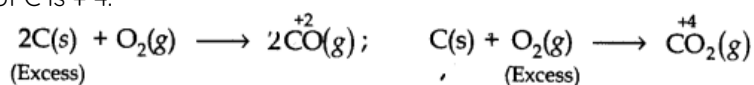


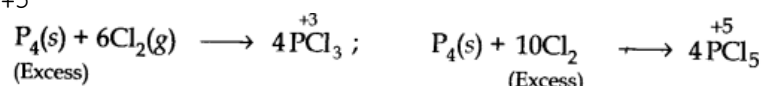


Question 11. Whenever a reaction between an oxidising agent and a reducing agent is carried out, a compound of lower oxidation state is formed if the reducing agent is in excess and a compound of higher oxidation state is formed if oxidising agent is in excess. Justify this statement giving three illustrations.

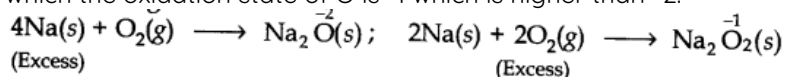
Answer: (i) C is a reducing agent while O_2 is an oxidising agent. If excess of carbon is burnt in a limited supply of O_2 , CO is formed in which the oxidation state of C is +2. If, however, excess of O_2 is used, the initially formed CO gets oxidised to CO_2 in which oxidation state of C is +4.



(ii) P_4 is a reducing agent while Cl_2 is an oxidising agent. When excess of P_4 is used, PCl_3 is formed in which the oxidation state of P is +3. If, however, excess of Cl_2 is used, the initially formed PCl_3 reacts further to form PCl_5 in which the oxidation state of P is +5



(iii) Na is a reducing agent while O_2 is an oxidising agent. When excess of Na is used, sodium oxide is formed in which the oxidation state of O is -2. If, however, excess of O_2 is used, Na_2O_2 is formed in which the oxidation state of O is -1 which is higher than -2.



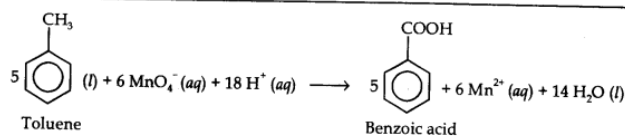
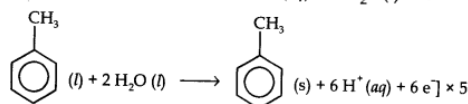
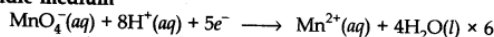
Question 12. How do you account for the following observations?

(a) Though alkaline potassium permanganate and acidic potassium permanganate both are used as oxidants, yet in the manufacture of benzoic acid from toluene we use alcoholic potassium permanganate as an oxidant. Why? Write a balanced redox equation for the reaction.

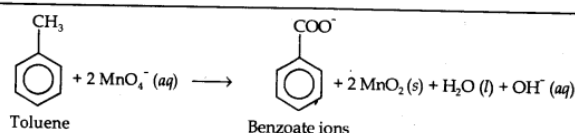
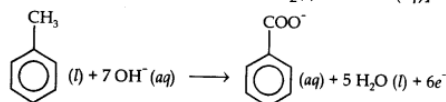
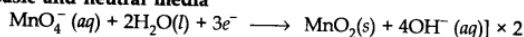
(b) When concentrated sulphuric acid is added to an inorganic mixture containing chloride, we get colourless pungent smelling gas HCl , but if the mixture contains bromide then we get red vapour of bromine. Why?

Answer: (a) Toluene can be oxidised to benzoic acid in acidic, basic and neutral media according to the following redox equations:

(i) **Acidic medium**



(ii) **Basic and neutral media**

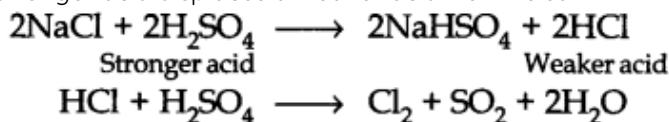


In the laboratory, benzoic acid is usually prepared by alkaline KMnO_4 oxidation of toluene. However, in industry alcoholic KMnO_4 is preferred over acidic or alkaline KMnO_4 because of the following reasons:

(i) The cost of adding an acid or the base is avoided because in the neutral medium, the base (OH^- ions) are produced in the reaction itself.

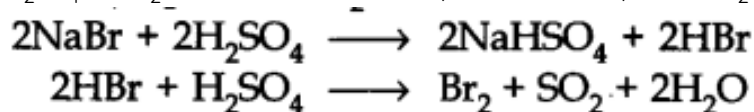
(ii) Since reactions occur faster in homogeneous medium than in heterogeneous medium, therefore, alcohol helps in mixing the two reactants, i.e., KMnO_4 (due to its polar nature) and toluene (because of its being an organic compound).

(b) When conc. H_2SO_4 is added to an inorganic mixture containing chloride, a pungent smelling gas HCl is produced because a stronger acid displaces a weaker acid from its salt.

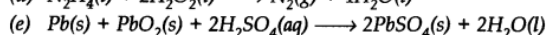
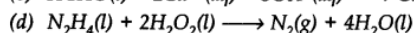
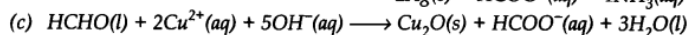
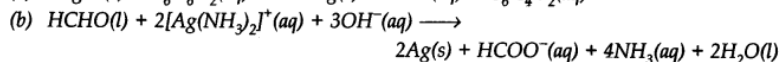
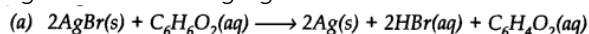


Since HCl is a very weak reducing agent, it can not reduce H_2SO_4 to SO_2 and hence HCl is not oxidised to Cl_2 .

However, when the mixture contains bromide ion, the initially produced HBr being a strong reducing agent than HCl reduces H_2SO_4 to SO_2 and is itself oxidised to produce red vapour of Br_2 .



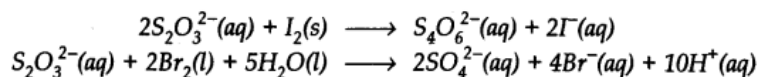
Question 13. Identify the substance oxidised, reduced, oxidising agent and reducing agent for each of the following reactions.



Answer:

Substance oxidised	Substance reduced	Oxidising agent	Reducing agent
(a) $\text{C}_6\text{H}_6\text{O}_2(\text{aq})$	$\text{AgBr}(\text{s})$	$\text{AgBr}(\text{s})$	$\text{C}_6\text{H}_6\text{O}_2(\text{aq})$
(b) $\text{HCHO}(\text{aq})$	$[\text{Ag}(\text{NH}_3)_2]^+$	$[\text{Ag}(\text{NH}_3)_2]^+$	$\text{HCHO}(\text{aq})$
(c) $\text{HCHO}(\text{aq})$	$\text{Cu}^{2+}(\text{aq})$	$\text{Cu}^{2+}(\text{aq})$	$\text{HCHO}(\text{aq})$
(d) $\text{N}_2\text{H}_4(\text{l})$	$\text{H}_2\text{O}_2(\text{l})$	$\text{H}_2\text{O}_2(\text{l})$	$\text{N}_2\text{H}_4(\text{l})$
(e) $\text{Pb}(\text{s})$	$\text{PbO}_2(\text{s})$	$\text{PbO}_2(\text{s})$	$\text{Pb}(\text{s})$

Question 14. Consider the reactions:



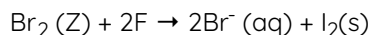
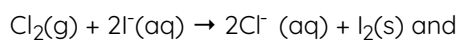
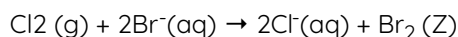
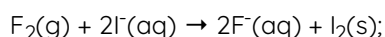
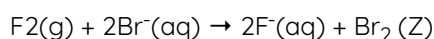
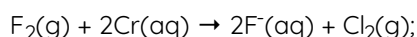
Why does the same reductant, thiosulphate react differently with iodine and bromine?

Answer: The average O.N. of S in $\text{S}_2\text{O}_3^{2-}$ is +2 while in $\text{S}_4\text{O}_6^{2-}$ it is +2.5. The O.N. of S in SO_4^{2-} is +6. Since Br_2 is a stronger oxidising agent than I_2 , it oxidises S of $\text{S}_2\text{O}_3^{2-}$ to a higher oxidation state of +6 and hence forms SO_4^{2-} ion. I_2 , however, being a weaker oxidising agent oxidises S of $\text{S}_2\text{O}_3^{2-}$ ion to a lower oxidation of +2.5 in $\text{S}_4\text{O}_6^{2-}$ ion. It is because of this reason that thiosulphate reacts differently with Br_2 and I_2 .

Question 15. Justify-giving reactions that among halogens, fluorine is the best oxidant and among hydrohalic compounds, hydroiodic acid is the best reductant.

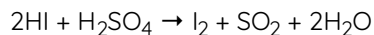
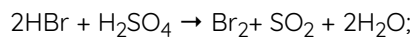
Answer: Halogens have a strong tendency to accept electrons. Therefore, they are strong oxidising agents. Their relative oxidising power is, however, measured in terms of their electrode potentials. Since the electrode potentials of halogens decrease in the order: F_2 (+2.87V) > Cl_2 (+1.36V) > Br_2 (+1.09V) > I_2 (+0.54V), therefore, their oxidising power decreases in the same order.

This is evident from the observation that F_2 oxidises Cl^- to Cl_2 , Br^- to Br_2 , I^- to I_2 ; Cl_2 oxidises Br^- to Br_2 and F^- to F_2 but not F^- to F_2 . Br_2 , however, oxidises F^- to F_2 but not F^- to F_2 , and Cl^- to Cl_2 .

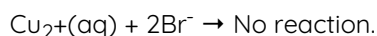
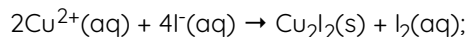


Thus, F_2 is the best oxidant.

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 order: I^- (-0.54 V) > Br^- (-1.09 V) > Cl^- (-1.36 V) > F^- (-2.87 V), therefore, the reducing power of the halide ions or their corresponding hydrohalic acids decreases in the same order: $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$. Thus, hydroiodic acid is the best reductant. This is supported by the following reactions. For example, HI and HBr reduce H_2SO_4 to SO_2 while HCl and HF do not.

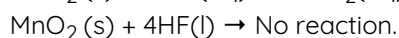


Further F^- reduces Cu^{2+} to Cu^+ but Br^- does not.



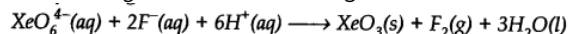
Thus, HI is a stronger reductant than HBr .

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.



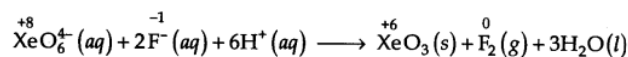
Thus, the reducing character of hydrohalic acids decreases in the order: $\text{HI} > \text{HBr} > \text{HCl} > \text{HF}$.

Question 16. Why does the following reaction occur?



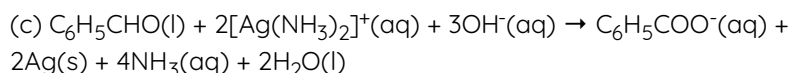
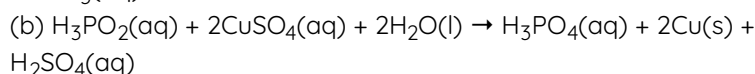
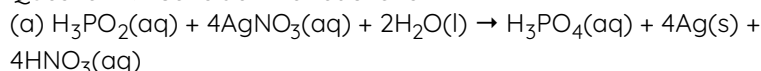
What conclusion about the compound Na_4XeO_6 (of which XeO_6^{4-} is a part) can be drawn from the reaction?

Answer:



Here, O.N. of Xe decreases from +8 in XeO_6^{4-} to +6 in XeO_3 while that of F increases from -1 in F^- to 0 in F_2 . Therefore, XeO_6^{4-} is reduced while F^- is oxidised. This reaction occurs because $\text{Na}_2\text{XeO}_6^{4-}$ (or XeO_6^{4-}) is a stronger oxidising agent than F_2 .

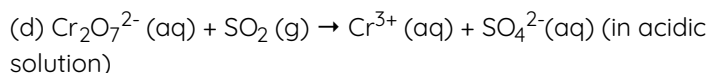
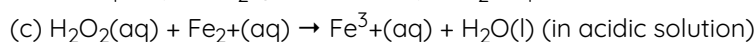
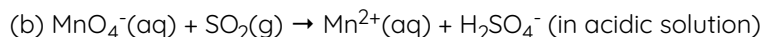
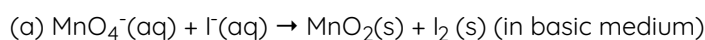
Question 17. Consider the reactions:



What inference do you draw about the behaviour of Ag^+ and Cu^{2+} from these reactions?

Answer: Reactions (a) and (b) indicate that H_3PO_2 (hypophosphorous acid) is a reducing agent and thus reduces both AgNO_3 and CuSO_4 to Ag and Cu respectively. Conversely, both AgNO_3 and CuSO_4 act as oxidising agent and thus oxidise H_3PO_2 to H_3PO_4 (orthophosphoric acid). Reaction (c) suggests that $[\text{Ag}(\text{NH}_3)_2]^+$ oxidises $\text{C}_6\text{H}_5\text{CHO}$ (benzaldehyde) to $\text{C}_6\text{H}_5\text{COO}^-$ (benzoate ion) but reaction (d) indicates that Cu^{2+} ions cannot oxidise $\text{C}_6\text{H}_5\text{CHO}$ to $\text{C}_6\text{H}_5\text{COO}^-$. Therefore, from the above reactions, we conclude that Ag^+ ion is a strong deoxidising agent than Cu^{2+} ion.

Question 18. Balance the following redox reactions by ion-electron method.

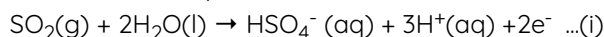


Answer:

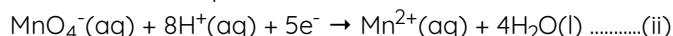
(a) Do it yourself.

(b) The balanced half reaction equations are:

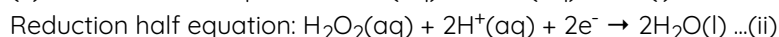
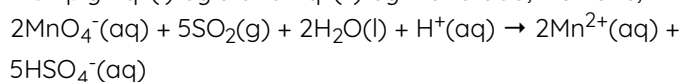
Oxidation half equation:



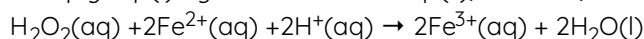
Reduction half equation:



Multiply Eq. (i) by 3 and Eq. (ii) by 2 and add, we have,

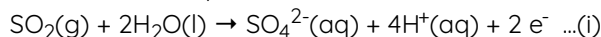


Multiply Eq. (i) by 2 and add it to Eq. (ii), we have,



(d) Following the procedure detailed on page 8/23, the balanced half reaction equations are:

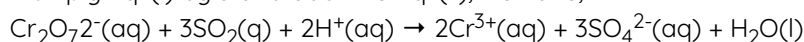
Oxidation half equation:



Reduction half equation:

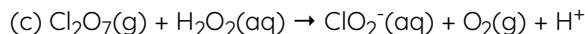
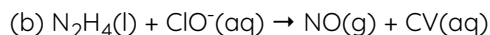
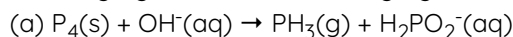


Multiply Eq. (i) by 3 and add it to Eq. (ii), we have,



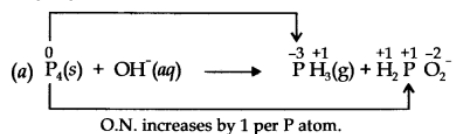
Question 19. Balance the following equation in basic medium by ion

electron method and oxidation number method and identify the oxidising agent and the reducing agent.



P_4 acts both as an oxidising as well as a reducing agent.

Answer:



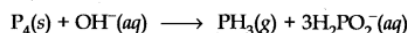
P_4 acts both as an oxidising as well as a reducing agent.

Oxidation number method:

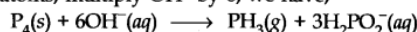
Total decrease in O.N. of P_4 in $\text{PH}_3 = 3 \times 4 = 12$

Total increase in O.N. of P_4 in $\text{H}_2\text{PO}_2^- = 1 \times 4 = 4$

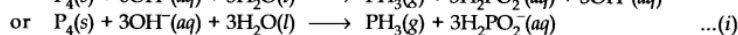
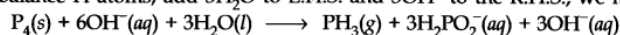
Therefore, to balance increases decreases in O.N. multiply PH_3 by 1 and H_2PO_2^- by 3, we have,



To balance O atoms, multiply OH^- by 6, we have,



To balance H atoms, add $3\text{H}_2\text{O}$ to L.H.S. and 3OH^- to the R.H.S., we have,



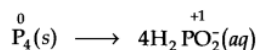
Thus, Eq. (i) represents the correct balanced equation.

Ion electron method. The two half reactions are:

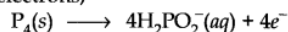
Oxidation half reaction:



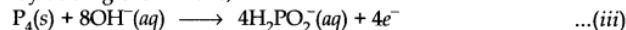
Balancing P atoms, we have,



Balance O.N. by adding electrons,



Balance charge by adding 8 OH^- ions,

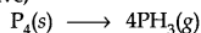


O and H get automatically balanced. Thus, Eq. (iii) represents the balanced oxidation half reaction.

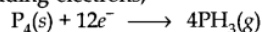
Reduction half reaction:



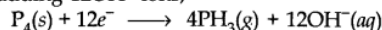
Balancing P atoms, we have,



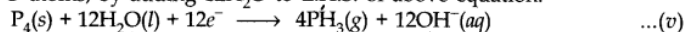
Balance O.N. by adding electrons,



Balance charge by adding 12 OH^- ions,



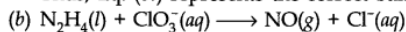
Balance O atoms, by adding $12\text{H}_2\text{O}$ to L.H.S. of above equation.



To cancel out electrons, multiply Eq. (iii) by 3 and add it to Eq. (v), we have,
 $4\text{P}_4(\text{s}) + 24\text{OH}^-(\text{aq}) + 12\text{H}_2\text{O}(\text{l}) \longrightarrow 4\text{PH}_3(\text{aq}) + 12\text{H}_2\text{PO}_2^-(\text{aq}) + 12\text{H}_2\text{O}(\text{l})$
 $+ 12\text{OH}^-(\text{aq})$

or $\text{P}_4(\text{g}) + 3\text{OH}^-(\text{aq}) + 3\text{H}_2\text{O}(\text{l}) \longrightarrow \text{PH}_3(\text{aq}) + 3\text{H}_2\text{PO}_2^-(\text{aq})$... (vi)

Thus, Eq. (vi) represents the correct balanced equation.

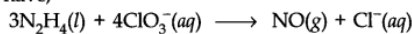


Oxidation number method

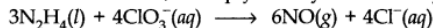
Total increase in O.N. of N = $2 \times 4 = 8$

Total decreases in O.N. of Cl = $1 \times 6 = 6$

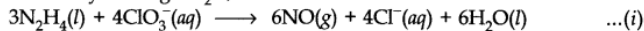
Therefore, to balance increase/decrease in O.N. multiply N_2H_4 by 3 and ClO_3^- by 4, we have,



To balance N and Cl atoms, multiply NO by 6 and Cl^- by 4, we have,

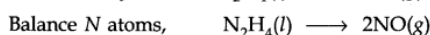
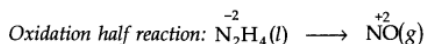


Balance O atoms by adding $6\text{H}_2\text{O}$,

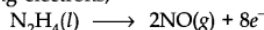


H atoms get automatically balanced and thus Eq. (i) represents the correct balanced equation.

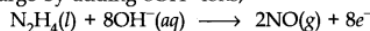
Ion electron method.



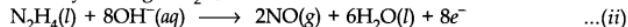
Balance O.N. by adding electrons,



Balance charge by adding 8OH^- ions,



Balance O atoms by adding $6\text{H}_2\text{O}$,

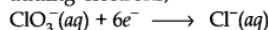


Thus, Eq. (ii) represents the correct balanced oxidation half equation.

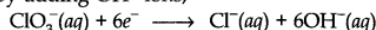
Reduction half reaction



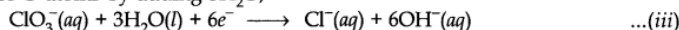
Balance O.N. by adding electrons,



Balance charge by adding OH^- ions,

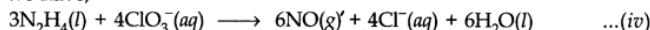


Balance O atoms by adding $3\text{H}_2\text{O}$,

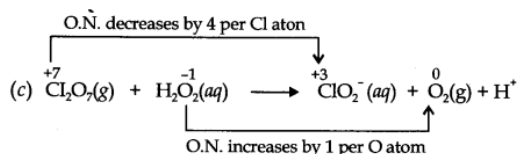


Thus, Eq. (iii) represents the correct balanced reduction half equation.

To cancel out electrons gained and lost, multiply Eq. (ii) by 3 and Eq. (iii) by 4 and add, we have,



Thus, Eq. (iv) represents the correct balanced equation



Thus, $\text{Cl}_2\text{O}_7(\text{g})$ acts an oxidising agent while $\text{H}_2\text{O}_2(\text{aq})$ as the reducing agent.

Oxidation number method

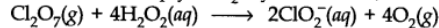
Total decrease in O.N. of $\text{Cl}_2\text{O}_7 = 4 \times 2 = 8$

Total increase in O.N. of $\text{H}_2\text{O}_2 = 2 \times 1 = 2$

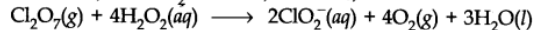
\therefore To balance increase/decrease in O.N. multiply H_2O_2 and O_2 by 4, we have,



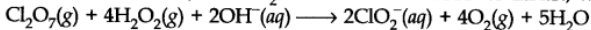
To balance Cl atoms, multiply ClO_2^- by 2, we have,



To balance O atoms, add $3\text{H}_2\text{O}$ R.H.S., we have,



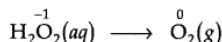
To balance H atoms, add $2\text{H}_2\text{O}$ to R.H.S. and 2OH^- to L.H.S., we have,



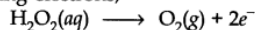
This represents the balanced redox equation.

Ion electron method

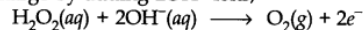
Oxidation half reaction:



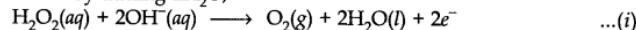
Balance O.N. by adding electrons,



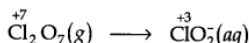
Balance charge by adding 2OH^- ions,



Balance O atoms by adding $2\text{H}_2\text{O}$,

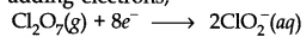


Reduction half reaction:

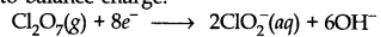


Balance Cl atoms; $\text{Cl}_2\text{O}_7(g) \longrightarrow 2\text{ClO}_2^-(aq)$

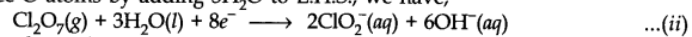
Balance O.N. by adding electrons,



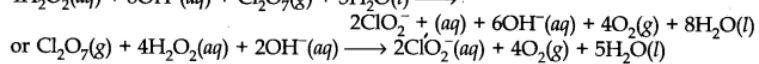
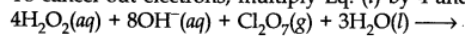
Add 6OH^- ions to balance charge:



Balance O atoms by adding $3\text{H}_2\text{O}$ to L.H.S., we have,



To cancel out electrons, multiply Eq. (i) by 4 and add it to Eq. (ii), we have,



***** END *****