

Short Answer Questions-II

Short Answer Questions-II (PYQ)

Q.1. Assign suitable reasons for the following:

Q. The Mn^{2+} compounds are more stable than Fe^{2+} towards oxidation to their +3 state.

Ans. The electronic configuration of Mn^{2+} is $[\text{Ar}] 3d^5$ which is half filled and hence stable. So Mn^{2+} cannot lose third electron easily. On the other hand, Fe^{2+} has electronic configuration $[\text{Ar}] 3d^6$. It tends to lose one electron to acquire stable $[\text{Ar}] 3d^5$ electronic configuration. Hence Mn^{2+} is more stable than Fe^{2+} towards oxidation.

Q. Sc^{3+} is colourless in aqueous solution whereas Ti^{3+} is coloured.

Ans. Ti^{3+} has one unpaired electron in d -orbitals ($3d^1$) which can absorb light in visible region for $d-d$ transition. Hence, it is coloured in aqueous solution. Sc^{3+} has no d electron ($3d^0$), therefore, no light is absorbed for $d-d$ transition. Hence, it is colourless in aqueous solution.

Q. The highest oxidation state is exhibited in oxo-anions of a metal.

[CBSE (F) 2014]

Ans.

Oxometal anions have the highest oxidation state, e.g., Cr in $\text{Cr}_2\text{O}_7^{2-}$ has an oxidation state of +6 whereas Mn in MnO_4^- has an oxidation state of +7. This is again due to the combination of the metal with oxygen, which is highly electronegative and oxidising element.

Q.2. The elements of $3d$ transition series are given as:

Sc Ti V Cr Mn Fe Co Ni Cu Zn

[CBSE East 2016]

Answer the following:

- i. Copper has exceptionally positive $E^\circ_{M^{2+}/M}$ value. Why?
- ii. Which element is a strong reducing agent in +2 oxidation state and why?
- iii. Zn^{2+} salts are colourless. Why?

Ans. (i) Because the sum of sublimation enthalpy and hydration enthalpy to convert $Cu(s)$ to $Cu^{2+}(aq)$ is so high that it is not balanced by its hydration enthalpy.

(ii) Cr is strongest reducing agent in +2 oxidation state. Cr^{2+} has configuration $3d^4$. After losing one electron it forms Cr^{3+} which has stable half filled t_{2g} level.

(iii) $Zn^{2+}(3d^{10})$ has completely filled d -orbitals. As a result of this, $d-d$ transition cannot occur and hence Zn^{2+} salts are colourless.

Q.3. Why do transition elements show variable oxidation states? How is the variability in oxidation states of d -block different from that of the p -block elements?

[CBSE Ajmer 2015]

Ans. In transition elements, the energies of $(n-1)d$ orbitals and ns orbitals are nearly same. Therefore, electrons from both can participate in bond formation and hence show variable oxidation states.

In transition elements, the oxidation states differ from each other by unity, e.g., Fe^{2+} and Fe^{3+} , Cu^+ and Cu^{2+} , etc. while in p -block elements the oxidation state differ by units of two, e.g., Sn^{2+} and Sn^{4+} , Pb^{2+} and Pb^{4+} , etc. In transition elements the higher oxidation states are more stable for heavier elements in a group, e.g., $Mo(VI)$ and $W(VI)$ are more stable than $Cr(VI)$ in group 6 whereas in p -block elements the lower oxidation states are more stable for heavier elements due to the inert pair effect, e.g., $Pb(II)$ is more stable than $Pb(IV)$ in group 16.

Q.4. How would you account for the following:

Q. Many of the transition elements and their compounds can act as good catalysts.

Ans. The catalytic activity of transition metals is attributed to the following reasons:

- a. Because of their variable oxidation states transition metals form unstable intermediate compounds and provide a new path with lower activation energy for the reaction.
- b. In some cases, the transition metal provides a suitable large surface area with free vacancies on which reactants are adsorbed.

Q. The metallic radii of the third (5d) series of transition elements are virtually the same as those of the corresponding members of the second series.

Ans. This is due to filling of 4f-orbitals which have poor shielding effect or due to lanthanoid contraction.

Q. There is a greater range of oxidation states among the actinoids than among the lanthanoids.

[CBSE (AI) 2009]

Ans. This is due to more comparable energies of 5f, 6d and 7s orbitals in actinoids.

Q.5. Answer the following questions:

Q. How would you account for the following:

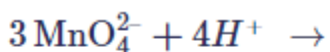
- Highest fluoride of Mn is MnF_4 whereas the highest oxide is Mn_2O_7 .**
- Transition metals and their compounds show catalytic properties.**

Ans. (a) As oxygen stabilises manganese more than fluorine by forming multiple bonds.

(b) The catalytic activity of transition metals and their compounds is attributed to the following reasons:

- Due to their tendency to show variable oxidation states transition metals form unstable intermediate compounds and provide a new path for the reaction with lower activation energy.
- In some cases, the transition metals provide a suitable large surface area with free valencies on which reactants are adsorbed.

Q. Complete the following equation:



[CBSE (F) 2015]

Ans.



Q.6.

$E^\circ\text{Mn}^{2+}/\text{Mn}$	Cr	Mn	Fe	Co	Ni	Cu
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	– 0.91	– 1.18	– 0.44	– 0.28	– 0.25	+ 0.34
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From the given data E° values, answer the following questions:

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

[CBSE Patna 2015] [HOTS]

Ans. (i) Copper has high enthalpy of atomisation and low enthalpy of hydration. Since the high energy to transform Cu (s) to $\text{Cu}^{2+} (\text{aq})$ is not balanced by hydration enthalpy, therefore, $E^\circ\text{Cu}^{2+}/\text{Cu}$ value is exceptionally positive.

(ii) This is due to extra stability of half-filled $3d$ -orbitals of $\text{Mn}^{2+}(3d^5)$.

(iii) Cr^{2+} , $d^4 \rightarrow d^3$ occurs in case of Cr^{2+} to Cr^{3+} while $d^6 \rightarrow d^5$ occurs in case of Fe^{2+} to Fe^{3+} . As in a medium like water d^3 is more stable as compared to d^5 , therefore, Cr^{2+} is stronger reducing agent than Fe^{2+} .

Q.7. Account for the following:

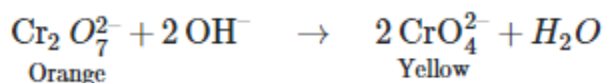
Q. Eu^{2+} is a strong reducing agent.

Ans. This is because Eu^{2+} tends to change to Eu^{3+} as +3 is the common oxidation state of lanthanoids.

Q. Orange colour of dichromate ion changes to yellow in alkaline medium.

Ans.

In alkaline medium, the orange colour of the solution changes to yellow due to conversion of dichromate ($\text{Cr}_2\text{O}_7^{2-}$) ion to chromate (CrO_4^{2-}) ion.



Q.

$E^\circ (M^{2+}/M)$ values for transition metals show irregular variation.

[CBSE (F) 2017]

Ans. The irregularity is due to the irregular variation of ionisation enthalpies ($\Delta_i H + \Delta_i H_2$) and also the sublimation enthalpies which are relatively much less for Mn (240 kJ mol^{-1}) and V (470 kJ mol^{-1}).

Q.8. When pyrolusite ore MnO_2 is fused with KOH in presence of air, a green coloured compound (A) is obtained which undergoes disproportionation reaction in acidic medium to give a purple coloured compound (B).

[CBSE South 2016] [HOTS]

- Write the formulae of the compounds (A) and (B).
- What happens when compound (B) is heated?

Ans.

- $A = \text{K}_2\text{MnO}_4$, $B = \text{KMnO}_4$
- $$\underset{\text{Potassium}}{2 \text{ KMnO}_4} \xrightarrow{513 \text{ K}} \underset{\text{Potassium}}{\text{K}_2 \text{ MnO}_4} + \text{MnO}_2 + \text{O}_2$$

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Short Answer Questions-II (OIQ)

Q.1. Describe the trends in the following properties of the first series of the transition elements:

- Oxidation states
- Atomic sizes
- Magnetic behaviour of dipositive gaseous ions (M^{2+}).

Ans. (i) As there is very little energy difference between $4s$ and $3d$ orbitals, electrons from both energy levels can be used for chemical bond formation. Therefore, all elements except Sc and Zn of the first transition series show a number of oxidation states.

(ii) Atomic radii of the first transition series decrease from Sc to Cr, then remains almost constant till Ni and then increases from Cu to Zn. The reason of this variation in atomic radii has been attributed to the increase in nuclear charge in the beginning of the series. But as the electrons continue to be filled in d -orbitals, they screen the outer $4s$ electrons from the influence of nuclear charge. When the increased nuclear charge and the increased screening effect balance each other in the middle of transition series, the

atomic radii become almost constant (Mn to Fe). Towards the end of the series, the repulsive interaction between electrons in orbitals become very dominant. As a result there is an expansion of the electron cloud; consequently, the atomic size increases.

(iii) Except Zn^{2+} , all other divalent gaseous ions of the first series of the transition elements contain unpaired electrons in their 3d-subshell and are therefore paramagnetic in nature.

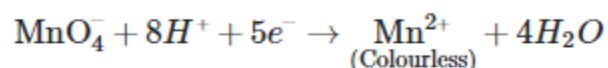
Q.2. A solution of KMnO_4 on reduction yields either a colourless solution or a brown precipitate or a green solution depending on pH of the solution. What different stages of the reduction do these represent and how are they carried out?

[NCERT Exemplar]

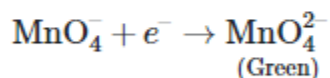
Ans.

Oxidising behaviour of KMnO_4 depends on pH of the solution.

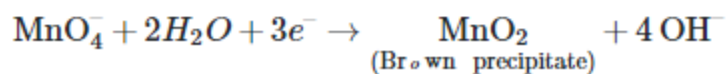
In acidic medium ($\text{pH} < 7$),



In alkaline medium ($\text{pH} > 7$),



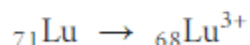
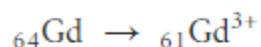
In neutral medium ($\text{pH} = 7$),



Q.3. Lanthanum, gadolinium and lutetium are extraordinarily stable in +3 oxidation state. Explain.

(Atomic number: La = 57, Gd = 64, Lu = 71)

Ans. ${}_{57}\text{La} \rightarrow {}_{57}\text{La}^{3+}$



From their electronic configurations, we find that La^{3+} , Gd^{3+} and Lu^{3+} have empty, exactly half-filled and fully filled valency shells, respectively, which make them extra stable.

Q.4. Assign reasons for the following:

Q. The second and third rows of transition elements resemble each other much more than they resemble the first row.

Ans. Due to lanthanoid contraction, the atomic radii of the second and third row transition elements is almost same. So they resemble each other much more as compared to first row elements.

Q. $\text{K}_2[\text{PtCl}_6]$ is a well-known compound whereas the corresponding Ni compound is not known.

Ans. The oxidation state of Pt in $\text{K}_2[\text{PtCl}_6]$ is +4, which is a stable oxidation state for Pt. The +4 oxidation state for Ni is very difficult to achieve because the sum of the first four ionisation enthalpies is very high. Hence, the corresponding Ni (II) compound is not formed.

Q.5. Explain the following observations:

Q. The enthalpies of atomisation of transition metals are quite high.

Ans. This is because transition metals have strong metallic bonds as they have large number of unpaired electrons.

Q. There is a close similarity in physical and chemical properties of the 4d and 5d series of the transition elements, much more than expected on the basis of usual family relationship.

Ans. This is because $5d$ and $4d$ -series elements have virtually the same atomic and ionic radii due to lanthanide contraction. Due to equality in size of Zr and Hf, Nb and Ta, Mo and W, etc., the two elements of each pair have the same properties.

Q. The members in the actinoid series exhibit larger number of oxidation states than the corresponding members in the lanthanoid series.

[NCERT Exemplar]

Ans. The members in the actinoid series exhibit larger number of oxidation states than the corresponding members in the lanthanide series due to the fact that the $5f$, $6d$ and $7s$ levels are of comparable energies.

Q.6. How would you account for the following:

Q. Transition metals sometimes exhibit very low oxidation state such as +1 and 0.

Ans. +1 oxidation state is shown by element like Cu because after loss of one electron, it acquires stable configuration of $3d^{10}$. Zero oxidation state is shown in forming metal carbonyl, because p -electrons donated by ligands are accepted into the empty d -orbitals.

Q. Cr^{2+} is reducing in nature while with the same d -orbital configuration (d^4) Mn^{3+} is an oxidising agent.

Ans. Cr^{2+} is reducing as its configuration changes from d^4 to d^3 , a more stable half-filled t_{2g} configuration while Mn^{3+} is oxidising as Mn^{3+} to Mn^{2+} change results in a more stable half-filled d^5 configuration.

Q. E° of Cu is +0.34 V while that of Zn is -0.76 V.

[HOTS]

Ans. High ionisation enthalpy to transform $\text{Cu}(s)$ to $\text{Cu}^{2+}(aq)$ is not balanced by its hydration enthalpy. However, in case of Zn after removal of electrons from $4s$ -orbital, stable $3d^{10}$ configuration is acquired.

Q.7. Answer the following questions:

Q. For M^{2+}/M and $\text{M}^{3+}/\text{M}^{2+}$ systems, E° values for some metals are as follows:

$$\text{Cr}^{2+}/\text{Cr} = -0.9 \text{ V}$$

$$\text{Cr}^{3+}/\text{Cr}^{2+} = -0.4 \text{ V}$$

$$\text{Mn}^{2+}/\text{Mn} = -1.2 \text{ V}$$

$$\text{Mn}^{3+}/\text{Mn}^{2+} = +1.5 \text{ V}$$

$$\text{Fe}^{2+}/\text{Fe} = -0.4 \text{ V}$$

$$\text{Fe}^{3+}/\text{Fe}^{2+} = +0.8 \text{ V}$$

Use this data to comment upon

- the stability of Fe^{3+} in acid solution as compared to that of Cr^{3+} and Mn^{3+} .
- the ease with which iron can be oxidised as compared to the similar process for either Cr or Mn metals.

Ans. (a) Higher the reduction potential of a species, greater is the ease with which it undergo reduction. Among these pairs, $\text{Mn}^{3+}/\text{Mn}^{2+}$ has largest positive reduction potential. Hence Mn^{3+} can be easily reduced to Mn^{2+} i.e., Mn^{3+} is least stable. $\text{Cr}^{3+}/\text{Cr}^{2+}$ has a negative E° value, therefore, Cr^{3+} is most stable. $\text{Fe}^{3+}/\text{Fe}^{2+}$ has a positive value but small. Hence, Fe^{3+} is more stable than Mn^{3+} but less stable than Cr^{3+} .

(b) Lower the reduction potential or higher the oxidation potential of a species, greater is the ease with which it undergo oxidation. Among these pairs, Mn^{2+}/Mn has the most negative reduction potential or most positive oxidation potential. Therefore, it will be most easily oxidised. Thus, the decreasing order of their ease of oxidation is $\text{Mn} > \text{Cr} > \text{Fe}$.

Q. What can be inferred from the magnetic moment of the complex $\text{K}_4[\text{Mn}(\text{CN})_6]$, Magnetic moment: 2.2 BM?

[CBSE Sample Paper 2016]

Ans. In the complex $\text{K}_4[\text{Mn}(\text{CN})_6]$, Mn is in +2 oxidation state. Magnetic moment 2.2 BM indicates that it has only one unpaired electron and hence forms inner orbital or low spin octahedral complex. In presence of CN^- , a strong ligand the hybridisation involved is d^2sp^3 .

Q.8. Account for the following:

Q. Mn_2O_7 is acidic whereas MnO is basic.

Ans. Mn has + 7 oxidation state in Mn_2O_7 and + 2 in MnO . In low oxidation state of the metal, some of the valence electrons of the metal atom are not involved in bonding. Hence, it can donate electrons and behave as a base. On the other hand, in higher oxidation state of the metal, valence electrons are involved in bonding and are not available. Instead effective nuclear charge is high and hence it can accept electrons and behave as an acid.

Q. Though copper has completely filled d -orbital (d^{10}) yet it is considered as a transition metal.

Ans. Copper exhibits +2 oxidation state wherein it will have incompletely filled d -orbitals ($3d^9$), hence a transition metal.

Q. Actinoids show wide range of oxidation states.

[CBSE (F) 2016]

Ans. This is due to comparable energies of $5f$, $6d$ and $7s$ orbitals.

Q.9. A mixed oxide of iron and chromium, FeOCr_2O_3 is fused with sodium carbonate in the presence of air to form a yellow coloured compound (A). On acidification the compound (A) forms an orange coloured compound (B), which is a strong oxidising agent.

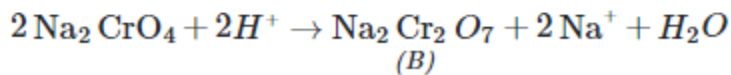
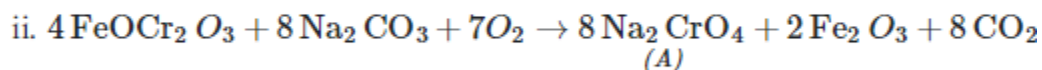
- Identify the compounds (A) and (B).
- Write balanced chemical equation for each step.

[HOTS]

Ans.

i. Compound A: Sodium chromate (Na_2CrO_4)

Compound B: Sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$)



Q.10. When a brown compound of manganese (A) is treated with HCl it gives a gas (B). The gas taken in excess, reacts with NH_3 to give an explosive compound (C). Identify compounds A and B.

[NCERT Exemplar] [HOTS]

Ans. A = MnO_2 , B = Cl_2 , C = NCl_3

