

TEXTBOOK QUESTIONS SOLVED

Question 1. Assign oxidation number to the underlined elements in each of the following species:

- (a) NaH₂PO₄
- (b) NaHSO4
- (c) $H_4\underline{P}_2O_7$
- (d) K_2MnO_4

- (e) Ca<u>O</u>₂
- (f) NaBH₄
- (g) $H_{2}S_{2}O_{7}$
- (h) $KAl(\underline{SO}_4)_2.12H_2O$

Answer:

(a)
$$\cdot$$
 +1 +1 x -2
P in Na H₂ P O₄
(+1) + 2(+1) + x + 4 (-2) = 0
 $x + 3 - 8$ or $x = +5$

(b) S in NaHSO₄

$$\begin{array}{r}
 +1 & +1 & x - 2 \\
 Na & H & S & O_4 \\
 & (+1) + (+1) + x + 4 & (-2) = 0 \\
 & x - 6 = 0 \\
 & x = +6
 \end{array}$$

- (c) P in H₄ P₂ O₇ $^{+1} x \sim ^{-2}$ H₄ P₂ O₇ 4 (+1) + 2x + 7 (-2) = 0 $^{2x} - 10 = 0$ $^{x} = +5$
- (d) Mn in K_2MnO_4 +1 x -2 K_2MnO_4 2 (+1) + x + 4 (-2) = 0 x - 6 = 0
 - x = +6 oxygen.

(e) Let the oxidation number of CaO_2 be x.

$$2 + 2x = 0$$
 (: oxy No. of $a = +2$)

Thus, oxidation number of O in $CaO_2 = -1$.

(f) In NaBH $_4$, H is present as hydride ion. Therefore, its oxidation number is -1. Thus,

+1
$$x$$
 -1
Na B H₄ \therefore 1 (+1) + x + 4 (-1) = 0 or x = +3
Thus, the oxidation number of B in NaBH₄ = +3.

- (g) +1 x -2 $H_2 S_2 O_7$ \therefore 2 (+1) + 2 (x) + 7 (-2) = 0 or x = +6 Thus, the oxidation number of S in $H_2 S_2 O_7 = + 6$.
- (h) +1+3 x -2 +1-2 K Al (S O₄)₂ 12 (H₂ O) or +1+3+2x+8 (-2) +12 (2 × 1 - 2) or x = +6 Alternatively, since H₂O is a neutral molecule, therefore, sum of oxidation numbers of all the atoms in H₂O may be taken as zero. As such water molecules may be ignored white computing the oxidation number of S.

$$\therefore$$
 + 1 + 3 + 2x - 16 = 0 or x = +6

Thus, the oxidation number of S in $KAl(SO_4)_2.12H_2O = +6$.

Question 2. What are the oxidation number of the underlined elements in each of the following and how do you rationalise your results?

(a)
$$KI_3$$
 (b) $H_2S_4O_6$ (c) \underline{Fe}_3O_4 (d) $\underline{CH}_3\underline{CH}_2OH$ (e) $\underline{CH}_3\underline{COOH}$.
Answer: (a) In KI_3 , since the oxidation number of K is +1, therefore,

the average oxidation number of iodine = -1/3. But the oxidation number cannot be fractional. Therefore, we must consider its structure, $K^+[I-I < -I]$. Here, a coordinate bond is formed between I_2 molecule and I^- ion. The oxidation number of two iodine atoms forming the I_2 molecule is zero while that of iodine forming the coordinate bond is -1. Thus, the O.N. of three I atoms, atoms in KI_3 are 0, 0 and -1 respectively.

(b) By conventional method. O.N. of S in
$$H_2S_4O_6 = H_2 S_4 O_6^{-2}$$

or $2(+1) + 4x + 6(-2) = 0$ or $x = +2.5$ (wrong)

But it is wrong because all the four S atoms cannot be in the same oxidation state.

By chemical bonding method. The structure of H₂S₄O₆ is shown below:

$$H - O \xrightarrow{+5} S - S - S - S - OH$$

The O.N. of each of the S-atoms linked with each other in the middle is zero while that of each of the remaining two S-atoms is +5.

- (c) By conventional method. O.N. of Fe in $\operatorname{Fe}_3 \operatorname{O}_4^2$ or 3x + 4 (-2) = 0 or x = 8/3. By stoichiometry. $\operatorname{Fe}_3 \operatorname{O}_4 \equiv \operatorname{Fe}_3 \operatorname{O} \cdot \operatorname{Fe}_2 \operatorname{O}_3^2$. \therefore O.N. of Fe in $\operatorname{Fe}_3 \operatorname{O}_4$ is + 2 and + 3
- (d) By conventional method. O.N. of C in $CH_3CH_2OH = C_2 H_6 O$ or 2x + 6 (+ 1) + 1 (- 2) = 0 or x = -2.
- (e) By conventional method. $CH_3COOH = C_2^x + H_4 C_2^2$ or 2x + 4 4 = 0 or x = 0By chemical bonding method, C_2 is attached to three *H*-atoms (less electronegative than carbon) and one – COOH group (more electronegative than carbon).

therefore, O.N. of $C_2 = 3 (+1) + x + 1 (-1) = 0$ or x = -2

 C_1 is, however, attached to one oxygen atom by a double bond, one OH (O.N. = -1) and one CH₃ (O.N. = +1) group, therefore, O.N. of C_1 = + 1 + x + 1 (-2) + 1 (-1) = 0 or x = +2

Question 3. Justify that the following reactions are redox reactions:

- (a) $CuO(s) + H_2(g) \rightarrow Cu(s) + H_2O(g)$
- (b) $Fe_2O_3(s) + 3CO(g) \rightarrow 2Fe(s) + 3CO_2(g)$
- (c) $4BCl_3(g) + 3LiAlH_4(s) \rightarrow 2B_2H_6(g) + 3LiCl(s) + 3AlCl_3(s)$
- (d) $2K(s) + F_2(g) \rightarrow 2K + F^-(s)$

Answer:

(a)
$$C_{uO(s)}^{+2-2} + H_{2}(g) \longrightarrow C_{u(s)}^{0} + H_{2O(g)}^{+1-2}$$

Here, O is removed from CuO, therefore, it is reduced to Cu while O is added to H_2 to form H_2O , therefore, it is oxidised. Further, O.N. of Cu decreases from + 2 in CuO to 0 in Cu but that of H increases from 0 in H_2 to +1 in H_2O . Therefore, CuO is reduced to Cu but H_2 is oxidised to H_2O . Thus, this is a redox reaction.

(b)
$$\text{Fe}_2 \overset{+3}{\text{O}_3} \overset{-2}{\text{O}_3} (s) + 3 \overset{+2}{\text{CO}} (g) \longrightarrow 2 \overset{0}{\text{Fe}} (s) + 3 \overset{+4}{\text{CO}_2} (g)$$

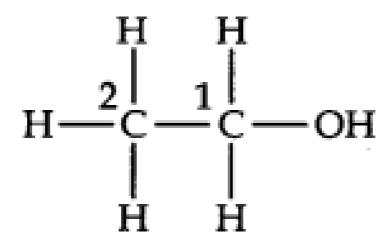
Here O.N. of Fe decreases from +3 if Fe_2O_3 to 0 in Fe while that of C increases from +2 in CO to +4 in CO_2 . Further, oxygen is removed from Fe_2O_3 and added to CO, therefore, Fe_2O_3 is reduced while CO is oxidised. Thus, this is a redox reaction.

(c)
$$4 \stackrel{+3-1}{BCl_3}(g) + \stackrel{+1+3-1}{LiAlH_4}(s) \longrightarrow 2 \stackrel{-3}{B_2} \stackrel{+1}{H_6}(g) + 3 \stackrel{+1}{LiCl}(s) + 3 \stackrel{+3}{Al} \stackrel{-1}{Cl_3}(s)$$

Here, O.N. of B decreases from +3 in $BrCl_3$ to -3 in B_2H_6 while that of H increases from -1 in $LiAlH_4$ to +1 in B_2H_6 . Therefore, BCl_3 is reduced while $LiAlH_4$ is oxidised. Further, H is added to BCl_3 but is removed from $LiAlH_4$, therefore, BCl_3 is reduced while $LiAlH_4$ is oxidised. Thus, it is a redox reaction.

Here, each K atom as lost one electron to form K^+ while F_2 has gained two electrons to form two F^- ions. Therefore, K is oxidised while F_2 is reduced. Thus, it is a redox reaction.

By chemical bonding, C_2 is attached to three H-atoms (less electronegative than carbon) and one CH_2OH group (more electronegative than carbon), therefore,



O.N. of C_2 = 3 (+1) + x + 1 (-1) = 0 or x = -2 G_2 is, however, attached to one OH (O.N. = -1) and one CH₃ (O.N. = +1) group, therefore, O.N. of C_4 = +1 + 2 (+1) + x + 1 (-1) = 0 or x = -2

Question 4. Fluorine reacts with ice and results in the change: $H_2O(S) + F_2(g) \rightarrow HF(g) + HOF(g)$

Justify that this reaction is a redox reaction.

Answer: Writing the O.N. of each atom above its symbol, we have,

$$\overset{+1}{\text{H}_2}\overset{-2}{\text{O}} + \overset{0}{\text{F}_2} \longrightarrow \overset{+1}{\text{H}}\overset{-1}{\text{F}} + \overset{+1}{\text{H}}\overset{-2}{\text{O}}\overset{+1}{\text{F}}$$

Here, the O.N. of F decreases from 0 in F_2 to -1 in HF and increases from 0 in F_2 to +1 in HOF. Therefore, F_2 is both reduced as well as oxidised. Thus, it is a redox reaction and more specifically, it is a disproportionation reaction.

Question 5. Calculate the oxidation number of sulphur, chromium and nitrogen in H_2SO_5 , Cr_2O_2 and NOT. Suggest structure of these compounds. Count for the fallacy.

Answer: O.N. of S in H_2SO_5 . By conventional method, the O.N. of S in H_2SO_5 is 2 (+1) + x + 5 (-2) = 0 or x = +8 This is impossible because the maximum O.N. of S cannot be more than six since it has only six electrons in the valence shell. This fallacy is overcome if we calculate the O.N. of S by chemical bonding method. The structure of H_2SO_5 is

$$H - O - S - O - O - H$$

$$2 \times (+1) + x + 2 (-1) + 3 \times (-2) = 0 \text{ or } x = +6$$

$$(\text{for H}) \quad (\text{for S}) \quad \text{for } (O - O) \text{ (for other O)}$$

$$atoms$$

$$Cr \text{ in } Cr_2O_7^{-2}$$

$$2x + (-2 \times 7) = -2$$

$$2x - 14 = -2$$

$$2x = -2 + 14 \qquad x = +6$$

$$x + 1 (-1) + 1 (-2) + 1 (-2) = 0 \text{ or } x + 5$$

$$(\text{for O}) \quad (\text{for = O)} \quad \text{for } \rightarrow O$$

Thus, there is no fallacy about the O.N. of N in NO₃⁻whether one calculates by conventional method or by chemical bonding method.

Question 6. Write formulas for the following compounds:

- (a) Mercury (II) chloride,
- (b) Nickel (II) sulphate,
- (c) Tin (IV) oxide,
- (d) Thallium (I) sulphate,
- (e) Iron (III) sulphate,
- (f) Chromium (III) oxide.

Answer:

- (a) $Hg(II) Cl_2$,
- (b) Ni(II) SO₄,
- (c) $S_n(IV) O_2$
- (4) T (1) CO
- (d) $T_{12}(I) SO_4$,
- (e) $Fe_2(III) (SO_4)_3$,
- (f) $Cr_2(III) O_3$.

Question 7. Suggest a list of substances where carbon can exhibit oxidation states from -4 to +4 and nitrogen from -3 to +5. Answer:

7 (110 17 01)			
Compound	O.N. of Carbon	Compound	O.N. of Nitrogen
CH ₄	-4	NH_3	-3
CH ₃ CH ₃	, -3	$NH_2 - NH_2$	-2
CH ₂ =CH ₂ or CH ₃ Cl	-2	NH=NH	-1
CH = CH	-1	N=N	0
CH ₂ Cl ₂ or C ₆ H ₁₂ O ₆	0	N_2O	+1
C2Cl2 or C6Cl6	+1	NO	+2
CO or CHCl ₃	+2	N_2O_3	+3
C2Cl6 or (COOH)2	+3	N_2O_4	+4
CO ₂ or CCl ₄	+4	N_2O_5	+5

Question 8. While sulphur dioxide and hydrogen peroxide can act as an oxidising as well as reducing agents in their reactions, ozone and nitric acid act only as oxidants. Why?

Answer:

- (i) In SO_2 , O.N. of S is +4. In principle, S can have a minimum O.N. of 2 and maximum of +6. Therefore, S in SO_2 can either decrease or increase its O.N. and hence can act both as an oxidising as well as a reducing agent.
- (ii) In H_2O_2 , the O.N. of O is -1. In principle, O can have a minimum O.N. of -2 and maximum of zero (+1 is possible in O_2F_2 and +2 in OF_2). Therefore, O in H_2O_2 can either decrease its O.N. from -1 to -2 or can increase its O.N. from -1 to zero. Therefore, H_2O_2 acts both as an oxidising as well as a reducing agent.
- (iii) In O_3 , the O.N. of O is zero. It can only decrease its O.N. from zero to -1 or -2, but cannot increase to +2. Therefore, O_3 acts only as an oxidant.
- (iv) In ${\rm HNO_3}$, O.N. of N is +5 which is maximum. Therefore, it can only decrease its O.N. and hence it acts as an oxidant only.

Question 9. Consider the reactions: (a) $6CO_2(g) + 6H_2O(I) \rightarrow C_6H_{12}O_6(s) + 6O_6(g)$ (b) $O_3(g) + H_2O_2(l) H_2O(l) + 2O_2(g)$

Why it is more appropriate to write these reactions as:

(a)
$$6CO_2(g) + 12H_2O(l) \rightarrow C_6H_{12}O_6(s) + 6H_2O(l) + 6O_2(g)$$

(b)
$$O_3(g) + H_2O_2(I) \rightarrow H_2O(I) + O_2(g) + O_2(g)$$

Also suggest a technique to investigate the path of above (a) and (b) redox reactions.

Answer:

- (a) Therefore, it is more appropriate to write the equation for photosynthesis as (iii) because it emphasises that $12H_2O$ are used per molecule of carbohydrate formed and $6H_2O$ are produced during the process.
- (b) The purpose of writing O_2 two times suggests that O_2 is being obtained from each of the two reactants.

$$\begin{array}{ccc}
O_3(g) & \longrightarrow & O_2(g) + O(g) \\
H_2O_2 + O(g) & \longrightarrow & H_2O(l) + O_2(g) \\
\hline
O_3(g) + H_2O_2(l) & \longrightarrow & H_2O(l) + O_2(g) + O_2(g)
\end{array}$$

The path of reactions (a) and (b) can be determined by using $\rm\,H_2O_2^{18}$ or $\rm\,D_2O$ in reaction

(a) or by using $H_2O_2^{18}$ or O_3^{18} in reaction (b).

Question 10. The compound ${\rm AgF_2}$ is unstable. However, if formed, the compound acts as a very strong oxidising agent. Why? Answer:

In ${\rm AgF_2}$ oxidation state of Ag is +2 which is very very unstable. Therefore, it quickly accepts an electron to form the more stable +1 oxidation state.

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

Therefore, AgF₂, if formed, will act as a strong oxidising agent.

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