Date: 16/10/2021

Q1. Complete the following reaction:

$$MnO_4^-(aq) + H_2O_2(aq) \longrightarrow$$

Q2. The compound AgF_2 is unstable, however if formed the compound acts as a very strong oxidising agent. Why?

Q3. MnO_4^{2-} undergoes disproportionation reaction in acidic medium but MnO_4^- does not. Why?

Q4. Complete the following reactions:

(a) $2S_2O_3^{2-} + I_2 \longrightarrow$ (b) $S_2O_3^{2-} + 2Br_2 + 5H_2O \longrightarrow$

Q5. Fluorine reacts with ice and results in the change

$$H_2O(s) + F_2(g) \longrightarrow HF(g) + HOF(g)$$

Justify that this reaction is a redox reaction.

Q6. Which of the following species do not show disproportionation?

$$ClO^-, \quad ClO_2^-, \quad ClO_3^- \quad \text{and} \quad ClO_4^-.$$

Q7. Can Fe^{3+} oxidises Br^- to Br_2 at 1 M concentration?

$$E°(Fe^{3+}/Fe^{2+}) = 0.77\,V \quad \text{and} \quad E°(Br/Br^-) = 1.09\,V.$$

Q8. Predict the product of electrolysis of an aqueous solution of $AgNO_3$ with platinum electrodes.

Q9. (a) How does Cu_2O act as both oxidant and reductant? Explain with proper reactions showing the change in oxidation numbers in each example.

(b) Find the value of n in $MnO_4^- + 8H^+ + ne^- \longrightarrow Mn^{2+} + 4H_2O$.

(c) Determine the oxidation number of iron in the following compound:

$$FeSO_4 . (NH_4)_2SO_4 \cdot 6H_2O$$

Q10. Justify that the following reactions are redox reactions:

(a) $CuO(s) + H_2(g) \longrightarrow Cu(s) + H_2O(g)$

(b) $Fe_2O_3(s) + 3CO(g) \longrightarrow 2Fe(s) + 3CO_2(g)$

(c) $4BCl_3(g) + 3LiAlH_4(s) \longrightarrow 2B_2H_6(g) + 3LiCl(s) + 3AlCl_3(s)$

Q11. Write balanced chemical equation for the reaction of liquid hydrazine (N_2H_4) with chlorate ion $[ClO_3]^-$ which produces nitric oxide gas and chloride ions. Balance this reaction in basic medium by oxidation number method.

Q12. Assign the oxidation number to the underlined elements in each of the following species:

(a) $NaH_2\underline{P}O_4$ (b) $H_2\underline{S}_4O_6$ (c) $KAl(\underline{S}O_4)_2 \cdot 12H_2O$

Q13. (a) Permanganate ion reacts with bromide ion in basic medium to give manganese dioxide and bromate ion. Write the balanced ionic equation for the reaction.

(b) Nitric acid is an oxidising agent and reacts with PbO but it does not react with PbO_2. Why?

Q14. Balance the following equation in basic medium and identify the oxidising and reducing agent:

$$P_4(s) + OH^-(aq) \longrightarrow PH_3(g) + H_2PO_2(aq)$$

Q15. Depict the galvanic cell in which the reaction,

$$Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$$

takes place, further show

(a) which of the electrode is negatively charged?

(b) the carriers of the current in the cell.

(c) individual reaction at each electrode.

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S1. $$2MnO_4^-(aq) + 5H_2O_2(aq) + 6H^+ \longrightarrow 2Mn^{2+} + 8H_2O + 5O_2$$

S2. In AgF_2, Ag is in + 2 oxidation state which is highly unstable. Therefore, it readily accepts an electron to attain more stable + 1 oxidation state.

$$Ag^{2+} + e^- \longrightarrow Ag^+$$

That's why, AgF_2, if formed acts as a strong oxidising agent.

S3. In MnO_4^-, Mn is in the highest oxidation state, *i.e.*, + 7 hence, it cannot be oxidised further but the oxidation state of Mn in MnO_4^{2-} is + 6 and it can increase to + 7 or decreases to lower values, (*i.e.*, + 4, + 3, + 2, 0).

Thus, MnO_4^{2-} undergoes disproportionation in acidic medium.

$$3\overset{+6}{Mn}O_4^{2-} + 4H^+ \longrightarrow 2\overset{+7}{Mn}O_4^- + \overset{+4}{Mn}O_2 + 2H_2O$$

OS increases by 1 per atom (oxidatation)

OS decreases by 2 per atom (reduction)

S4. (a) $2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$

(b) $S_2O_3^{2-}(aq) + 2Br_2(l) + 5H_2O \longrightarrow 2SO_4^{2-}(aq) + 4Br^-(aq) + 10H^+(aq)$

Bromine being stronger oxidising agent than I_2, oxidises S of $S_2O_3^{2-}$, whereas I_2 oxidises it only into $S_4O_6^{2-}$ ion.

S5. $$\overset{+1}{H_2}\overset{-2}{O}(s) + \overset{0}{F_2}(g) \longrightarrow \overset{+1}{H}\overset{-1}{F}(g) + 2\overset{+1}{H}\overset{-2}{O}\overset{+1}{F}(g) \longrightarrow \overset{+1}{H}\overset{-1}{F} + \overset{+1}{H_2}\overset{-2}{O} + \overset{+2}{O}\overset{-1}{F_2}$$

Oxidation number of F decreases from zero (in F_2) to – 1 (in HF) and of O increases from – 2 to + 2 (in OF_2). This shows that F_2 is reduced. It is not a disproportionation reaction but only a redox reaction. In a disproportionation reaction, an element in one oxidation state is simultaneously reduced and oxidised.

S6. The oxidation state of Cl in all the given species are:

$$\underset{(+1)}{ClO^-},\quad \underset{(+3)}{ClO_2^-},\quad \underset{(+5)}{ClO_3^-} \quad \text{and} \quad \underset{(+7)}{ClO_4^-}.$$

Among all the species, ClO_4^- do not undergo disproportionation, since in this oxoanion chlorine has maximum possible oxidation state (*i.e.*, + 7) and hence, cannot be oxidised further through it can be reduced to oxidation state equal to – 1.

S7. $E°(Fe^{3+}/Fe^{2+})$ is lower thant thant of $E°(Br/Br^-)$. Therefore, Fe^{2+} can reduce Br_2 but Br^- cannot reduce Fe^{3+}. Thus Fe^{2+} cannot oxidise Br^- to Br_2.

S8. Platinum is an inert electrode and does not undergo oxidation easily. So, at anode, oxidation of water takes place. As a result, O_2 is released at anode. At cathode, reduction of Ag^+ ions takes place.

Therefore, on electrolysis of aqueous $AgNO_3$ solution with platinum electrodes, O_2 is released at anode and Ag^+ ions from solution get deposited at cathode.

S9. (a) Cu undergoes disproportionation to form Cu^{2+} and Cu.

(i) When heated in air, Cu_2O is oxidised to CuO.

$$2\overset{+1}{Cu_2}\overset{-2}{O} + \frac{1}{2}\overset{0}{O_2} \longrightarrow 2\overset{+2}{Cu}\overset{-2}{O}$$

i.e., Cu_2O actsas a reductant and reduces O_2 to O^{2-}.

(ii) When heated with Cu_2S, it oxidised S^{2-} to SO_2 and hence, Cu_2O acts as an oxidant.

$$2\overset{+1}{Cu_2}\overset{-2}{O} + \overset{+1}{Cu_2}\overset{-2}{S} \longrightarrow 6\overset{0}{Cu} + \overset{+4}{S}O_2$$

(b)
$$MnO_4^- + 8H^+ + ne^- \longrightarrow Mn^{2+} + 4H_2O$$
$$-1 + 8 - n = +2$$
$$\Rightarrow \quad -1 - 2 + 8 - n = 0 \quad \Rightarrow \quad n = 5$$

(c) Let the oxidation number of Fe = x

Sum of oxidation number for $(NH_4)_2SO_4 = 0$

Sum of oxidation number for $H_2O = 0$

Sum of oxidation number for $SO_4^{2-} = -2$

Therefore, $\quad x = (-2) + 0 + 6\,(0) = 0$

$$x = +2.$$

S10. (a)
$$\overset{+2}{Cu}\,\overset{-2}{O}(s) + \overset{0}{H_2}(g) \longrightarrow \overset{0}{Cu}(s) + \overset{+1}{H_2}\overset{-2}{O}(g)$$

Oxidation number of Cu in CuO is +2. It decreases from +2 to zero while oxidation number of hydrogen increases from 0 (in H_2) to +1 (in H_2O). This shows that CuO is reduced to Cu but H_2 oxidised to $_H2O$. Hence, it is a redox reaction.

(b)
$$\overset{+3}{Fe_2}\overset{-2}{O_3}(s) + 3\overset{+2}{C}\,\overset{-2}{O}(g) \longrightarrow 2\overset{0}{Fe}(s) + 3\overset{+4}{C}\,\overset{-2}{O_2}(g)$$

Oxidation number of Fe decreases from +3 (in Fe_2O_3) to zero in (Fe) and oxidation number of C increases from +2 (in CO) to +4 (in CO_2). This shows that Fe_2O_3 s reduced to Fe and CO is oxidised to CO_2.

(c)
$$4\overset{+3}{B}\,\overset{-1}{Cl_3}(g) + 3\overset{+1}{Li}\,\overset{+1}{Al}\,\overset{-1}{H_4}(s) \longrightarrow 2\overset{-3}{B_2}\overset{+1}{H_6}(g) + 3\overset{+1}{Li}\,\overset{-1}{Cl}(s) + 3\overset{+3}{Al}\,\overset{-1}{Cl_3}(s)$$

Oxidation number of B decreases from +3 (in BCl_3) to −3 (in B_2H_6) and oxidation number of H increases from −1 (in $LiAlH_4$) to +1 (in B_2H_6). This shows that BCl_3 is reduced to B_2H_6 and $LiAlH_4$ is oxidised. Hence, it is a redox reaction.

S11. Oxidation number method: Write the skeleton equation for the given reaction.

$$\overset{-2}{N_2}H_4(l) + ClO_3^-(aq) \longrightarrow \overset{+2}{N}O(g) + Cl^-(aq)$$

On increases by 4 per N-atom

$$N_2H_4(l) + \overset{+5}{Cl}O_3^-(aq) \longrightarrow \overset{+2}{N}O(g) + \overset{-1}{Cl}^-(aq)$$

On decreases by 6 per Cl-atom

Multiply NO by 2 because in N_2H_4. there are two N-atoms.

$$N_2H_4(l) + ClO_3^-(aq) \longrightarrow 2NO(g) + Cl^-(aq)$$

Total increase in ON of N = $2 \times 4 = 8$ ($8e^-$ lost)

Total decrease in ON of Cl = $1 \times 6 = 6$ ($6e^-$ gain)

Therefore, to balance increase or decrease in ON, multiply N_2H_4 by 3, 2NO by 3 and ClO_3^- and Cl^- by 4.

$$3N_2H_4(l) + 4ClO_3^-(aq) \longrightarrow 6NO(g) + 4Cl^-(aq)$$

Balance O and H-atoms by adding $6H_2O$ to RHS

$$3N_2H_4(l) + 4ClO_3^-(aq) \longrightarrow 6NO(g) + 4Cl^-(aq) + 6H_2O(l).$$

S12. (a) $NaH_2\underline{P}O_4$

Let the oxidation number of P be x.

Writting the oxidation number of each atom abocw its symbol, we get $\overset{+1}{Na}\,\overset{+1}{H_2}\,\overset{x}{P}\overset{-2}{O_4}$.

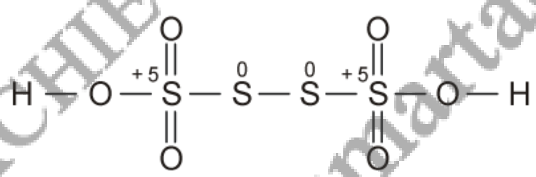
In neutral compounds, the sum of the oxidation numbers of all the atoms is zero.

$$\therefore \quad 1(+1) + 2(+1) + x + 4(-2) = 0$$
$$3 + x + (-8) = 0$$
$$x = 8 - 3 = 5$$

Hence, the oxidation number of P in NaH_2PO_4 is +5.

(b) $H_2\underline{S}_4O_6$

The structure of $H_2S_4O_6$ is shown below:



As each of the two terminal sulphur atoms is linked to two O-atoms by a double bond and one oxygen atom by a single bond. therefore oxidation state of terminal sulphur atoms is +5 while the oxidation number (or state) of middle S-atoms is zero as they are linked by S — S single bonds.

(c) $KAl(\underline{S}O_4)_2 \cdot 12H_2O$

Let the oxidation number of S in $KAl(SO_4)_2 \cdot 12H_2O$ be x.

$$\overset{+1}{K}\,\overset{+3}{Al}\,(\overset{x}{S}\overset{-2}{O_4})_2 \cdot 12\overset{+1}{H_2}\overset{-2}{O}$$

$$1(+1) + 1(+3) + 2x + 8(-2) + 12(2 \times 1 + 1(-2)) = 0$$

$$4 + 2x - 16 = 0, \qquad 2x = +12 \quad \text{or} \quad x = +6$$

Hence, the oxidation number of S in $KAl(SO_4)_2 \cdot 12H_2O$ is $+6$.

Note: H_2O is a neutral molecule, therefore sum of oxidation numbers of all atoms in H_2O is zero.

S13. (a) **Step I:** The skeletal ionic equation is

$$MnO_4^-(aq) + Br^-(aq) \longrightarrow MnO_2(s) + BrO_3^-(aq)$$

Step II: Assigning oxidation numbers for Mn and Br

$$\overset{+7}{Mn}O_4^-(aq) + \overset{-1}{Br^-}(aq) \longrightarrow \overset{+4}{Mn}O_2(s) + \overset{+5}{Br}O_3^-(aq)$$

This indicates that permangananate ion is the oxidant and bromide ion is the reductant.

Step III: Calculating the increase and decrease of oxidation number, and make the increase equal to the decrease.

$$2\overset{+7}{Mn}O_4^-(aq) + \overset{-1}{Br^-}(aq) \longrightarrow 2\overset{+4}{Mn}O_2(s) + \overset{+5}{Br}O_3^-(aq)$$

Step IV: As the reaction occurs in the basic medium and the ionic charges are not equal on both sides, we add 2OH– ions on the right to make ionic charges equal.

$$2MNO_4^-(aq) + Br^-(aq) \longrightarrow 2MNO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$$

Step V: Finally, we count the hydrogen atoms and add appropriate number of water molecules (*i.e.*, one H_2O molecule) on the left side to achieve balanced redox change.

$$2MNO_4^-(aq) + Br^-(aq) + H_2O(l) \longrightarrow 2MnO_2(s) + BrO_3^-(aq) + 2OH^-(aq)$$

(b) As in PbO_2, Pb is in maximum oxidation state of $+4$ and in HNO_3, N is in maximum oxidation state of $+5$. Therefore, none of them can oxidise each other. In other words, PbO_2 is passive towards HNO_3 and hence no reaction takes place in contrast, PbO being basic undergoes an acid-base reaction to form $Pb(NO_3)_2$ and H_2O.

S14.

ON decrease by 3 per P-atom

$$\overset{0}{P_4}(s) + OH^-(aq) \longrightarrow \overset{-3}{P}\overset{+1}{H_3}(g) + \overset{+1}{H_2}\overset{+1}{P}\overset{-2}{O_2^-}(aq)$$

ON increases by 1 per P-atom

Thus, P_4 acts as both oxidising as well as reducing agent. It can be balanced by oxidation number method as:

Total decrease in ON on P_4 om $PH_3 = 3 \times 4 = 12$,

Total increase in ON of P_4 in $H_2PO_2^- = 1 \times 4 = 4$.

Therefore, to balance increase or decrease in ON, multiply PH_3 by 1 and $H_2PO_2^-$ by 3, thus we get

$$P_4(s) + OH^-(aq) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq)$$

To balance O-atoms, multiply OH^- by 3, we get

$$P_4(s) + 3OH^-(aq) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq)$$

To balance H-atoms, add $3H_2O$ to LHS, wqe get

$$P_4(s) + 3OH^-(aq) + 3H_2O(l) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq)$$

S15. The given redox reaction for the galvanic cell is

$$Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s)$$

Since, Zn is oxidised to Zn^{2+} ions and Ag^+ ions are reduced to Ag metal. Therefore, oxidation occurs at zinc electrode and reduction occurs at the silver electrode. Hence, zinc act as anode and silver acts as cathode. Thus, galvanic cell for the above rtedox reaction may be depicted an $Zn\,|\,Zn^{2+}(aq)\,||\,Ag^+(aq)\,|\,Ag$.

(a) Zn electrode is negatively charged because of the oxidation of Zn to Zn^{2+} ions, electrons are accumulated on zinc electrode.

(b) The ions carry current in the cell. Current should flow from Ag electrode to Zn electrode, while electrons flow from Zn electrode to Ag electrode.

(c) Individual reactions occuring at each electrode ae:

Anode $\quad Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

Cathode $\quad Ag^+(aq) + e^- \longrightarrow Ag(s)$