THE VILLAGE INTERNATIONAL SCHOOL
"We Nurture Dreams"
AIM HIGH, TOGETHER WE FLY

REDOX REACTIONS

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

(a) $NaH_2\underline{P}O_4$ (b) $NaH\underline{S}O_4$ (c) $H_4\underline{P}_2O_7$ (d) $K_2\underline{Mn}O_4$
(e) $Ca\underline{O}_2$ (f) $Na\underline{B}H_4$ (g) $H_2\underline{S}_2O_7$ (h) $KAl(\underline{S}O_4)_2.12H_2O$

Answer:

(a) P in $\overset{+1}{Na}\,\overset{+1}{H_2}\,\overset{x}{P}\,\overset{-2}{O_4}$

$$(+1) + 2(+1) + x + 4(-2) = 0$$
$$x + 3 - 8 \text{ or } x = +5$$

(b) S in $NaHSO_4$

$\overset{+1}{Na}\,\overset{+1}{H}\,\overset{x}{S}\,\overset{-2}{O_4}$

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

(c) P in $H_4P_2O_7$

$\overset{+1}{H_4}\,\overset{x}{P_2}\,\overset{-2}{O_7}$

$$4(+1) + 2x + 7(-2) = 0$$
$$2x - 10 = 0$$
$$x = +5$$

(d) Mn in K_2MnO_4

$\overset{+1}{K_2}\overset{x}{Mn}\overset{-2}{O_4}$

$$2(+1) + x + 4(-2) = 0$$
$$x - 6 = 0$$
$$x = +6 \text{ oxygen.}$$

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

$$2 + 2x = 0 \quad (\because \text{oxy No. of } a = +2)$$
$$x = -1$$

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,

$\overset{+1}{Na}\ \overset{x}{B}\ \overset{-1}{H_4}$ $\quad \therefore \quad 1(+1) + x + 4(-1) = 0$ or $x = +3$

Thus, the oxidation number of B in $NaBH_4$ = **+ 3.**

(g) $\overset{+1}{H_2}\ \overset{x}{S_2}\ \overset{-2}{O_7}$ $\quad \therefore \quad 2(+1) + 2(x) + 7(-2) = 0$ or $x = +6$

Thus, the oxidation number of S in $H_2S_2O_7$ = **+ 6.**

(h) $\overset{+1}{K}\ \overset{+3}{Al}\ (\overset{x}{S}\ \overset{-2}{O_4})_2\ 12\ (\overset{+1}{H_2}\ \overset{-2}{O})$ or $+1 + 3 + 2x + 8(-2) + 12(2 \times 1 - 2)$ or $x = +6$

Alternatively, since H_2O is a neutral molecule, therefore, sum of oxidation numbers of all the atoms in H_2O 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) $K\underline{I}_3$ *(b)* $H_2\underline{S}_4O_6$ *(c)* $\underline{Fe}_3O_4$ *(d)* $\underline{C}H_3\underline{C}H_2OH$ *(e)* $\underline{C}H_3\underline{C}OOH$.

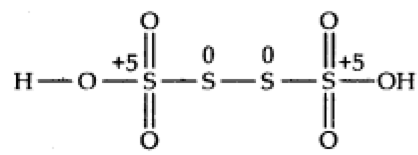
Answer: (a) In KI_3, since the oxidation number of K is +1, therefore, the average oxidation number of iodine = -1/3. But the oxidation number cannot be fractional. Therefore, we must consider its structure, $K^+[I — I \leftarrow I]^-$. Here, a coordinate bond is formed between I_2 molecule and I^- ion. 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 $H_2S_4O_6 = \overset{+1}{H_2}\overset{x}{S_4}\overset{-2}{O_6}$

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 $H_2S_4O_6$ is shown below:



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 $\overset{x}{Fe_3}\overset{-2}{O_4}$ or $3x + 4(-2) = 0$ or $x = 8/3$.

By stoichiometry. $Fe_3O_4 \equiv \overset{+2}{Fe_3}\overset{-2}{O}\cdot\overset{+3}{Fe_2}\overset{-2}{O_3}$.

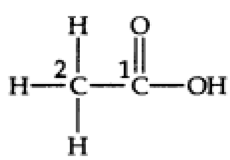
$\therefore$ O.N. of Fe in Fe_3O_4 is + 2 and + 3

(*d*) *By conventional method.* O.N. of C in $CH_3CH_2OH = \overset{x}{C_2}\overset{+1}{H_6}\overset{-2}{O}$

or $2x + 6(+1) + 1(-2) = 0$ or $x = -2$.

(*e*) *By conventional method.* $CH_3COOH = \overset{x}{C_2}\overset{+1}{H_4}\overset{-2}{O_2}$ or $2x + 4 - 4 = 0$ or $x = 0$

By 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 CH_3 (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) $CuO(s) + H_2(g) \longrightarrow Cu(s) + H_20(g)$

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

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

(d) $2K(s) + F_2(g) \longrightarrow 2K^+F^-(s)$

Answer:

(a) $\overset{+2-2}{CuO}(s) + \overset{0}{H_2}(g) \longrightarrow \overset{0}{Cu}(s) + \overset{+1-2}{H_2O}(g)$

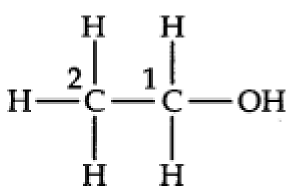
Here, O is removed from CuO, therefore, it is reduced to Cu while O is added to H_2 to form H_20, therefore, it is oxidised. Further, O.N. of Cu decreases from + 2 in CuO to 0 in Cu but that of H increases from 0 in H_2 to +1 in H_20. Therefore, CuO is reduced to Cu but H_2 is oxidised to H_20. Thus, this is a redox reaction.

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

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) $4\overset{+3-1}{BCl_3}(g) + \overset{+1+3-1}{LiAlH_4}(s) \longrightarrow 2\overset{-3}{B_2}\overset{+1}{H_6}(g) + 3\overset{+1}{Li}\overset{-1}{Cl}(s) + 3\overset{+3}{Al}\overset{-1}{Cl_3}(s)$

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, BC13 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,

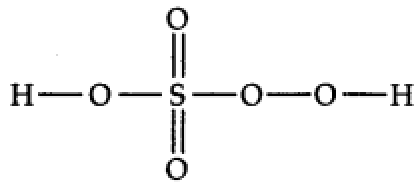


O.N. of C_2 = 3 (+1) + x + 1 (-1) = 0 or x = -2 C_2 is, however, attached to one OH (O.N. = -1) and one CH_3 (O.N. = +1) group, therefore, O.N. of C_4 = + 1 + 2 (+1) + x + 1 (-1) = 0 or x = -2

Question 4. Fluorine reacts with ice and results in the change:
$H_20(S) + F_2\ (g)$ ——-> 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,
$\overset{+1}{H_2}\overset{-2}{O} + \overset{0}{F_2} \longrightarrow \overset{+1}{H}\overset{-1}{F} + \overset{+1}{H}\overset{-2}{O}\overset{+1}{F}$
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



$$\underset{\text{(for H)}}{2 \times (+1)} + \underset{\text{(for S)}}{x} + \underset{\text{for (O – O)}}{2\,(-1)} + \underset{\text{(for other O atoms)}}{3 \times (-2)} = 0 \text{ or } x = +6$$

Cr in $Cr_2O_7^{2-}$

$$2x + (-2 \times 7) = -2$$
$$2x - 14 = -2$$
$$2x = -2 + 14 \qquad x = +6$$

$$\underset{\text{(for O}^-\text{)}}{x + 1\,(-1)} + \underset{\text{(for = O)}}{1\,(-2)} + \underset{\text{for} \rightarrow \text{O}}{1\,(-2)} = 0 \quad \text{or } x + 5$$

Thus, there is no fallacy about the O.N. of N in $N0_3^-$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)SO_4, (c)S_n(IV)O_2 (d) T_{12}(I)SO_4, (e) Fe_2(III)$(S0_4)_3$, (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:

Compound	O.N. of Carbon	Compound	O.N. of Nitrogen
CH_4	–4	NH_3	–3
CH_3CH_3	–3	NH_2-NH_2	–2
$CH_2{=}CH_2$ or CH_3Cl	–2	$NH{=}NH$	–1
$CH{\equiv}CH$	–1	$N{\equiv}N$	0
CH_2Cl_2 or $C_6H_{12}O_6$	0	N_2O	+1
C_2Cl_2 or C_6Cl_6	+1	NO	+2
CO or $CHCl_3$	+2	N_2O_3	+3
C_2Cl_6 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 $S0_2$, O.N. of S is +4. In principle, S can have a minimum O.N. of -2 and maximum of +6. **Question 18. Balance the following redox reactions by ion-electron method.**
(a) $MnO_4^-(aq) + I^-(aq)$ ———> $Mn0_2(s) + I_2 (s)$ (in basic medium)
(b) $MnO_4^-(aq)$ + S02(g) ——-> $Mn^{2+}(aq) + H_2S0_4^-$(in acidic solution)
(c) $H_2O_2(aq)$ + Fe2+(aq) ———-> Fe^3+(aq) + $H_2O(l)$ (in acidic solution)
(d) $Cr_2O_7^{2-}$ (aq) + $S0_2$ (g)——> Cr^{3+} (aq) + $SO_4^{2-}(aq)$ (in acidic solution)
Answer: (a) Do it yourself.
(b) The balanced half reaction equations are:
Oxidation half equation:
$S0_2(g) + 2H_2O(l)$ ——–> $HS0_4^-$ (aq) + $3H^+(aq) + 2e^-$ …(i)
Reduction half equation:
$MnO_4^-(aq) + 8H^+(aq) + 5e^-$ ——–> $Mn^{2+}(aq) + 4H_2O(l)$ ……….(ii)
Multiply Eq. (i) by 3 and Eq. (ii) by 2 and add, we have,
$2MnO_4^-(aq) + 5S0_2(g) + 2H_20(l) + H^+(aq)$ ————> $2Mn^{2+}(aq) + 5HSO_4^-(aq)$
(c) Oxidation half equation: $Fe^{2+}(aq)$ ———> $Fe^{3+}(aq) + e^-$ …(i)
Reduction half equation: $H_2O_2(aq) + 2H^+(aq) + 2e^-$ ———> $2H_2O(l)$ …(ii)
Multiply Eq. (i) by 2 and add it to Eq. (ii), we have,
$H_2O_2(aq) + 2Fe^{2+}(aq) + 2H^+(aq)$ ——-> $2Fe^{3+}(aq) + 2H_2O(l)$
(d) Following the procedure detailed on page 8/23, the balanced half reaction equations are:
Oxidation half equation:

$SO_2(g) + 2H_2O(l)$ ————> $SO_4^{2-}(aq) + 4H^+(aq) + 2\ e^-$ …(i)
Reduction half equation:
$Cr_2O_72^-(aq) + 14H^+(aq) + 6e^-$ ————> $2Cr^{3+}(aq) + 7H_20(l)$ …(ii)
Multiply Eq. (i) by 3 and add it to Eq. (ii), we have,
$Cr_2O_72^-(aq) + 3SO_2(q) + 2H^{+\cdots}(aq)$ ————> $2Cr^{3+}(aq) + 3SO_4^{2-}(aq) + H_20(l)$

………………………………………………………………………………..