2Cr_2O_7 + 2KCl \rightarrow K_2Cr_2O_7 + 2NaCl$ 

The chromates and dichromates are interconvertible in aqueous solution depending upon pH of the solution. The oxidation state of chromium in chromate and dichromate is the same.

2 
$$\text{CrO}_4^{2-}$$
 + 2H<sup>+</sup>→  $\text{Cr}_2\text{O}_7^{2-}$  + H<sub>2</sub>O  
Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> + 2 OH<sup>-</sup>→ 2  $\text{CrO}_4^{2-}$  + H<sub>2</sub>O

The combined reaction can be shown like:

 $\begin{array}{c} 2CrO_4^{2-} \xleftarrow{Acid}{Alkali} 2HCrO_4^- \xleftarrow{Acid}{Alkali} Cr_2O_7^{2-} \\ Chromate \end{array} \end{array}$ (Yellow) chromate (Orange)

ii. Potassium permanganate  $(KMnO_4)$  can be prepared from pyrolusite. $(MnO_2)$ The ore is fused with KOH in the presence of either atmospheric oxygen or an oxidising agent, such as  $KNO_3$  or  $KClO_4$  to give  $K_2MnO_4$ 

$$2MnO_2 + 4KOH + O_2 \xrightarrow[(Green)]{heat} 2K_2MnO_4 + 2H_2O$$

This produces the dark green K<sub>2</sub>MnO<sub>4</sub> which disproportionates in a neutral or acidic solution to give permanganate.

$$3MnO_4^{2-} + 4H^+ \rightarrow 2MnO_4^- + MnO_2 + 2H_2O$$

Commercially it is prepared by the alkaline oxidative fusion of MnO<sub>2</sub> followed by

the electrolytic oxidation of manganate (Vl).

$$MnO_2 \xrightarrow{fused with KOH and oxidised by KNO_3 or air} MnO_4^{2-} MnO_4^{2-} \xrightarrow{electrolytic oxidation in alkaline solution} MnO_4^{-}$$

In the laboratory, a manganese (II) ion salt is oxidised by peroxodisulphate to permanganate.

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