Solution

REDOX REACTIONS

Class 11 - Chemistry

1. According to the Modern electronic concept, Reduction is a reaction in which an electron is gained by an element.

   For example, Cl + e^- $\rightarrow$ Cl^- , here reduction of chlorine atom takes place by gaining one electron and it forms an anion.
2. $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{cathode}} - E^{\circ}_{\text{anode}}$
   $= E^{\circ}_{\text{Ag}^+/\text{Ag}} - E^{\circ}_{\text{Cu}^{2+}/\text{Cu}}$ = +0.80 - (+0.34) = 0.46 V
3. Fluorine is the strongest oxidizing agent with the largest positive standard electrode potential.
4. In a redox reaction, the total number of electrons lost during oxidation reaction must be equal to the total number of electrons gained during reduction reaction.
5. In a disproportionation reaction an element in one oxidation state is simultaneously oxidized and reduced. For such redox reaction to occur the reacting species must contain an element which has at least three oxidation states.
6. According to the Modern electronic concept, the oxidation reaction is the reaction in which electron gets lost during the chemical reaction.

   For example,

   Na $\rightarrow$ Na^+ + e^-, here oxidation of sodium atom takes place by losing an electron and it forms sodium cation.
7. Oxidising agent is a substance which has ability to oxidize other substance. It can gain electrons easily. F_2 is the best oxidizing agent.
8. No, the oxidation number of an element in any species is an arbitrary charge present on the atom and it does not represent the total charge present on a polyatomic ion.
9. As per the rules to find oxidation number, let the oxidation number of Mn be x.

   We know, Oxidation number of K = +1 while Oxidation number of O = -2. By putting the value we get

   1 + x + 4(-2) = 0

   x = +7
10. Since the reduction potential of copper is less than that of Ag, so Cu electrode behaves as anode and Ag electrode as cathode

    Cu|Cu^{2+} (aq)||Ag^+(aq)|Ag.
11. i. The given redox reaction is ,

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

       Since Zn (s) gets oxidized, to Zn^{2+} (aq) ions, and Ag^+ (aq) ions gets reduced to Ag (s) metal, therefore, oxidation occurs at the zinc electrode *(*acting as anode*)* and reduction occurs at the silver electrode (as cathode*)*. Thus, the galvanic cell corresponding to the above redox reaction is depicted as:

       $Zn_{(s)}$ | Zn^{2+} (aq) || Ag^+ (aq) | $Ag_{(s)}$

    ii. a. Since oxidation occurs at the zinc electrode, therefore, electrons accumulate on the zinc electrode,/ anode. Hence, zinc electrode is negatively charged.

        b. Electrons move from Zn anode to Ag cathode in the external circuit. Since the direction of current in the external circuit is opposite to that of the electrons so,

           The carriers of current are silver cathode and Zinc anode through an external circuit in a direction from silver cathode to zinc anode.

        c. The reactions occurring at the two electrodes are

           At anode:

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

           At cathode

           Ag^+ (aq) + e^- $\longrightarrow$ Ag (s)
12. By applying various rules of calculating the oxidation number of the desired element in a compound, the oxidation number of each metallic element in its compound is as follows:

    $HAuCl_4$ $\longrightarrow$ Au has 3

    Tl_2O $\longrightarrow$ Tl has 1

    FeO $\longrightarrow$ Fe has 2

$Fe_2O_3 \longrightarrow$ Fe has 3

$CuI \longrightarrow$ Cu has 1

$CuO \longrightarrow$ Cu has 2

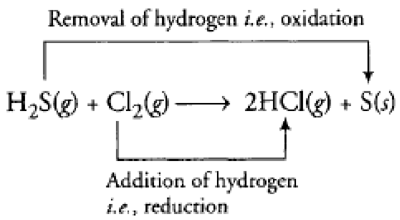
$MnO \longrightarrow$ Mn has 2

$MnO_2 \longrightarrow$ Mn has 4

Therefore, these compounds may be represented as:

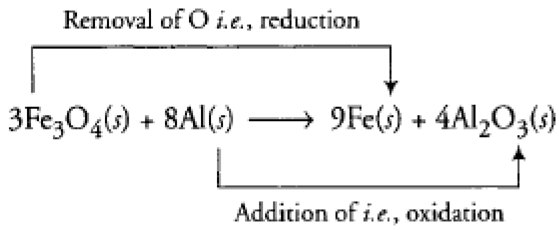
$HAu(III)Cl_4$, $Tl_2(I)O$, Fe(II)O, $Fe_2(III)O_3$, Cu(I)I, Cu(II)O, Mn(II)O, $Mn(IV)O_2$.

13. i.



Thus, here, H_2S undergoes oxidation because oxidation number of Sulphur atom get increased from -2 to 0 while Cl_2 undergoes reduction because oxidation number of Cl atom get decreased from 0 to -1.

ii.



Thus, here Fe_3O_4 undergoes reduction because oxidation number of Fe atom get decreased while AI atom undergoes oxidation because Oxidation number of Al atom get increased from 0 to +3.

iii. 2 Na(s) + H_2(g) $\rightarrow$ 2 NaH(s)

Since Na is more electro-positive than H so, here Na atom get oxidised by losing electron while H-atom get reduced by accepting electron.

14. i. In this redox reaction, H in $LiAlH_4$ gets oxidised because of the addition of oxygen atom that leads to the formation of OH^-.

Propanone (CH_3COCH_3) gets reduced because of addition of hydrogen atom to give propan-2-ol ($CH_3CH(OH)CH_3$).

ii. This is not a redox reaction as neither hydrogen or oxygen or electron is removed or added.

iii. This is not a redox reaction as neither hydrogen or oxygen or electron is removed or added.

15. i. Halogens have a strong tendency to accept electrons. Therefore, they are strong oxidizing agents. Their relative oxidizing power is however, measured in terms of their electrode potentials.

Since the electrode potentials of halogens decrease in the order :

F_2 < (2.87V) > Cl_2(+1.36V) > Br_2(+1.09V) > I_2(+0.54V),

Therefore, their oxidizing power decreases in the same order.

This is evident from the observation that

a. F_2 oxidizes Cl^- to Cl_2, Br^- to Br_2, I^- to I_2

b. Cl_2 oxidizes Br^- to Br_2 and I^- to I_2 but not F^- to F_2.

c. Br_2, however oxidizes I^- to I_2. But Br_2 fails to oxidise F^- to F_2 and Cl^- to Cl_2

The related above reactions are,

$F_2(g) + 2Cl^-(aq) \rightarrow 2F^-(aq) + Cl_2(g)$; $F_2(g) + 2Br^-(aq) \rightarrow 2F^-(aq) + Br_2(l)$

$F_2(g) + 2I^-(aq) \rightarrow 2F^-(aq) + I_2(s)$; $Cl_2(g) + 2Br^-(aq) \rightarrow 2Cl^-(aq) + Br_2(l)$

$Cl_2(g) + 2I^-(aq) \rightarrow 2Cl^-(aq) + I_2(s)$ and $Br_2(l) + 2I^- \rightarrow 2Br^-(aq) + I_2(s)$

Thus, **F_2 is the best oxidant.**

ii. Conversely, halide ions have a tendency to lose electrons and hence can act as reducing agents. Since the electrode potentials of halide ions decrease in the following order,

I^-(-0.54 V) > Br^-(-1.09V) > Cl^-(-1.36V) > F^- (-2.87 V),

Therefore, the reducing power of the halide ions or their corresponding hydrohalic acids decreases in the same order: HI > HBr > HCl > HF.

Thus, hydroiodic acid is the best reductant. This is supported by the following reactions.

For example,

HI and HBr reduces H_2SO_4 to SO_2 while HCI and HF do not.

$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$; $2HI + H_2SO_4 \rightarrow I_2 + SO_2 + 2H_2O$

Further I^- reduces Cu^{2+} to Cu^+ but Br^- does not.

$2Cu^{2+}(aq) + 4I^-(aq) \rightarrow Cu_2I_2(s) + I_2(aq)$;

$Cu^{2+}(aq) + 2Br^- \rightarrow$ No reaction

So, HI is a stronger reductant than HBr.

Further, among HCl and HF, HCl is a stronger reducing agent than HF because HCl reduces MnO_2 to Mn^{2+} but HF does not.

$MnO_2(s) + 4HCl(aq) \rightarrow MnCl_2(aq) + Cl_2(g) + 2H_2O$

$MnO_2(s) + 4HF(l) \not\rightarrow$ No reaction

Thus, the reducing character of hydrohalic acids decreases in the order: **HI > HBr > HCl > HF.**

16. For spontaneity of the reaction, E_{cell} value must be positive because the relation between standard Gibbs free energy and E_{cell} value is given as $\Delta G = -n F E_{cell}$

From the formula it is clear that higher the positive value of E_{cell}, more negative will be the value of ΔG and higher will be the spontaneity.

To calculate E_{cell}, the following formula is used:

$E_{cell} = E^o_{cathode} - E^o_{anode}$

Here both E^o values are of standard reduction potential.

It may be noted that whenever any half-reaction equation is multiplied by an integer, its E° is not multiplied by that integer.

i. Fe^{3+}(aq) and I^-(aq)

The possible reaction between Fe^{3+}(aq) and I^-(aq) is as follows:

$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(s)$

Oxidation half-reaction:

$2I^-(aq) \longrightarrow I_2(s) + 2e^-$; E° = -0.54 V

Reduction half-reaction:

$2Fe^{3+}(aq) + 2e^- \longrightarrow 2Fe^{2+}(aq)$; E° = + 0.77 V

Overall reaction

$2Fe^{3+}(aq) + 2I^-(aq) \longrightarrow 2Fe^{2+}(aq) + I_2(s)$; E° = + 0.23 V

Positive emf indicates that the reaction is feasible because ΔG will be negative.

ii. The possible reaction between Ag^+ (aq) and Cu(s) is as follows:

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

Separate the equation into two half reactions and write electrode potential for each half-reaction.

Oxidation half-reaction:

$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$; E° = - 0.34 V

Reduction half reaction:

$2Ag^+(aq) + 2e^- \longrightarrow 2Ag(s)$; E° = + 0.80 V

Overall reaction:

$Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag$; E° = + 0.46 V

Positive emf indicates that the reaction is feasible because ΔG will be negative.

iii. The possible reaction between Fe^{3+}(aq) and Cu(s) occurs according to the following equation,

$2Fe^{3+}(aq) + Cu(s) \longrightarrow 2Fe^{2+} + Cu^{2+}$

Oxidation half-reaction:

$Cu(s) \longrightarrow Cu^{2+} + 2e^-$; E° = -0.34 V

Reduction half-reaction:

$2Fe^{3+}(aq) + 2e^- \longrightarrow 2Fe^{2+}(aq)$; E° = + 0.77 V

Overall reaction:

$Cu(s) + 2Fe^{3+}(aq) \longrightarrow Cu^{2+}(aq) + 2Fe^{2+}(aq)$; E° = + 0.43 V

Positive emf indicates that the reaction is feasible because ΔG will be negative.

iv. The possible reaction between Fe^{3+}(aq) and Ag(s) occurs according to the following equation

$Ag(s) + Fe^{3+}(aq) \longrightarrow Ag^+(aq) + Fe^{2+}(aq)$

oxidation half-reaction

$Ag(s) \longrightarrow Ag^+(aq) + e^-$; E^o = -0.80 V

Reduction half-reaction

$Fe^{3+}(aq) + e^- \longrightarrow Fe^{2+}(aq)$; E° = + 0.77 V

Overall reaction

$Ag(s) + Fe^{3+}(aq) \longrightarrow Ag^+(aq) + Fe^{2+}(aq)$; E° = - 0.03 V

Negative emf indicates that the reaction is not feasible because ΔG will be positive.

v. The possible reaction between Br_2(aq) and Fe^{2+} (aq) occurs according to the following equation.

$Br_2(aq) + 2Fe^{2+}(aq) \longrightarrow 2Br^- + 2Fe^{3+}(aq)$

Oxidation half reaction

$2Fe^{2+}(aq) \longrightarrow 2Fe^{3+}(aq) + 2e^-$; E° = - 0.77 V

Reduction half reaction

$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$; E° = + 1.09 V

Overall reaction

$2Fe^{2+}(aq) + Br_2(aq) \longrightarrow 2Fe^{3+}(aq) + 2Br^-(aq)$; E° = + 0.32 V

Positive emf indicates that the reaction is feasible because ΔG will be negative.

17. In reaction (a), the compound nitric oxide is formed by the combination of the elemental substances, nitrogen, and oxygen; therefore, this is an example of combination redox reactions.
The reaction (b) involves the breaking down of lead nitrate into three components; therefore, this is categorized under decomposition redox reaction.
In reaction (c), hydrogen of water has been displaced by hydride ion into dihydrogen gas. Therefore, this may be called a displacement redox reaction.
The reaction (d) involves disproportionation of NO_2 (+4 state) into NO_2^- (+3 state) and NO_2^- (+5 state). Therefore reaction (d) is an example of a disproportionation redox reaction.

18. We need to write a skeletal equation for the reaction of chlorine with sulphur dioxide in water and balance the skeletal equation by ion-electron method
The skeletal equation is:

$\mathrm{Cl}_2(aq) + \mathrm{SO}_2(aq) + \mathrm{H}_2\mathrm{O}(l) \longrightarrow Cl^-(aq) + SO_2(aq)$

In order to balance the skeletal equation by ion-electron method, the steps followed are, F
Write reduction half cell equation and oxidation half cell equation separately.
Reduction half equation is:

$Cl_2(aq) \longrightarrow Cl^-(aq)$

Balance Cl atoms,

$\overset{0}{Cl}_2(aq) \rightarrow 2\,\overset{-1}{Cl^-}(aq)$

Balance oxidation number of chlorine by adding electrons:

$Cl_2(aq) + 2e^- \longrightarrow 2Cl^-(aq)$ ....(i)

Oxidation half-equation:

$\overset{+4}{S}O_2(aq) \rightarrow \overset{+6}{S}O_4^{2-}(aq) + 2e^-$

Balance oxidation number of S by adding electrons:

$SO_2(aq) \rightarrow SO_4^{2-}(aq) + 2e^-$

Balance charge by adding $4H^+$ ions

$SO_2(aq) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$

Balance O atoms by adding $2H_2O$ at a side opposite to that of H^+

$SO_2(aq) + 2H_2O(l) \rightarrow SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$ .... (ii)

Now adding eq. (i) and eq. (ii), we have,

$Cl_2(aq) + SO_2(aq) + SO_2(aq) + 2H_2O(l) \longrightarrow 2Cl^-(aq) + SO_4^{2-}(aq) + 4H^+(aq)$

The above equation represents a balanced redox equation for the reaction of chlorine iwth sulphur dioxide in water.

19. The substances where carbon can exhibit oxidation states from - 4 to + 4 are following :-

Let the O.N. of C be 'x'

Substances	O.N. of carbon	Calculation
CH_4	-4	x + 4(+1) = 0 x = -4
$H_3C\text{-}CH_3$	-3	3(1) + x + x + 3(1) = 0 x = -3
CH_3Cl	-2	x + 3(+1) + 1(-1) = 0 x = -2
HC = CH	-1	1 + x + x + 1 = 0 x = -1
CH_2Cl_2	0	x + 2(1) + 2(-1) = 0 x = 0
ClC = CCl	+1	1(-1) + x + x + 1(-1) = 0 x = +1
CO	+2	x + 1(-2) = 0 x = +2
$Cl_3C\text{-}CCl_3$	+3	3(-1) + x + x + 3(-1) = 0 x = +3
CCl_4	+4	x + 4(-1) = 0 x = +4

The substances where Nitrogen can exhibit oxidation states from -3 to + 5 are following :-

Let the O.N. of N be 'y'

Substances	O.N. of N	Calculations
NH_3	-3	y + 3(1) = 0 y = -3
N_2H_4	-2	2y + 4(1) = 0 y = -2
N_2H_2	-1	2y + 2(1) = 0 y = -1
N_2	0	2y = 0 y = 0
N_2O	+1	2y + 1(-2) = 0 y = +1

NO	+2	y + 1(-2) = 0 y = +2
N_2O_3	+3	2y + 3(-2) = 0 y = +3
NO_2	+4	y + 2(-2) = 0 y = +4
N_2O_5	+5	2y + 5(-2) = 0 y = +5