The d and f-Block Elements

Case Study Based Questions

Case Study 1

When an orange coloured crystalline compound [A] was heated with common salt and concentrated sulphuric acid, an orange red coloured gas [B] was evolved. The gas [B] on passing through NaOH solution gave a yellow solution [C]. The solution on reacting with an aqueous solution of lead acetate gave a yellow precipitate. Read the given passage carefully and give the

Answer of the following questions:

Q1. The crystalline compound [A] is:

a. cobalt nitrate

b. manganese sulphate

c. potassium dichromate

d. ammonium dichromate

Q2. The gas [B] is:

a. chlorine

c. chromyl chloride

b. bromine

d. nitrogen peroxide

Q3. What happens when potassium iodide reacts with acidic solution of potassium dichromate?

a. It liberates iodine

b. Potassium sulphate is formed

c. Chromium sulphate is formed

d. All the above products are formed

Q4. One mole of acidified K_2Cr_2O7, on reaction with excess KI will liberate ....mole (s) of 12.

a. 3

b. 1

c. 7
d. 2

Answers

1. (c) potassium dichromate
2. (c) chromyl chloride
3. (d) All the above products are formed
4. (a) 3

Case Study 2

In basic solution with pH 6, CrO_3 forms the tetrahedral yellow chromate ion, CrO_4^{2-}. Between pH 2 and 6, HCr_4- and the orange red dichromate ion, $Cr_2O_7^{2-}$ are in equilibrium. At pH values below 1, the main species is H_2CrO_4. The equilibria are:

$$HCr_4^- \rightleftharpoons CrO_4^{2-} + H^+, K = 10^{-5.9}$$
$$HCr_4^- \rightleftharpoons HCrO_4^- + H^+, K = 4.1$$
$$Cr_2O_7^{2-} + H_2O \rightleftharpoons 2HCrO_4^-, \ K = 10^{-2.2}$$

In addition, these are base-hydrolysis equilibria

$$Cr_2O_7^{2-} + OH^- \rightleftharpoons HCrO_4^- + CrO_4^{2-}$$
$$HCr_2O_4^- + OH^- \rightleftharpoons CrO_4^- + H_2O$$

The pH dependent equilibria are quite labile and on addition of cations that form insoluble chromates (e.g., Ba_{2+}, Pb_{2+} and A_{g+}), the chromates and not the dichromates are precipitated.

Read the given passage carefully and give the answer of the following questions:

Q1. Which of the following statement is correct?
a. Acid solutions of dichromate are strong oxidants
b. In alkaline solution, the chromate ion is strong oxidant
c. Acid solutions of dichromate are poor oxidants
d. Both a. and b.

Q2. In the redox reaction involving $Cr_2$072- and Fe2+ ions, the number of electrons absorbed per chromium atoms is:
a. 1
b. 3

c. 4
d. 6

Q3. What happens when a solution of potassium chromate is treated with an excess of dilute nitric acid?

a. Cr^{3}+ and $Cr_20_7^{2}$- are formed
b. $Cr_20_7^{2-}$and H2O are formed
c. CrO_7^{2-} is reduced to +3 state of Cr
d. CrO_7^{2-} is oxidised to +7 state of Cr

Q4. When acidified K_2Cr_2O, solution is added to Sn2+ salts, then Sn^2+ changes to:
a. Sn
b. Sn^3+
c. Sn4+
d. Sn+

Answers

1. (a) Acid solutions of dichromate are strong oxidants

2. (b) 3

3. (b) Cr_202 and H2O are formed

4. (c) Sn4+

Case Study 3

The d-block occupies the large middle section flanked between s- and p-blocks in the periodic table. The name 'transition' given to the elements of d-block is only because of their position between s and p-block elements. The d-orbitals of the penultimate energy level in their atoms receive electrons giving rise to the three rows of the transition metals, i.e., 3d, 4d, and 5d. The fourth row of 6d is still incomplete. First transition series or 3d-series: Scandium (Sc) to Zinc (Zn). Second transition series or d-series: Yttrium (Y) to Cadmium (Cd). Third transition series or 5d-series: Lanthanum (La) to Mercury (Hg) excluding Ce to Lu. Fourth transition series or 6d-series: Actinium (Ac) to Copernicium (Cn) excluding Th to Lr.

Read the given passage carefully and give the answer of the following questions:

Q1. Silver atom has completely filled d-orbitals (4d10) in its ground state. How can you say that it is a transition element?

Q2. In the series Sc (Z= 21) to Zn (Z = 30), the enthalpy of atomisation of zinc is lowest, i.e., 126 kJ mol-^{1}. Why?

Q3. Why is the highest oxidation state of a metal exhibited in its oxide or fluoride only?

OR

The E° $_{M2+/M}$ value of copper is positive (+0.34V). What is the possible reason for this?

Answers

1. Silver in its +1 oxidation state, exhibits $4d^{10}55^{0}$ configuration. But in some compounds, it also shows +2 oxidation state, so the configuration becomes 4d9 55^{0}. Here, d-orbital is not completely filled. Therefore, silver is a transition element.

2. Zinc has stable ground state due to its completely filled d-orbitals. It therefore, has least tendency to form metallic bonds, in the series and thus requires least enthalpy of atomisation to get atomised.

3. Oxygen and fluorine both have small size and high value of electronegativity. So, they can oxidise the metal to their highest oxidation states.

OR

E° M^{2}/M value of copper is positive as value of hydration enthalpy is less than the sum of values of ionisation enthalpy and enthalpy of ionisation.

Solutions for Questions 4 to 8 are Given Below

Case Study 4

Read the passage given below and answer the following questions :

The transition elements have incompletely filled *d*-subshells in their ground state or in any of their oxidation states. The transition elements occupy position in between *s*- and *p*-blocks in groups 3-12 of the Periodic table. Starting from fourth period, transition elements consists of four complete series : Sc to Zn, Y to Cd and La, Hf to Hg and Ac, Rf to Cn. In general, the electronic configuration of outer orbitals of these elements is $(n-1)\,d^{1-10}\,ns^{1-2}$. The electronic configurations of outer orbitals of Zn, Cd, Hg and Cn are represented by the general formula $(n-1)d^{10}\,ns^2$. All the transition elements have typical metallic properties such as high tensile strength, ductility, malleability. Except mercury, which is liquid at room temperature, other transition elements have typical metallic structures. The transition metals and their compounds also exhibit catalytic property and paramagnetic behaviour. Transition metal also forms alloys. An alloy is a blend of metals prepared by mixing the components. Alloys may be homogeneous solid solutions in which the atoms of one metal are distributed randomly among the atoms of the other.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Which of the following characteristics of transition metals is associated with higher catalytic activity?

(a) High enthalpy of atomisation
(b) Variable oxidation states
(c) Paramagnetic behaviour
(d) Colour of hydrated ions

(ii) Transition elements form alloys easily because they have

(a) same atomic number
(b) same electronic configuration
(c) nearly same atomic size
(d) same oxidation states.

(iii) The electronic configuration of tantalum (Ta) is

(a) $[Xe]4f^0\,5d^1\,6s^2$
(b) $[Xe)4f^{14}\,5d^2\,6s^2$
(c) $[Xe]4f^{14}\,5d^3\,6s^2$
(d) $[Xe[4f^{14}\,5d^4\,6s^2$

(iv) Which one of the following outer orbital configurations may exhibit the largest number of oxidation states?

(a) $3d^5 4s^1$
(b) $3d^5 4s^2$
(c) $3d^2 4s^2$
(d) $3d^3 4s^2$

OR

The correct statement(s) among the following is/are

(i) all *d*- and *f*-block elements are metals

(ii) all *d*- and *f*-block elements form coloured ions

(iii) all *d*- and *f*-block elements are paramagnetic.

(a) (i) only
(b) (i) and (ii) only
(c) (ii) and (iii) only
(d) (i), (ii) and (iii)

Case Study 5

Read the passage given below and answer the following questions :

The unique behaviour of Cu, having a positive E° accounts for its inability to liberate H_2 from acids. Only oxidising acids (nitric and hot concentrated sulphuric acid) react with Cu, the acids being reduced. The stability of the half-filled (d^5) subshell in Mn^{2+} and the completely filled (d^{10}) configuration in Zn^{2+} are related to their E° (M^{3+}/M^{2+}) values. The low value for Sc reflects the stability of Sc^{3+} which has a noble gas configuration. The comparatively high value for Mn shows that $Mn^{2+}(d^5)$ is particularly stable, whereas a comparatively low value for Fe shows the extra stability of Fe^{3+} (d^5). The comparatively low value for V is related to the stability of V^{2+} (half-filled t_{2g} level).

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Standard reduction electrode potential of Zn^{2+}/Zn is – 0.76 V. This means

(a) ZnO cannot be reduced to Zn by H_2 under standard conditions

(b) Zn cannot liberate H_2 with concentrated acids

(c) Zn is generally the anode in an electrochemical cell

(d) Zn is generally the cathode in an electrochemical cell.

(ii) E° values for the couples Cr^{3+}/Cr^{2+} and Mn^{3+}/Mn^{2+} are –0.41 and +1.51 volts respectively. These values suggest that

(a) Cr^{2+} acts as a reducing agent whereas Mn^{3+} acts as an oxidizing agent

(b) Cr^{2+} is more stable than Cr^{3+} state

(c) Mn^{3+} is more stable than Mn^{2+}

(d) Cr^{2+} acts as an oxidizing agent whereas Mn^{3+} acts as a reducing agent.

(iii) The reduction potential values of *M*, *N* and *O* are +2.46, –1.13 and –3.13 V respectively. Which of the following order is correct regarding their reducing property?

(a) $O > N > M$
(b) $O > M > N$
(c) $M > N > O$
(d) $M > O > N$

(iv) Which of the following statements are true?

(i) Mn^{2+} compounds are more stable than Fe^{2+} towards oxidation to +3 state.

(ii) Titanium and copper both in the first series of transition metals exhibits +1 oxidation state most frequently.

(iii) Cu^+ ion is stable in aqueous solutions.

(iv) The E° value for the Mn^{3+}/Mn^{2+} couple is much more positive than that for Cr^{3+}/Cr^{2+} or Fe^{3+}/Fe^{2+}.

(a) (ii) and (iii)
(b) (i) and (iv)
(c) (i) and (iii)
(d) (ii) and (iv)

OR

The stability of $Cu^{2+}_{(aq)}$ rather than $Cu^{+}_{(aq)}$ is due to

(a) more negative $\Delta_{hyd} H^\circ$ of $Cu^{2+}_{(aq)}$
(b) less negative $\Delta_{hyd} H^\circ$ of $Cu^{2+}_{(aq)}$
(c) more positive $\Delta_{hyd} H^\circ$ of $Cu^{2+}_{(aq)}$
(d) less positive $\Delta_{hyd} H^\circ$ of $Cu^{2+}_{(aq)}$.

Case Study 6

Read the passage given below and answer the following questions :

The *f*-block elements are those in which the differentiating electron enters the $(n-2)f$ orbital. There are two series of *f*-block elements corresponding to filling of 4*f* and 5*f*-orbitals. The series of 4*f*-orbitals is called lanthanides. Lanthanides show different oxidation states depending upon stability of f^0, f^7 and f^{14} configurations, though the most common oxidation states is +3. There is a regular decrease in size of lanthanides ions with increase in atomic number which is known as lanthanide contraction.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) The atomic numbers of three lanthanide elements *X*, *Y* and *Z* are 65, 68 and 70 respectively, their Ln^{3+} electronic configuration is

(a) $4f^8, 4f^{11}, 4f^{13}$ (b) $4f^{11}, 4f^8, 4f^{13}$ (c) $4f^0, 4f^2, 4f^{11}$ (d) $4f^3, 4f^7, 4f^9$

(ii) Lanthanide contraction is observed in

(a) Gd (b) At (c) Xe (d) Te

(iii) Which of the following is not the configuration of lanthanoid?

(a) $[Xe]4f^{10}6s^2$ (b) $[Xe]4f^15d^16s^2$ (c) $[Xe]4d^{14}5d^{10}6s^2$ (d) $[Xe]4f^75d^16s^2$

OR

Name a member of the lanthanoid series which is well known to exhibit +4 oxidation state.

(a) Cerium ($Z = 58$) (b) Europium ($Z = 63$) (c) Lanthanum ($Z = 57$) (d) Gadolinium ($Z = 64$)

(iv) Identify the incorrect statement among the following.

(a) Lanthanoid contraction is the accumulation of successive shrinkages.
(b) The different radii of Zr and Hf due to consequence of the lanthanoid contraction.
(c) Shielding power of 4*f* electrons is quite weak.
(d) There is a decrease in the radii of the atoms or ions as one proceeds from La to Lu.

Case Study 7

Read the passage given below and answer the following questions :

Transition metal oxides are compounds formed by the reaction of metals with oxygen at high temperature. The highest oxidation number in the oxides coincides with the group number. In vanadium, there is a gradual change from the basic V_2O_3 to less basic V_2O_4 and to amphoteric V_2O_5·V_2O_4 dissolves in acids to give VO^{2+} salts. Transition metal oxides are commonly utilized for their catalytic activity and semiconductive properties. Transition metal oxides are also frequently used as pigments in paints and plastic. Most notably titatnium dioxide. One of the earliest application of transition metal oxides to chemical industry involved the use of vanadium oxide for catalytic oxidation of sulfur dioxide to sulphuric acid. Since then, many other applications have emerged, which include benzene oxidation to maleic anhydride on vandium oxides; cyclohexane oxidation to adipic acid on cobalt oxides. An important property of the catalyst material used in these processes is the ability of transition metals to change their oxidation state under a given chemical potential of reductants and oxidants.

The following questions are multiple choice questions. Choose the most appropriate answer :

(i) Which oxide of vanadium is most likely to be basic and ionic ?

(a) VO (b) V_2O_3 (c) VO_2 (d) V_2O_5

(ii) Vanadyl ion is

(a) VO^{2+} (b) VO_2^+ (c) V_2O^+ (d) VO_4^{3-}

OR

Which of the following statements is false?

(a) With fluorine vanadium can form VF_5.

(b) With chlorine vanadium can form VCl_5.

(c) Vanadium exhibits highest oxidation state in oxohalides $VOCl_3$, $VOBr_3$ and fluoride VF_5.

(d) With iodine vanadium cannot form VI_5 due to oxidising power of V^{5+} and reducing nature of I^-.

(iii) The oxidation state of vanadium in V_2O_5 is

(a) +5/2 (b) +7 (c) +5 (d) +6

(iv) Identify the oxidising agent in the following reaction.

$V_2O_5 + 5Ca \longrightarrow 2V + 5CaO$

(a) V_2O_5 (b) Ca (c) V (d) None of these

Case Study 8

Read the passage given below and answer the following questions :

Transition elements are elements that have partially filled *d*-orbitals. The configuration of these elements corresponds to $(n-1)d^{1-10}\,ns^{1-2}$. It is important to note that the elements mercury, cadmium and zinc are not considered transition elements because of their electronic configurations, which corresponds to $(n-1)d^{10}\,ns^2$.
Some general properties of transition elements are :
These elements can form coloured compounds and ions due to *d*-*d* transition;
These elements exhibit many oxidation states;
A large variety of ligands can bind themselves to these elements, due to this, a wide variety of stable complexes formed by these ions. The boiling and melting point of these elements are high. These elements have a large ratio of charge to the radius.

In these questions (Q. No. i-iv), a statement of assertion followed by a statement of reason is given. Choose the correct answer out of the following choices.

(a) Assertion and reason both are correct statements and reason is correct explanation for assertion.

(b) Assertion and reason both are correct statements but reason is not correct explanation for assertion.

(c) Assertion is correct statement but reason is wrong statement.

(d) Assertion is wrong statement but reason is correct statement.

(i) **Assertion :** Tungsten has very high melting point.
Reason : Tungsten is a covalent compound.

(ii) **Assertion :** Zn, Cd and Hg are normally not considered transition metals.
Reason : *d*-Orbitals in Zn, Cd and Hg elements are completely filled, hence these metals do not show the general characteristics properties of the transition elements.

(iii) **Assertion :** Copper metal gets readily corroded in acidic aqueous solution such as HCl and dil. H_2SO_4.
Reason : Free energy change for this process is positive.

(iv) **Assertion :** Tailing of mercury occurs on passing ozone through it.
Reason : Due to oxidation of mercury.

OR

Assertion : Transition metals are poor reducing agents.
Reason : Transition metals form numerous alloys with other metals.

4. (i) (b): The transition metals and their compounds are known for their catalytic activity. This activity is ascribed to their ability to adopt multiple oxidation states to form complexes.

(ii) (c) : Because of similar radii and other characteristics of transition metals, alloys are readily formed by these metals.

(iii) (c)

(iv) (b): Greater the number of valence electrons, more will be the number of oxidation states exhibited by the element.

OR

(a) : All the *d*-block elements are metals, they exhibit most properties of metals like lustre, malleability, ductility, high density, high melting and boiling point, hardness, conduction of heat and electricity, etc. All the *f*-block elements are also metals but they are not good conductors of heat and electricity.

5. (i) (a)

(ii) (a): Lesser and negative reduction potential indicates that Cr^{2+} is a reducing agent. Higher and positive reduction potential indicates that Mn^{3+} is a stronger oxidizing agent.

(iii) (a): The electrode which has more reduction potential is a good oxidizing agent and has least reducing power.

(iv) (b): (i) It is because Mn^{2+} has $3d^5$ electronic configuration which has extra stability.
(ii) Not titanium but copper, because with +1 oxidation state an extra stable configuration, $3d^{10}$ results.
(iii) It is not stable as it undergoes disproportionation; $2Cu^{+}_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$. The $E°$ value for this is favourable.
(iv) Much larger third ionisation energy of Mn (where the required change is d^5 to d^4) is mainly responsible for this.

OR

(a) : The stability of $Cu^{2+}_{(aq)}$ rather than $Cu^{+}_{(aq)}$ is due to the much more negative $\Delta_{Hyd}H°$ of $Cu^{2}_{(aq)}$ than Cu^{+}, which more than compensates for the second ionisation enthalpy of Cu.

6. (i) (a): Terbium (65), $4f^8$; Dysprosium (Dy), $4f^9$; Ytterbium (Yb), $4f^{13}$.

(ii) (a)

(iii) (c)

OR

(a)

(iv) (b): The almost identical radii of Zr (160 pm) and Hf (159 pm), a consequence of lanthanoid contraction.

7. (i) (a): Oxide of V in lowest oxidation state, *i.e.*, VO is basic and ionic in character.

(ii) (a): Vanadyl ion is VO^{2+} where V is in +4 oxidation state.

OR

(b)

(iii) (c)

(iv) (a)

8. (i) (c): Tungsten is a transition element and is very hard due to high metallic bonding.

(ii) (a)

(iii) (d): Non-oxidising acids (HCl and dil. H_2SO_4) do not have any effect on copper. However they dissolve the metal in presence of air. As it is a non-spontaneous process so, ΔG cannot be –ve.

(iv) (a): When mercury is exposed to ozone it gets superficially oxidised and loses its meniscus and sticks to the glass.

OR

(b): In actual practice transition metals react with acid very slowly and act as poor reducing agents. This is due to the protection of metal as a result of formation of thin oxide protective film. Further, their poor tendency as reducing agent is due to high ionisation energy, high heat of vapourisation and low heat of hydration.