

Chapter: The d and f Block Elements

Introduction to d block elements

Question 1

In Tc (Z = 43) and Tb(Z = 65) which one is inner transition metal and which one is transition metal and why?

Ans.

The outer Electronic configuration of Tc (Z = 43) is $4d^65s^1$ and that of Tb (Z = 65) is $4f^95d^06s^2$. Since in Tc there is incompletely filled d orbitals hence it is Transition metal or d-block element and in Tb there is incompletely filled f orbitals hence it is inner transition metal or f-block element.

Question 2

Why the melting points of transition metals are very high and what is the trend of melting point across the period of 3d series?

Ans.

The high melting points of transition metals are due to the involvement of greater number of electrons of $(n-1)d$ in addition to the n electrons in the interatomic metallic bonding. In a period of 3d series the melting points of these metals increases to a maximum at d^5 except for anomalous values of Mn and decreases regularly as the atomic number increases.

Question 3

Why scandium (Z = 21) is a transition element but zinc (Z = 30) is not?

Ans.

The outer electronic configuration of scandium (Z = 21) is $3d^14s^2$ while that of zinc (Z = 30) is $3d^{10}4s^2$. Since scandium has incompletely filled d orbital in its ground state it is regarded as transition metal while zinc do not have incompletely filled d-orbital in either ground state or any of its oxidized state so it is not regarded as transition metal.

Question 4

Silver atom has completely filled d orbitals ($4d^{10}$) in its ground state. How can you say that it is a transition element?

Ans.

Silver Ag(Z = 47) have outer electronic configuration $5s^14d^{10}$ in its ground state showing that it is not transition metal in first instance but in +2 oxidation state its electronic configuration is $5s^04d^9$, proving that it is transition metal with incompletely filled d orbital.

Question 5

Why the 4s orbitals fill prior to 3d orbitals.

Ans.

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The 3d orbitals of the transition elements project to the periphery of an atom more than the 4s orbitals. Thus it has higher energy than 4s orbitals. This is the reason 4s orbitals fills prior to 3d orbitals.

Question 6

Why the d-block elements are called transition elements?

Ans.

The d-block occupies the large middle section of the periodic table and flanked by s- and p- blocks elements. The name 'transition' given to the elements of d-block is because of their position between s- and p- block elements and thus showing transition in properties of s and p block elements.

Question 7

Define transition elements.

Ans.

A transition element is defined as the one which has incompletely filled d orbitals in its ground state or in any one of its oxidation states.

Question 8

Give the names of two series of inner transition metals.

Ans.

The two series of inner transition metal are 4f series or lanthanoids and 5f series or actinoids.

Question 9

Write down the electronic configuration of Mn.

Ans.

Mn(25): $1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^5, 4s^2$

Question 10

Write down the three series of the transition metals.

Ans.

The three series of transition metals are:

- i. 3d series (Sc to Zn)
- ii. 4d series (Y to Cd)
- iii. 5d series (La to Hg, omitting Ce to Lu).

Properties of d-Block elements

Question 1

How would you account for the following?

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- (i) The atomic radii of the metals of the third (5d) series of transition elements are virtually the same as those of the corresponding members of the second (4d) series.
- (ii) The E° value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} couple or Fe^{3+}/Fe^{2+} couple.
- (iii) The highest oxidation state of a metal is exhibited in its oxide or fluoride.

Ans.

(i) Due to lanthanoid contraction.

(ii) Because Mn^{3+} has the outer electronic configuration of $3d^4$ and Mn^{2+} has the outer electronic configuration of $3d^5$. Thus, the conversion of Mn^{3+} to Mn^{2+} will be a favourable reaction since $3d^5$ is a very stable configuration as it is half filled configuration. Hence, E° value for Mn^{3+}/Mn^{2+} couple is positive.

Cr^{3+} to Cr^{2+} undergoes a change in outer electronic configuration from $3d^3$ to $3d^4$. Fe^{3+} to Fe^{2+} undergoes a change in outer electronic configuration from $3d^5$ to $3d^6$. Both these configurations of the resultant are not stable and hence have a lower E° value.

(iii) Because of small size and high electronegativity oxygen or fluorine can oxidise the metal to its highest oxidation state.

Question 2

Explain the following observations:

- (i) Generally there is an increase in density of elements from titanium (Z=22) to copper (Z=29) in the first series of transition elements.
- (ii) Transition elements and their compounds are generally found to be good catalysts in chemical reactions.

Ans.

(i) The decrease in metallic radius coupled with increase in atomic mass results in a general increase in the density of the elements from titanium (Z=22) to copper (Z=29) in the first series of transition elements.

(ii) Transition elements and their compounds are generally found to be good catalysts in chemical reaction because transition elements have the ability to adopt multiple oxidation states and form complexes.

Question 3

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Explain the following observations giving an appropriate reason for each.

- (i) The enthalpies of atomization of transition elements are quite high.
- (ii) There occurs much more frequent metal-metal bonding in compounds of heavy transition metals (i.e. 3rd series).
- (iii) Mn^{2+} is much more resistant than Fe^{2+} towards oxidation.

Ans.

- I. They have large number of unpaired electrons in their atoms; hence they have stronger interatomic interaction and stronger bonding between atoms which results in higher enthalpies of atomisation.
- II. The transition metals form a large number of compounds with metal metal bonding. This is due to the comparatively smaller sizes of the metal ions, their high ionic charges and the availability of *d* orbitals for bond formation.
- III. Mn^{2+} is much more resistant to oxidation than Fe^{2+} because Mn^{2+} has a stable half filled configuration which gets disturbed when oxidation of Mn^{2+} occurs and Mn^{3+} is formed. Whereas in case of oxidation of Fe^{2+} , Fe^{3+} is formed which has a stable half filled configuration.

Question 4

Why do the transition elements exhibit higher enthalpies of atomisation and why is enthalpy of atomisation of zinc is the lowest in 3d series?

Ans.

The value of enthalpy of atomisation increases as the interatomic interaction increases. Further the interatomic interaction is affected by the number of unpaired electrons. The greater the number of unpaired electrons greater is interatomic interaction and greater will be the enthalpy of atomisation. Since transition elements have unpaired electrons they have greater interatomic interaction and exhibit higher enthalpies of atomisation. Zinc contains no unpaired electrons hence enthalpy of atomisation of zinc is the lowest.

Question 5

Which of the 3d series of the transition element exhibit the largest number of oxidation states and why?

Ans.

Manganese exhibit the largest number of oxidation states. It shows the oxidation states +2, +3, +4, +5, +6, and +7. The reason for that is the maximum number of unpaired electrons present in its outermost shell i.e. $3d^5 4s^2$.

Question 6

What is Lanthanoid contraction and what is the factor responsible for that?

Ans.

There is an increase in radii from the first (3*d*) to the second (4*d*) series of the elements but the radii of the third (5*d*) series are virtually the same as those of the corresponding members of the second series. This phenomenon is called Lanthanoids contraction. The possible reason for that is the intervention of the 4*f* orbitals which must be filled before

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the 5d series of elements begins. The imperfect shielding of one 4f electron by another result in the decrease in the size of the entire 4fⁿ orbitals as the nuclear charge increases along the series.

Question 7

Why Cr²⁺ is reducing agent and Mn³⁺ an oxidizing agent although both have d⁴ configuration?

Ans.

Cr²⁺ is reducing agent as its configuration changes from d⁴ to d³, when it oxidized to Cr³⁺. The d³ configuration have a half-filled t_{2g} level which is very stable. On the other hand, the reduction of Mn³⁺ to Mn²⁺ results in the half-filled (d⁵) configuration which has extra stability hence Mn³⁺ acts as oxidizing agent.

Question 8

Why the element of 3d series forms coloured ions?

Ans.

When an electron of a lower energy d orbital of the transition metal ion is excited to a higher energy d orbital, the energy of excitation corresponds to the frequency of light absorbed. Since this frequency lies in the visible region hence the corresponding complementary color of the absorbed light can be observed.

Question 9

Name the compound in which Ni and Fe show zero oxidation state and Why?

Ans.

In Ni(CO)₄ and Fe(CO)₅, the oxidation state of nickel and iron is zero because the ligand CO is capable of π-acceptor character in addition to the σ-bonding.

Question 10

Name the oxometal anions of the first series of the transition metals in which the metal exhibits the oxidation state equal to its group number.

Ans.

In permanganate ion (MnO₄⁻) the metal exhibits the oxidation state equal to its group number.

Question 11

Which element of 3d series does not exhibit variable oxidation state?

Ans.

Scandium (Z = 21) of 3d series does not exhibit variable oxidation states.

Question 12

Among oxygen and fluorine which one has the greater stability to stabilize high oxidation states?

Ans.

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The ability of oxygen to stabilize high oxidation states is greater than that of fluorine.

Question 13

Name the element of 3d series which have lowest enthalpy of atomisation.

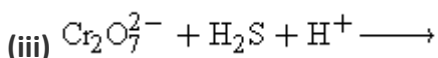
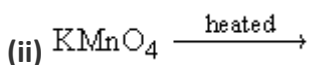
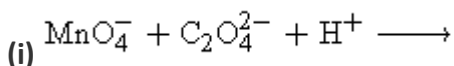
Ans.

In 3d series enthalpy of atomisation of zinc is the lowest.

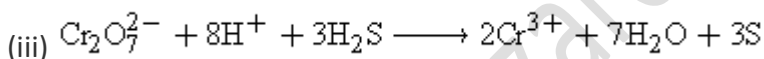
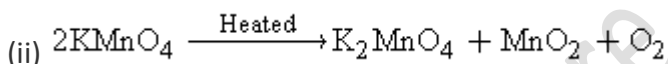
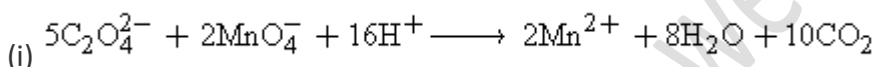
Important compounds of d block

Question 1

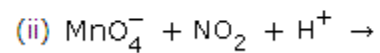
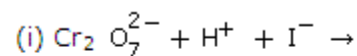
Complete the following chemical equations:



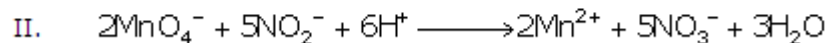
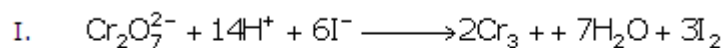
Ans.



Question 2



Ans.



Question 3

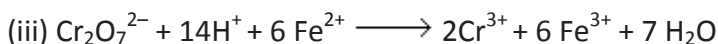
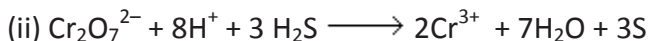
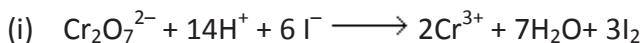
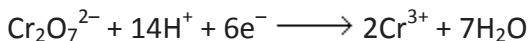
Describe the oxidising action of potassium dichromate and write the ionic equations for its reaction with:

(i) Iodide (ii) Iron (II) solution and (iii) H_2S .

Ans.

In acidic solution, the oxidising action of Potassium dichromate can be represented as follows:

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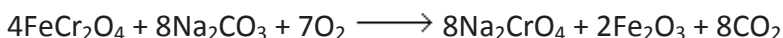


Question 4

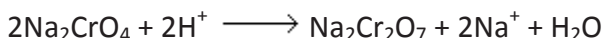
Give the method of preparation of potassium dichromate.

Ans.

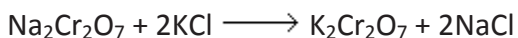
Dichromates are generally prepared from chromate, which is obtained by the fusion of chromite ore (FeCr_2O_4) with sodium or potassium carbonate in free access of air.



Solution of sodium chromate is filtered and acidified with sulphuric acid to give solution from which $\text{Na}_2\text{Cr}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ can be crystallized



Potassium dichromate can be prepared by treating the solution of sodium dichromate with potassium chloride.



Question 5

What are interstitial compounds? Give their characteristics.

Ans.

Interstitial compounds are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals. The atoms in interstitial compounds are usually in non stoichiometric ratio and are neither typically ionic nor covalent.

Characteristics:

(i) They have high melting points.

(ii) They are very hard.

(iii) They retain metallic conductivity.

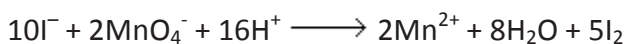
(iv) They are chemically inert.

Question 6

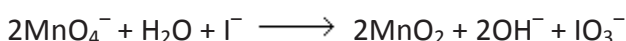
Give reaction of KMnO_4 with KI in (i) Acidic medium, (ii) Alkaline medium.

Ans.

Acidic medium: Iodine is liberated from potassium iodide



Alkaline medium: Iodide is oxidized to iodate



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Question 7

What are alloys and how these are formed by the elements of transition metals?

Ans.

Alloys are homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other. Alloys are formed by atoms with almost similar metallic radii. Transition metals readily form alloys because of similar radii. The alloys so formed are hard, have high melting points and improved quality than original metal.

Question 8

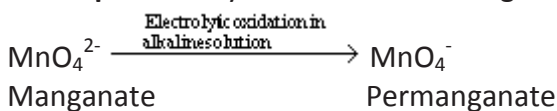
Give the commercial method for the preparation of KMnO_4 .

Ans.

Ist step: Fusion of MnO_2 with an alkali metal hydroxide and an oxidising agent like KNO_3



IInd step: Electrolytic oxidation of manganate



Question 9

What is the difference between manganate and permanganate ion?

Ans.

The manganate ion (MnO_4^{2-}) is green colored and paramagnetic while permanganate ion (MnO_4^-) is purple coloured and diamagnetic.

Question 10

Give the name of two acidic oxide and their corresponding acid formed by the elements of 3d transition series.

Ans.

Mn_2O_7 gives HMnO_4 acid and CrO_3 gives H_2CrO_4 acid.

Question 11

Name the elements which can be used in the production of alloy steel.

Ans.

Iron, chromium, vanadium, tungsten, molybdenum and manganese.

Question 12

Give two examples of interstitial compounds.

Ans.

Fe_3H and Mn_4N

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Lanthanoids & Actinoids

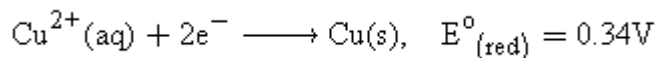
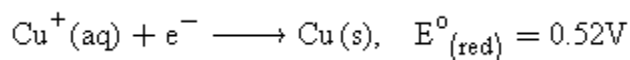
Question 1

Assign reasons for the following:

- (i) Copper (I) ion is not known in aqueous solution.
(ii) Actinoids exhibits greater range of oxidation states than Lanthanoids.

Ans.

- (i) In aqueous solution, Cu^+ ion undergoes oxidation to Cu^{2+} ion. The relative stability of different oxidation states can be seen from their electrode potentials.



Due to more reduction electrode potential value of Cu^+ , it undergoes oxidation reaction quite feasibly. Hence, Copper (I) ion is not known in aqueous solution.

- (ii) The actinoids show a larger number of oxidation states because of very small energy gap between the 5f, 6d and 7s sub-shells.
Hence all their electrons can take part in bond formation.

Question 2

Write a note on the Ionisation Enthalpy for lanthanoids.

Ans.

The first ionisation enthalpies of the lanthanoids are around 600 kJ mol^{-1} , the second is obviously greater than the first i.e. about 1200 kJ mol^{-1} . The third ionisation enthalpies is abnormally low for lanthanum, gadolinium and lutetium because a certain degree of stability attained due to empty, half-filled and completely filled orbitals of f level.

Question 3

Write the electronic configuration of the following elements of lanthanoid and their possible oxidation state other than +3: (a) Eu and (b) Yb.

Ans.

(a) Eu (63): $4f^7 6s^2$ the possible oxidation state other than +3 is +2 having $4f^7$ configuration.

(b) Yb (70): $4f^{14} 6s^2$ the possible oxidation state other than +3 is +2 having $4f^{14}$ configuration.

Question 4

Why it is very difficult to study the chemistry of Actinoid?

Ans.

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The actinoids are radioactive elements having relatively short half-lives. The elements of actinoid series could be prepared only in nanogram quantities. This is the reason why their study is more difficult.

Question 5

What is mischmetall and what is its use?

Ans.

Mischmetall is an alloy of a lanthanoid metal (~ 95%) and iron (~ 5%) and traces of S, C, Ca and Al. A large quantity of mischmetall is used in Mg-based alloy to produce bullets, shell and lighter flint.

Question 6

Why Ce^{4+} behaves as good oxidising agent although being a stable species?

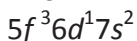
Ans.

The formation of Ce^{4+} is favoured by its noble gas configuration, but it is a strong oxidant reverting to the common +3 state because the E° value for Ce^{4+}/Ce^{3+} is + 1.74 V which is positive.

Question 7

Write down the outer electronic configuration of Uranium.

Ans.



Question 8

Write down the number of electrons in 4f, 5d and 6s orbital of Ce in +4 oxidation state.

Ans.

The outer electronic configuration of Ce in +4 oxidation state is $4f^0 5d^0 6s^2$. Hence the number of electron possessed by 4f, 5d and 6s orbital is zero.

Question 9

Write down the most common oxidation state for lanthanoids.

Ans.

Write down the most common oxidation state for lanthanoids.

Question 10

Why do Zr and Hf occur together in nature?

Ans.

The atomic radii of Zr (160 pm) and Hf (159 pm) is almost identical due to lanthanoid contraction. So they occur together in nature.

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