

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

$$P_4(s) + 6Cl_2(g) \longrightarrow 4 \stackrel{+3}{PCl_3}; \qquad P_4(s) + 10Cl_2 \longrightarrow 4 \stackrel{+5}{PCl_5}$$
(Excess)

(iii) Na is a reducing agent while 02 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 O2 is used, Na_2O_2 is formed in which the oxidation state of O is -1 which is higher than -2.

$$4\text{Na}(s) + \text{O}_2(g) \longrightarrow \text{Na}_2 \overset{-2}{\text{O}}(s); 2\text{Na}(s) + 2\text{O}_2(g) \longrightarrow \text{Na}_2 \overset{-1}{\text{O}}_2(s)$$
(Excess)

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
$$MnO_{4}^{-}(aq) + 8H^{+}(aq) + 5e^{-} \longrightarrow Mn^{2+}(aq) + 4H_{2}O(l) \times 6$$

$$CH_{3} \longrightarrow CH_{3}$$

$$(l) + 2H_{2}O(l) \longrightarrow (s) + 6H^{+}(aq) + 6e^{-} \times 5$$

$$COOH \longrightarrow Following Benzoic acid$$
(ii) Basic and neutral media
$$MnO_{4}^{-}(aq) + 2H_{2}O(l) + 3e^{-} \longrightarrow MnO_{2}(s) + 4OH^{-}(aq)] \times 2$$

$$CH_{3} \longrightarrow COO^{-} \longrightarrow CH_{3} \longrightarrow COO^{-} \longrightarrow COO^{-$$

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 cone. $\rm H_2SO_4$ 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.

$$\begin{array}{ccc} \text{2NaCl} + 2\text{H}_2\text{SO}_4 & \longrightarrow & \text{2NaHSO}_4 + 2\text{HCl} \\ \text{Stronger acid} & & \text{Weaker acid} \\ \text{HCl} + \text{H}_2\text{SO}_4 & \longrightarrow & \text{Cl}_2 + \text{SO}_2 + 2\text{H}_2\text{O} \end{array}$$

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

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

$$2NaBr + 2H_2SO_4 \longrightarrow 2NaHSO_4 + 2HBr$$

 $2HBr + H_2SO_4 \longrightarrow Br_2 + SO_2 + 2H_2O$

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

(a)
$$2AgBr(s) + C_6H_6O_2(aq) \longrightarrow 2Ag(s) + 2HBr(aq) + C_6H_4O_2(aq)$$

(b)
$$HCHO(l) + 2[Ag(NH_3)_2]^+(aq) + 3OH^-(aq) \longrightarrow 2Ag(s) + HCOO^-(aq) + 4NH_3(aq) + 2H_3O(l)$$

(c)
$$HCHO(l) + 2Cu^{2+}(aq) + 5OH^{-}(aq) \longrightarrow Cu_{2}O(s) + HCOO^{-}(aq) + 3H_{2}O(l)$$

(d) $N_2H_4(1) + 2H_2O_2(1) \longrightarrow N_2(g) + 4H_2O(1)$

(e)
$$Pb(s) + PbO_2(s) + 2H_2SO_4(aq) \longrightarrow 2PbSO_4(s) + 2H_2O(l)$$

Answer:

Substance oxidised	Substance reduced	Oxidising agent	Reducing agent
(a) $C_6H_6O_2(aq)$	AgBr(s)	AgBr(s)	$C_6H_6O_2(aq)$
(b) HCHO(aq)	$[Ag (NH_3)_2]^+$	[Ag (NH3)2]+	HCHO(aq)
(c) HCHO(aq)	$Cu^{2+}(aq)$	$Cu^{2+}(aq)$	HCHO(aq)
$(d) \cdot N_2H_4(l)$	$H_2O_2(l)$	$H_2O_2(l)$	$N_2H_4(l)$
(e) Pb(s)	$PbO_2(s)$	$PbO_2(s)$	Pb(s)

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

Answer: The average O.N. of S in $S_2O_3^{2-}$ is +2 while in $S_4O_6^{2-}$ it is + 2.5. The O.N. of S in SO_4^{2-} is +6. Since Br_2 is a stronger oxidising agent that I_2 , it oxidises S of $S_2O_3^{2-}$ to a higher oxidation state of +6 and hence forms SO_4^{2-} ion. I_2 , however, being weaker oxidising agent oxidises S of $S_2O_3^{2-}$ ion to a lower oxidation of +2.5 in $S_4O_6^{2-}$ 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 add 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: $F_2 \ (+2.87V) \ > \ Cl_2 \ (+1.36V) \ > \ Br_2 \ (+1.09V) \ > \ l_2 \ (+0.54V), \ therefore, \ their oxidising power decreases in the same order.$

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 I_2 but not F^- to F_2 . Br_2 , however, oxidises F to I_2 but not F^- to F_2 , and Cl^- to Cl_2 .

$$F_2(g) + 2Cr(aq) \rightarrow 2F^-(aq) + Cl_2(g);$$

$$F2(g) + 2Br^{-}(aq) \rightarrow 2F^{-}(aq) + Br_{2}(Z)$$

$$F_2(g) + 2I^-(aq) \rightarrow 2F^-(aq) + I_2(s);$$

Cl2 (g) +
$$2Br^{-}(aq) \rightarrow 2Cl^{-}(aq) + Br_{2}(Z)$$

$$Cl_2(g) + 2l^-(aq) \rightarrow 2Cl^-(aq) + l_2(s)$$
 and

$$Br_2(Z) + 2F \rightarrow 2Br^-(aq) + I_2(s)$$

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 decreases in the order: $I^-(-0.54 \text{ V}) > Br^-(-1.09 \text{ V}) > Cl^-(-1.36 \text{ V}) > I_2 (-2.87 \text{ V})$, 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 reduce H_2SO_4 to SO_2 while HCl 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 F reduces Cu²⁺ to Cu⁺ but Br does not.

$$2Cu^{2+}(aq) + 4l^{-}(aq) \rightarrow Cu_{2}l_{2}(s) + l_{2}(aq);$$

 $Cu_2+(aq) + 2Br^- \rightarrow No reaction.$

Thus, HI is a stronger reductant than HB_r.

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

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

 $MnO_2(s) + 4HF(l) \rightarrow No reaction.$

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

Question 16. Why does the following reaction occur?

$$XeO_6^{4-}(aq) + 2F^{-}(aq) + 6H^{+}(aq) \longrightarrow XeO_3(s) + F_2(g) + 3H_2O(l)$$

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

Answer:

 $XeO_6^{4-}(aq) + 2F^{-}(aq) + 6H^{+}(aq) \longrightarrow XeO_3(s) + F_2(g) + 3H_2O(l)$

Here, O.N. of Xe decreases from +8 in XeO_6^{4-} to +6 in XeO_3 while that of F increases from -I in F^- to 0 in F_2 . Therefore, XeO_6^{4-} is reduced while F^- is oxidised. This reaction occurs because Na₂XeO₆⁴⁻ (or XeO₆⁴⁻) is a stronger oxidising agent than F₂.

Question 17. Consider the reactions:

- (a) $H_3PO_2(aq) + 4AgNO_3(aq) + 2H_2O(l) \rightarrow H_3PO_4(aq) + 4Ag(s) +$ $4HNO_3(aq)$
- (b) $H_3PO_2(aq) + 2CuSO_4(aq) + 2H_2O(1) \rightarrow H_3PO_4(aq) + 2Cu(s) +$ $H_2SO_4(aq)$
- (c) $C_6H_5CHO(1) + 2[Ag(NH_3)_2]^+(aq) + 3OH^-(aq) \rightarrow C_6H_5COO^-(aq) +$ $2Ag(s) + 4NH_3(aq) + 2H_2O(l)$
- (d) $C_6H_5CHO(1) + 2Cu^{2+}(aq) + 5OH^{-}(aq) \rightarrow No change observed$ What inference do you draw about the behaviour of Ag⁺ and Cu^{2+} from these reactions?

Answer: Reactions (a) and (b) indicate that H₃PO₂ (hypophosphorous acid) is a reducing agent and thus reduces both AgNO₃ and CuSO₄ to Ag and Cu respectively. Conversely, both AgNO₃ and CuSO₄ act as oxidising agent and thus oxidise H_3PO_2 to H_3PO_4 (orthophosphoric acid) Reaction (c) suggests that $[Ag(NH_3)_2]^+$ oxidises C_6H_5CHO (benzaldehyde) to $C_6H_5COO^-$ (benzoate ion) but reaction (d) indicates that Cv^{2+} ions cannot oxidise C_6H_5CHO to $C_6H_5COO^{-}$. Therefore, from the above reactions, we conclude that Ag⁺ ion is a strong deoxidising agent

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

- (a) $MnO_4^-(aq) + I^-(aq) \rightarrow MnO_2(s) + I_2(s)$ (in basic medium)
- (b) $MnO_4^-(aq) + SO_2(g) \rightarrow Mn^{2+}(aq) + H_2SO_4^-$ (in acidic solution)
- (c) $H_2O_2(aq) + Fe_2+(aq) \rightarrow Fe^3+(aq) + H_2O(1)$ (in acidic solution)
- (d) $Cr_2O_7^{2-}$ (aq) + SO_2 (g) $\rightarrow Cr^{3+}$ (aq) + SO_4^{2-} (aq) (in acidic solution)

Answer:

(a) Do it yourself.

than Cu^{2+} ion.

(b) The balanced half reaction equations are:

Oxidation half equation:

$$SO_2(g) + 2H_2O(I) \rightarrow HSO_4^-(aq) + 3H^+(aq) + 2e^- ...(i)$$

Reduction half equation:

$$MnO_4^-(aq) + 8H^+(aq) + 5e^- \rightarrow Mn^{2+}(aq) + 4H_2O(l)$$
(ii)

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

$$2MnO_4^{-}(aq) + 5SO_2(g) + 2H_2O(l) + H^{+}(aq) \rightarrow 2Mn^{2+}(aq) + 5HSO_4^{-}(aq)$$

(c) Oxidation half equation:
$$Fe^{2+}(aq) \rightarrow Fe^{3+}(aq) + e^{-}...(i)$$

Reduction half equation:
$$H_2O_2(aq) + 2H^+(aq) + 2e^- \rightarrow 2H_2O(1)$$
 ...(ii)

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

$$H_2O_2(aq) + 2Fe^{2+}(aq) + 2H^+(aq) \rightarrow 2Fe^{3+}(aq) + 2H_2O(1)$$

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

Oxidation half equation:

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

Reduction half equation:

$$Cr_2O_72^-(aq) + 14H^+(aq) + 6e^- \rightarrow 2Cr^{3+}(aq) + 7H_2O(l)$$
 ...(ii)

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

$$\text{Cr}_2\text{O}_7\text{2-}(\text{aq}) + 3\text{SO}_2(\text{q}) + 2\text{H}^+(\text{aq}) \rightarrow 2\text{Cr}^{3+}(\text{aq}) + 3\text{SO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{I})$$

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.

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

(b)
$$N_2H_4(I) + CIO^-(aq) \rightarrow NO(g) + CV(aq)$$

(c)
$$Cl_2O_7(g) + H_2O_2(aq) \rightarrow ClO_2^-(aq) + O_2(g) + H^+$$

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

Answer:

(a)
$$P_4(s) + OH^-(aq)$$
 \longrightarrow $P_3(g) + H_2 P_1 O_2$

P4 acts both as an oxidising as well as a reducing agent.

Oxidation number method:

Total decrease in O.N. of P_4 in $PH_3 = 3 \times 4 = 12$

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

Therefore, to balance increases decreases in O.N. multiply PH₃ by 1 and H₂PO₂ by 3, we have,

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

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

$$P_4(s) + 6OH^-(aq) \longrightarrow PH_3(g) + 3H_2PO_2^-(aq)$$

To balance H atoms, add 3H₂O 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:

$$P_4(s) \longrightarrow H_2PO_2^-(aq)$$
 ...(ii)

Balancing P atoms, we have,

$$\stackrel{0}{P_4}(s) \longrightarrow 4H_2 \stackrel{+1}{PO_2}(aq)$$

Balance O.N. by adding electrons,

$$P_4(s) \longrightarrow 4H_2PO_2^-(aq) + 4e^-$$

Balance charge by adding 8 OH ions,

$$P_4(s) + 8OH^-(aq) \longrightarrow 4H_2PO_2^-(aq) + 4e^- \qquad ...(iii)$$

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

Reduction half reaction:

$$\stackrel{0}{P_4}(s) \longrightarrow \stackrel{-3}{PH_3}(g) \qquad ...(iv)$$

Balancing P atoms, we have,

$$P_4(s) \longrightarrow 4PH_3(g)$$

Balance O.N. by adding electrons, $P_4(s) + 12e^-$

$$P_4(s) + 12e^- \longrightarrow 4PH_3(g)$$

Balance charge by adding 12OH⁻ ions, $P_4(s) + 12e^- \longrightarrow 4PH_3(g) + 12OH^-(aq)$

$$(s) + 12e^- \longrightarrow 4PH_3(g) + 12OH^-(aq)$$

Balance O atoms, by adding 12H₂O to L.H.S. of above equation.

$$P_4(s) + 12H_2O(l) + 12e^- \longrightarrow 4PH_3(g) + 12OH^-(aq)$$
 ...(v)

To cancel out electrons, multiply Eq. (iii) by 3 and add it to Eq. (v), we have, $4P_4(s) + 24OH^-(aq) + 12H_2O(l) \longrightarrow 4PH_3(aq) + 12H_2PO_2^-(aq) + 12H_2O(l)$ + 12OH-(aq) or $P_4(g) + 3OH^-(aq) + 3H_2O(l) \longrightarrow PH_3(aq) + 3H_2PO_2^-(aq)$...(vi) Thus, Eq. (vi) represents the correct balanced equation. (b) $N_2H_4(l) + ClO_3^-(aq) \longrightarrow NO(g) + Cl^-(aq)$ 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 N₂H₄ by 3 and ClO₃ by 4, we have, $3N_2H_4(l) + 4ClO_3^-(aq) \longrightarrow NO(g) + Cl^-(aq)$ To balance N and Cl atoms, multiply NO by 6 and Cl by 4, we have, $3N_2H_4(l) + 4ClO_3^-(aq) \longrightarrow 6NO(g) + 4Cl^-(aq)$ Balance O atoms by adding 6H₂O, $3N_2H_4(l) + 4ClO_3^-(aq) \longrightarrow 6NO(g) + 4Cl^-(aq) + 6H_2O(l)$ H atoms get automatically balanced and thus Eq. (i) represents the correct balanced equation. Ion electron method. Oxidation half reaction: $N_2H_4(l) \longrightarrow NO(g)$ Balance N atoms, $N_2H_4(l) \longrightarrow 2NO(g)$ Balance O.N. by adding electrons, $N_2H_4(l) \longrightarrow 2NO(g) + 8e^{-l}$ Balance charge by adding 8OH ions, $N_2H_4(l) + 8OH^-(aq) \longrightarrow 2NO(g) + 8e^-$ Balance O atoms by adding 6 H₂O, $N_2H_4(l) + 8OH^-(aq) \longrightarrow 2NO(g) + 6H_2O(l) + 8e^-$...(ii) Thus, Eq. (ii) represents the correct balanced oxidation half equation. Reduction half reaction $ClO_3^-(aq) \longrightarrow Cl^-(aq)$ Balance O.N. by adding electrons, $ClO_3^-(aq) + 6e^- \longrightarrow Cl^-(aq)$ Balance charge by adding OH ions, $CIO_3^-(aq) + 6e^- \longrightarrow CI^-(aq) + 6OH^-(aq)$ Balance O atoms by adding 3H₂O, $ClO_3^-(aq) + 3H_2O(l) + 6e^- \longrightarrow Cl^-(aq) + 6OH^-(aq)$...(iii) 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, $3N_2H_4(l) + 4ClO_3^-(aq) \longrightarrow 6NO(g)' + 4Cl^-(aq) + 6H_2O(l)$...(iv) Thus, Eq. (iv) represents the correct balanced equation O.N. decreases by 4 per Cl aton $\longrightarrow ClO_2(aq) + O_2(g) + H^*$ Thus, Cl₂O₇(g) acts an oxidising agent while H₂O₂(aq) as the reducing agent. Oxidation number method Total decrease in O.N. of $Cl_2O_7 = 4 \times 2 = 8$ Total increase in O.N. of $H_2O_2 = 2 \times 1 = 2$.: To balance increase/decrease in O.N. multiply H₂O₂ and O₂ by 4, we have, $Cl_2O_7(g) + 4H_2O_2(aq) \longrightarrow ClO_2^-(aq) + 4O_2(g)$ To balance Cl atoms, multiply ClO₂ by 2, we have, $Cl_2O_7(g) + 4H_2O_2(aq) \longrightarrow 2ClO_2^-(aq) + 4O_2(g)$ To balance O atoms, add 3H2O R.H.S., we have, $\text{Cl}_2\text{O}_7(g) \,+\, 4\text{H}_2\text{O}_2(\tilde{aq}) \,\,\longrightarrow\,\, 2\text{ClO}_2^-(aq) \,+\, 4\text{O}_2(g) \,+\, 3\text{H}_2\text{O}(l)$ To balance H atoms, add 2H2O to R.H.S. and 2OH to L.H.S., we have, $Cl_2O_7(g) + 4H_2O_2(g) + 2OH^{-}(aq) \longrightarrow 2ClO_2^{-}(aq) + 4O_2(g) + 5H_2O$ This represents the balanced redox equation. Ion electron method Oxidation half reaction: $H_2^{-1}O_2(aq) \longrightarrow O_2(g)$ Balance O.N. by adding electrons, $H_2O_2(aq) \longrightarrow O_2(g) + 2e^-$ Balance charge by adding 2OH $^-$ ions, $H_2O_2(aq) + 2OH^-(aq) \longrightarrow O_2(g) + 2e^-$ Balance O atoms by adding $2H_2O$, $H_2O_2(aq) + 2OH^-(aq) \longrightarrow O_2(g) + 2H_2O(l) + 2e^-$...(i) Reduction half reaction:

 $Cl_2 O_7(g) \longrightarrow ClO_7(aq)$

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Balance Cl atoms; Cl_2O_7(g) \longrightarrow 2ClO_2^-(aq)

Balance O.N. by adding electrons, Cl_2O_7(g) + 8e^- \longrightarrow 2ClO_2^-(aq)

Add 6OH ions to balance charge: Cl_2O_7(g) + 8e^- \longrightarrow 2ClO_2^-(aq) + 6OH^-

Balance O atoms by adding 3H_2O to L.H.S., we have, Cl_2O_7(g) + 3H_2O(l) + 8e^- \longrightarrow 2ClO_2^-(aq) + 6OH^-(aq) ...(ii)

To cancel out electrons, multiply Eq. (i) by 4 and add it to Eq. (ii), we have, 4H_2O_2(aq) + 8OH^-(aq) + Cl_2O_7(g) + 3H_2O(l) \longrightarrow 2ClO_2^- + (aq) + 6OH^-(aq) + 4O_2(g) + 8H_2O(l)

or Cl_2O_7(g) + 4H_2O_2(aq) + 2OH^-(aq) \longrightarrow 2ClO_2^-(aq) + 4O_2(g) + 5H_2O(l)
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