

CHEMISTRY STUDY MATERIALS FOR CLASS 12 (NCERT BASED QUESTIONS WITH ANSWERS)

GANESH KUMAR

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The d & f - Block Elements

Solution 19: From the above table, it is evident that the maximum number of oxidation states is shown by Mn, varying from +2 to +7. The number of oxidation states increases on moving from Sc to Mn. On moving from Mn to Zn, the number of oxidation states decreases due to a decrease in the number of available unpaired electrons. The relative stability of the +2 oxidation state increases on moving from top to bottom. This is because on moving from top to bottom, it becomes more and more difficult to remove the third electron from the **d-orbital**.

Question 20: Compare the chemistry of actinoids with that of the lanthanoids with special reference to: (i) electronic configuration (ii) oxidation state (iii) atomic and ionic sizes and (iv) chemical reactivity.

Solution 20:

(i) Electronic configuration:

The general electronic configuration for lanthanoids is $[Xe] 4f^{0-14} 5d^{0-1} 6s^2$ and that for actinoids is $[Rn] 5f^{0-14} 6d^{0-1} 7s^2$. Unlike 4f orbitals, 5f orbitals are not deeply buried and participate in bonding to a greater extent.

(ii) Oxidation states

The principal oxidation state of lanthanoids is (+3). However, sometimes we also encounter oxidation states of +2 and +4. This is because of extra stability of fully-filled and half-filled orbitals. Actinoids exhibit a greater range of oxidation states. This is because the 5f, 6d, and 7s levels are of comparable energies. Again, (+3) is the principal oxidation state for actinoids. Actinoids such as lanthanoids have more compounds in +3 state than in +4 state.

(iii) Atomic and Ionic sizes

Similar to lanthanoids, actinoids also exhibit actinoid contraction (overall decrease in atomic and ionic radii). The contraction is greater due to the poor shielding effect of 5f orbitals.

(iv). Chemical reactivity

In the lanthanide series, the earlier members of the series are more reactive. They have reactivity that is comparable to Ca. With an increase in the atomic number, the lanthanides start behaving similar to Al. Actinoids, on the other hand, are highly reactive metals, especially when they are finely divided. When they are added to boiling water, they give a mixture of oxide and hydride. Actinoids combine with most of the non-metals at moderate temperatures. Alkalies have no action on these actinoids. In case of acids, they are slightly affected by nitric acid (because of the formation of a protective oxide layer).

Question 21: How would you account for the following?

- (i) Of the d^4 species, Cr^{2+} is strongly reducing while manganese (II) is strongly oxidizing.
- (ii) Cobalt(II) is stable in aqueous solution but in the presence of complexing reagents it is easily oxidized.
- (iii) The d^1 configuration is very unstable in ions.

Solution 21:

- (i) Cr^{2+} is strongly reducing in nature. It has a d^4 configuration. While acting as a reducing agent, it gets oxidized to Cr^{3+} (electronic configuration, d^3). This d^3 configuration can be written as $t^3 e^0$ configuration, which is a more stable configuration. In the case of Mn^{3+} (d^4) it acts as an oxidizing agent and gets reduced to Mn^{2+} (d^5). This has an exactly half-filled d -orbital and is highly stable.
- (ii) Co (II) is stable in aqueous solutions. However, in the presence of strong field complexing reagents, it is oxidized to Co (III). Although the 3rd ionization energy for Co is high, but the higher amount of crystal field stabilization energy (CFSE) released in the presence of strong field ligands overcomes this ionization energy.
- (iii) The ions in d^1 configuration tend to lose one more electron to get into stable d^0 configuration. Also, the hydration or lattice energy is more than sufficient to remove the only electron present in the d -orbital of these ions. Therefore, they act as reducing agents.

Question 22: Which metal in the first series of transition metals exhibits +1 oxidation state most frequently and why?

Solution 22: In the first transition series, Cu exhibits +1 oxidation state very frequently. It is because Cu (+1) has an electronic configuration of $[\text{Ar}] 3d^{10}$. The completely filled d -orbital makes it highly stable.

Question 23: Calculate the number of unpaired electrons in the following gaseous ions: Mn^{3+} , Cr^{3+} , V^{3+} and Ti^{3+} . Which one of these is the most stable in aqueous solution?

Solution 23: Cr^{3+} is the most stable in aqueous solutions owing to a half filled f^3 configuration.

S.No.	Gaseous ions	Number of unpaired electrons
(i)	Mn^{3+} , $[\text{Ar}]3d^4$	4
(ii)	Cr^{3+} , $[\text{Ar}]3d^3$	3
(iii)	V^{3+} , $[\text{Ar}]3d^2$	2
(iv)	Ti^{2+} , $[\text{Ar}]3d^1$	1

Question 24: Give examples and suggest reasons for the following features of the transition metal chemistry:

- (i) The lowest oxide of transition metal is basic, the highest is amphoteric/acidic.
- (ii) A transition metal exhibits highest oxidation state in oxides and fluorides.
- (iii) The highest oxidation state is exhibited in oxoanions of a metal.

Solution 24:

(i) In the case of a lower oxide of a transition metal, the metal atom has a low oxidation state. This means that some of the valence electrons of the metal atom are not involved in bonding. As a result, it can donate electrons and behave as a base. On the other hand, in the case of a higher oxide of a transition metal, the metal atom has a high oxidation state. This means that the valence electrons are involved in bonding and so, they are unavailable. There is also a high effective nuclear charge. As a result, it can accept electrons and behave as an acid. For example, Fe^{II}O is basic and Fe^{VI}O is acidic. For example, Mn^{II}O is basic and Mn^{VII}O is acidic.

(ii) Oxygen and fluorine act as strong oxidizing agents because of their high electro negativities and small sizes. Hence, they bring out the highest oxidation states from the transition metals. In other words, a transition metal exhibits higher oxidation states in oxides and fluorides. For example, in OsF_6 and V_2O_5 , the oxidation states of Os and V are +6 and +5 respectively.

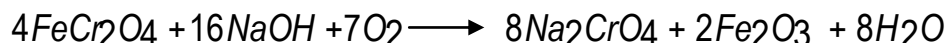
(iii) Oxygen is a strong oxidizing agent due to its high electronegativity and small size. So, oxo- anions of a metal have the highest oxidation state. For example in MnO_4^- , the oxidation state of Mn is +7.

Question 25: Indicate the steps in the preparation of:

- (i) $K_2Cr_2O_7$ from chromite ore. (ii) $KMnO_4$ from pyrolusite ore.

Solution 25: (i) Potassium dichromate is prepared from chromite ore $FeCr_2O_4$ in the following steps.

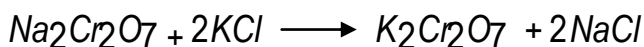
Step (1): Preparation of sodium chromate



Step (2): Conversion of sodium chromate into sodium dichromate

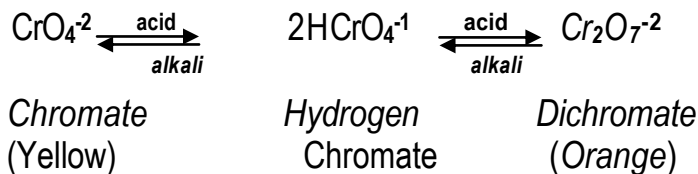


Step(3): Conversion of sodium dichromate to potassium dichromate

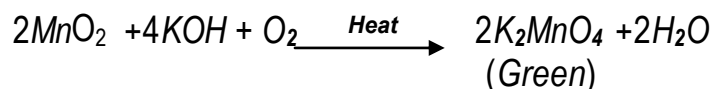


Potassium chloride being less soluble than sodium chloride is obtained in the form of orange coloured crystals and can be removed by filtration. The dichromate ion $Cr_2O_7^{2-}$ exists in equilibrium with chromate

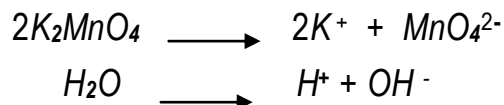
CrO_4^{2-} ion at pH 4. However, by changing the pH, they can be interconverted.



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



The green mass can be extracted with water and then oxidized either electrolytically or by passing chlorine/ozone into the solution. Electrolytic oxidation.



At anode, manganate ions are oxidized to permanganate ions.

