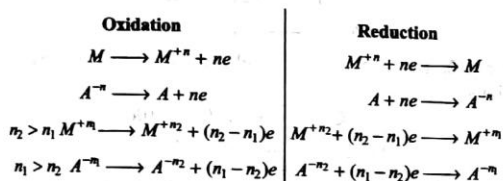


[A] Oxidation-reduction

(1) Oxidation is a process which liberates electrons, *i.e.*, de-electronation.

(2) Reduction is a process which gains electrons, *i.e.*, electronation.



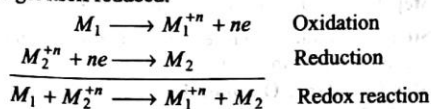
(3) Oxidants are substances which:
 (a) oxidize other.
 (b) reduced themselves.
 (c) show electronation.
 (d) show a decrease in oxidation no. during a redox change.

(e) has higher oxidation no. in a conjugate pair of redox.

(4) Reductants are substances which:
 (a) reduce other.
 (b) oxidized themselves.
 (c) show de-electronation.
 (d) show an increase in oxidation no. during a redox change.

(e) has lower oxidation no. in a conjugate pair of redox.

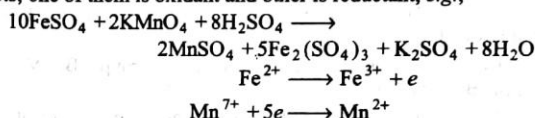
(5) A redox change is one in which a reductant is oxidized to liberate electrons, which are then used up by an oxidant to get itself reduced.



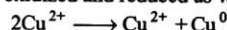
(6) A redox change occurs simultaneously.

[B] Types of Redox changes

(1) **Intermolecular redox reactions** : Two substances reacts; one of them is oxidant and other is reductant, *e.g.*,

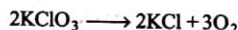


(2) **Auto redox reactions or disproportionation** : The same element is oxidized and reduced as well, *e.g.*,

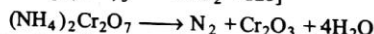
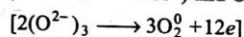


Cu^+ is oxidized to Cu^{2+} and Cu^+ is reduced to Cu .

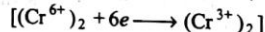
(3) **Intramolecular redox reactions** : One element of a compound is oxidized and other element of the same compound is reduced, *e.g.*,



Cl is reduced ($\text{Cl}^{5+} + 6e \longrightarrow \text{Cl}^-$) and O is oxidized



N is oxidized ($2\text{N}^{3-} \longrightarrow \text{N}_2^0 + 6e$) and Cr is reduced

**[C] Oxidation Number**

(1) Oxidation no. of an element in a particular compound represents the no. of electrons lost or gained by an element during its change from free state into that compound.

or Oxidation no. of an element in a particular compound represents the extent of oxidation or reduction of an element during its change from free state into that compound.

(2) Oxidation no. is given positive sign if electrons are lost. Oxidation no. is given negative sign if electrons are gained.

(3) Oxidation no. represents real charge in case of ionic compounds. However, in covalent compounds it represents imaginary charge.

[D] Rules for Deriving Oxidation Number

Following rules have been arbitrarily adopted to decide oxidation no. of elements on the basis of their periodic properties.

- (1) In uncombined state or free state, oxidation no. of an element is zero.
- (2) In combined state oxidation no. of
 - (a)F is always -1.
 - (b)O is -2. In peroxides it is -1. However in F_2O it is +2.
 - (c)H is +1. In ionic hydrides it is -1. (i.e., IA, IIA and IIIA metals)
 - (d)halogens as halide is always -1.
 - (e)sulphur as sulphide is always -2.
 - (f)metals is always +ve.
 - (g)alkali metals (i.e., IA group—Li, Na, K, Rb, Cs, Fr) is always +1.
 - (h)alkaline earth metals (i.e., IIA group—Be, Mg, Ca, Sr, Ba, Ra) is always +2.
- (3) The algebraic sum of all the oxidation no. of elements in a compound is equal to zero, e.g., $KMnO_4$.
 $Ox. no. of K + Ox. no. of Mn + (Ox. no. of O) \times 4 = 0$
- (4) The algebraic sum of all the oxidation no. of elements in a radical is equal to the net charge on the radical, e.g., CO_3^{2-} .
 $Oxidation no. of C + 3 \times (Oxidation no. of O) = -2$
- (5) Oxidation number can be zero, +ve, -ve (integer or fraction).
- (6) Maximum oxidation no. of an element is = Group no. (Except O and F)
 Minimum oxidation no. of an element is = Group no. - 8 (Except metals)

[E] Oxidation State

It is defined as oxidation no. per atom, e.g., in $KMnO_4$

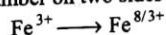
Oxidation no. of Mn is = +7

Oxidation state of Mn is = Mn^{7+}

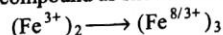
[F] Balancing a half reaction

Consider for example : $Fe_2O_3 \longrightarrow Fe_3O_4$

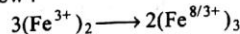
Step I : Write down the symbol of element with its oxidation number on two sides of reaction.



Step II : Write the elemental form of element in which it exist in that compound as shown below.



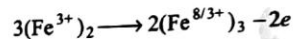
Step III : Make the number of atoms same on two sides as reported below :



Step IV : Multiply the all digits on right hand side [i.e., $2 \times 3 \times \left(+\frac{8}{3}\right) = +16$] and on left hand side [i.e., $3 \times 2 \times$

$(+3) = +18$] than subtract the value of left hand side from right hand side [i.e., $+16 - (+18) = -2$].

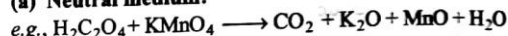
Put this number (-2) with electron on right hand side, with its sign.

**[G] Balancing of Redox Equations**

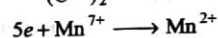
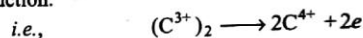
Two methods are commonly used for this purpose.

1. Ion Electron Method

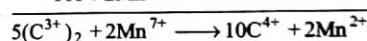
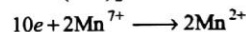
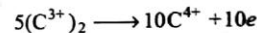
It involves three sets of rules depending upon the nature of medium (i.e., neutral, acid or alkaline) in which reaction occurs.

(a) Neutral medium:

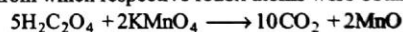
Step 1. Select the oxidant, reductant atoms and write their half reactions, one representing oxidation and other reduction.



Step 2. Balance the no. of electrons and add the two equations.

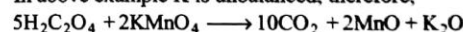


Step 3. Write complete molecule of the reductant and oxidant from which respective redox atoms were obtained.



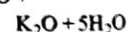
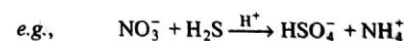
Step 4. Balance other atoms if any (except H and O).

In above example K is unbalanced, therefore,

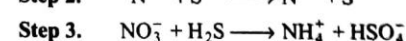
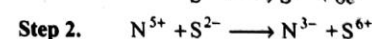
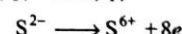
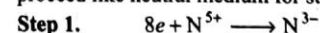


(mentioned as product)

Step 5. Balance O-atom using H_2O on desired side.

**(b) Acidic medium:**

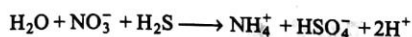
proceed like neutral medium for step 1 to step 4.



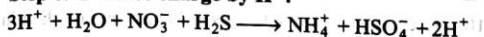
Step 4. No other atom (except H and O) is unbalanced and thus, no need for this step.

Step 5. Balance O-atom: Balancing of O-atom is made by using H_2O and H^+ ions.

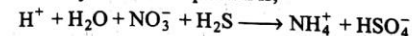
Add desired molecules of H_2O on the side deficient with O-atom and double H^+ on opposite side. Therefore,



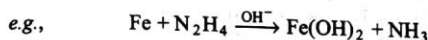
Step 6. Balance charge by H^+ :



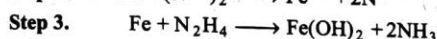
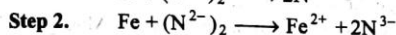
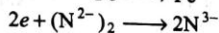
$\therefore$ Finally balanced equation is,



(c) **Alkaline medium:**



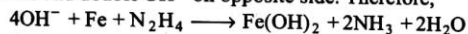
Proceed like neutral medium for step 1 to step 4.



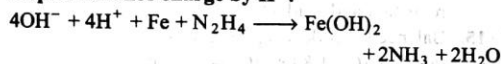
Step 4. No other atom (except H and O) is unbalanced and thus, no need for this step.

Step 5. Balance O-atom: Balancing of O-atom is made by using H_2O and OH^- ions.

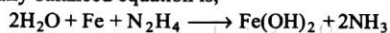
Add desired molecules of H_2O on the side rich with O-atoms and double OH^- on opposite side. Therefore,



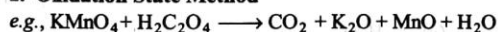
Step 6. Balance charge by H^+ :



$\therefore$ Finally balanced equation is,



2. Oxidation State Method



The initial step 1 should be written as

Step 1. $\text{Mn}^{7+} \longrightarrow \text{Mn}^{2+}$ i.e., change in oxidation no. of

Mn (+7 $\longrightarrow$ +2) = 5 units

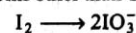
$(\text{C}^{3+})_2 \longrightarrow 2\text{C}^{4+}$ i.e., change in oxidation no. of C (+6 $\longrightarrow$ +8) = 2 units

Step 2. Proceed from step 2 to last step for neutral, acidic or alkaline medium as in ion electron method.

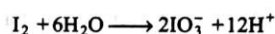
[H] Balancing of Half Reactions

Example 1. $\text{I}_2 \longrightarrow \text{IO}_3^-$ (Acid medium)

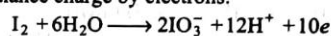
Step 1. Balance atoms other than O and H if needed, i.e.,



Step 2. Balance O-atoms using H^+ and H_2O as reported earlier.



Step 3. Balance charge by electrons.



This is balanced half reaction.

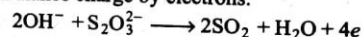
Example 2. $\text{S}_2\text{O}_3^{2-} \longrightarrow \text{SO}_2$ (Basic medium)

Step 1. As above $\text{S}_2\text{O}_3^{2-} \longrightarrow 2\text{SO}_2$

Step 2. Balance O-atom by H_2O and OH^- as reported earlier.



Step 3. Balance charge by electrons.



This is balanced half reaction.

● NUMERICAL PROBLEMS ●

- Determine the oxidation no. of following elements given in bold letters:
 (a) KMnO_4 , (b) H_2SO_5 , (c) $\text{H}_2\text{S}_2\text{O}_8$, (d) NH_4NO_3 ,
 (e) $\text{K}_4\text{Fe}(\text{CN})_6$, (f) OsO_4 , (g) HCN , (h) HNC ,
 (i) HNO_3 , (j) KO_2 , (k) Fe_3O_4 , (l) KI_3 , (m) OCN^- ,
 (n) $\text{Fe}(\text{CO})_5$, (o) $\text{Fe}_{0.94}\text{O}$, (p) $\text{NH}_2 \cdot \text{NH}_2$,
 (q) $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ (r) NOCl , (s) NOClO_4 ,
 (t) $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$, (u) $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]\text{SO}_4$,
 (v) $\text{Na}_2\text{S}_4\text{O}_6$, (w) Dimethyl sulphoxide or $(\text{CH}_3)_2\text{SO}$,
 (x) $\text{Na}_2\text{S}_2\text{O}_3$, (y) CrO_5 or $\text{CrO}(\text{O}_2)_2$, (z) CaOCl_2 .
- Determine the oxidation number of following elements given in bold letters :
 (a) CuH , (b) $\text{Na}_2\text{S}_3\text{O}_6$, (c) N_2O , (d) Ba_2XeO_6 ,
 (e) C_3O_2 , (f) $\text{V}(\text{BrO}_2)_2$, (g) $\text{Ca}(\text{ClO}_2)_2$,
 (h) $\text{Cs}_4\text{Na}(\text{HV}_{10}\text{O}_{28})$, (i) LiAlH_4 ,
 (j) $\text{K}[\text{Co}(\text{C}_2\text{O}_4)_2 \cdot (\text{NH}_3)_2]$, (k) $[\text{Ni}(\text{CN})_4]^{2-}$,
 (l) Na_2S_2 , (m) $[\text{XeO}_6]^{4-}$, (n) HOCN , (o) $(\text{CN})_2$.
- Find the oxidation number of Fe in Fe_3O_4 and in $\text{Fe}(\text{III})_4[\text{Fe}(\text{II})(\text{CN})_6]_3$.
- Find out the value of n in:

$$\text{MnO}_4^- + 8\text{H}^+ + ne \longrightarrow \text{Mn}^{2+} + 4\text{H}_2\text{O}$$
- Calculate the oxidation number of Mn in the product formed on strongly heating Mn_2O_7 .
- Calculate the oxidation number of Mn in the product of alkaline oxidative fusion of MnO_2 . (IIT 2009)
- One mole of N_2H_4 loses 10 mole electrons to form a new compound Y. Assuming that all the N₂ appears in new compound, what is oxidation state of N in Y?
- In the reaction, $\text{Al} + \text{Fe}_3\text{O}_4 \longrightarrow \text{Al}_2\text{O}_3 + \text{Fe}$
 (a) Which element is oxidized and which is reduced?
 (b) Total no. of electrons transferred during the change.
- The composition of a sample of wustite is $\text{Fe}_{0.93}\text{O}_{1.00}$. What percentage of iron is present in the form of Fe (III)? (IIT 1994)
- Select the species acting as reductant and oxidant in the reaction given below:

$$\text{PCl}_3 + \text{Cl}_2 \longrightarrow \text{PCl}_5$$
- Identify the substance acting as oxidant or reductant reduced if any in the following :
 (i) $\text{AlCl}_3 + 3\text{K} \longrightarrow \text{Al} + 3\text{KCl}$
 (ii) $\text{SO}_2 + 2\text{H}_2\text{S} \longrightarrow 3\text{S} + \text{H}_2\text{O}$
 (iii) $\text{BaCl}_2 + \text{Na}_2\text{SO}_4 \longrightarrow \text{BaSO}_4 + 2\text{NaCl}$
 (iv) $3\text{I}_2 + 6\text{NaOH} \longrightarrow \text{NaIO}_3 + 5\text{NaI} + 3\text{H}_2\text{O}$
- Arrange the following in order of:
 (a) Increasing oxidation no. of Mn: MnCl_2 , MnO_2 , $\text{Mn}(\text{OH})_3$, KMnO_4
 (b) Decreasing oxidation no. of X: H_2XO_4 , HXO_3 , HXO_2 , HXO
 (c) Increasing oxidation no. of I: I_2 , HI , HIO_4 , ICl (IIT 1986)
- Which of the following are oxidants and which are reductants? Justify your answer with half equations?
 Fe^{3+} , SO_3 , NO_3^- , I^- , Na
- HNO_3 acts only as oxidant whereas, HNO_2 acts as reductant and oxidant both.
- Balance the following equations:
 (a) $\text{BaCrO}_4 + \text{KI} + \text{HCl} \longrightarrow \text{BaCl}_2 + \text{I}_2 + \text{KCl} + \text{CrCl}_3 + \text{H}_2\text{O}$
 (b) $\text{SO}_2 + \text{Na}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + \text{Cr}_2(\text{SO}_4)_3 + \text{H}_2\text{O}$
 (c) $\text{C}_2\text{H}_5\text{OH} + \text{I}_2 + \text{OH}^- \longrightarrow \text{CHI}_3 + \text{HCO}_2^- + \text{H}_2\text{O} + \text{I}^-$ (Basic)
- Write down the disproportionation of HNO_2 in cold water.
- Eight mole of chlorine (Cl_2) undergoes a loss and gain of 14 mole of electrons to form two oxidation state of chlorine (Cl). Write down the two half reaction and equation for disproportionation of chlorine, Cl_2 .

SOLUTIONS (Numerical Problems)

1. (a)
- KMnO_4
- : Ox. no. of K = +1 by rules

$$\text{Ox. no. of Mn} = a$$

$$\text{Ox. no. of O} = -2 \text{ by rules}$$

$$\therefore 1 + a + 4 \times (-2) = 0$$

$$\therefore a = +7$$

- (b)
- H_2SO_5
- : Ox. no. of H = +1

$$\text{Ox. no. of O} = -2$$

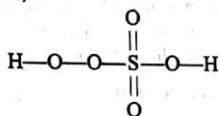
$$\text{Ox. no. of S} = a$$

$$\therefore 2 \times 1 + a + 5 \times (-2) = 0$$

$$a = +8$$

(wrong)

But this cannot be true as maximum ox. no. for S (VI gp) stands +6. The exceptional value is due to the fact that two O-atoms in H_2SO_5 show peroxide linkage, i.e.,

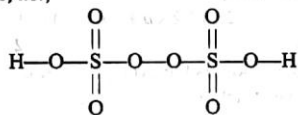


Thus, evaluation of ox. no. of S should be made as

$$2 \times 1 + a + 3 \times (-2) + 2 \times (-1) = 0$$

$$\therefore a = +6$$

- (c)
- $\text{H}_2\text{S}_2\text{O}_8$
- : Here too, two O-atoms form peroxide linkage, i.e.,



$$\therefore 2 \times 1 + 2a + 6 \times (-2) + 2 \times (-1) = 0$$

$$\therefore a = +6$$

- (d)
- NH_4NO_3
- :
- $2 \times a + 4 \times 1 + 3 \times (-2) = 0$
- by rules

$$a = +1$$

(wrong)

No doubt there are two N-atoms in NH_4NO_3 , but one N-atom has negative ox. no. (attached to H) and the other has positive ox. no. (attached to O). Therefore, evaluation should be made separately as

$$\text{Ox. no. of N in } \text{NH}_4^+ \quad \text{and} \quad \text{Ox. no. of N in } \text{NO}_3^-$$

$$a + 4 \times (+1) = +1$$

$$\therefore a = -3$$

$$a + 3 \times (-2) = -1$$

$$\therefore a = +5$$

- (e)
- $\text{K}_4\text{Fe}(\text{CN})_6$
- : By rules, Ox. no. of K = +1 (MLNR 1986)

$$\text{Ox. no. of } \text{CN}^{-1} = -1$$

$$\text{Ox. no. of Fe} = a$$

$$\therefore 4 \times 1 + a + 6 \times (-1) = 0$$

$$\therefore a = +2$$

- (f)
- OsO_4
- :
- $a + 4 \times (-2) = 0$

$$\therefore a = +8$$

Note : 1. The element Os and Ru show highest oxidation state, i.e., +8.

2. Recently Ba_2XeO_6 has been reported in which ox. no. of Xe is +8.

- (g)
- HCN
- : The evaluation cannot be made directly in some cases, e.g.,
- HCN
- by using rules proposed earlier since we have no rule for ox. no. of both N and C. In all such cases evaluation of ox. no. should be made using indirect concept or using fundamentals by which rules have been framed.

(1) Each covalent bond contributes one unit for ox. no.

(2) Covalently bonded atoms with less electronegativity acquires positive ox. no. whereas other with more electronegativity acquires negative ox. no.

(3) In case of co-ordinate bond, give +2 value for ox. no. to atom from which co-ordinate bond is directed to a more electronegative atom and -2 value to more electronegative atom.

If co-ordinate bond is directed from more electronegative to less electronegative atom, then neglect contribution of co-ordinate bond for both atoms in which co-ordinate bond exist.

$$\text{Thus, } \text{H}-\text{C} \equiv \text{N}$$

$$1 + a + 3 \times (-1) = 0$$

$$a = +2$$

$\therefore$ Three bonds on N-atom and N is more electronegative
 $\therefore$ Ox. no. of N = $3 \times (-1) = -3$

- (h)
- HNC
- :
- $\text{H}-\text{N} \equiv \text{C}$

$$\text{Ox. no. of H} = +1$$

$$\text{Ox. no. of N} = [-2 + (-1) + 0] = -3$$

for covalent bond with C [for covalent bond with H] No. contribution for co-ordinate bond (According to fundamental concept)

$$= -3$$

$$\therefore 1 + (-3) + a = 0$$

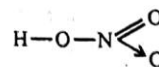
$$\therefore a = +2$$

- (i)
- HNO_3
- : By rules

$$1 + a + 3 \times (-2) = 0$$

$$\therefore a = +5$$

By fundamental approach



$$\text{Ox. no. of H} = +1$$

$$\text{Ox. no. of N} = +1 + (+2) + (+2) = +5$$

Covalent bond with O Two covalent bond with O Co-ordinate bond

$\therefore$ N being less electronegative than O.

(j) KO_2 : A super oxide of K; (MLNR 1988)

Ox. no. of K = +1

Ox. no. of O = a

$$1 + 2 \times a = 0$$

$$\therefore a = -\frac{1}{2}$$

(k) Fe_3O_4 : $3 \times a + 4 \times (-2) = 0$

$$\therefore a = +\frac{8}{3}$$

or Fe_3O_4 is a mixed oxide of $\text{FeO} \cdot \text{Fe}_2\text{O}_3$

$\therefore$ Fe has two oxidation no. +2 and +3 separately. However, factually speaking ox. no. of Fe in Fe_3O_4 is an average of two values (i.e., +2 and +3)

$$\text{Average ox. no.} = \frac{+2 + 2 \times (+3)}{3} = +\frac{8}{3}$$

(l) KI_3 : $1 + 3 \times (a) = 0$

$$a = -\frac{1}{3}$$

or KI_3 is $\text{KI} + \text{I}_2$

$\therefore$ I has two oxidation no. -1 and 0 respectively. However, factually speaking ox. no. of I in KI_3 is an average of two values -1 and 0.

$$\text{Average Ox. no.} = \frac{-1 + 2 \times (0)}{3} = -\frac{1}{3}$$

(m) OCN^- : $\text{O}=\text{C} \equiv \text{N}$

$$a + 4 - 3 = -1 \quad (\text{Follow covalent rules})$$

$$\therefore a = -2$$

(n) $\text{Fe}(\text{CO})_5$: Sum of ox. no. of CO = 0

$$\therefore a + 5 \times (0) = 0$$

$$\therefore a = 0$$

(o) $\text{Fe}_{0.94}\text{O}$: $0.94 \times a + (-2) = 0$

$$a = \frac{200}{94}$$

(p) $\text{NH}_2 \cdot \text{NH}_2$: Both N have same nature.

$$a + 2 + a + 2 = 0$$

$$\therefore a = -2$$

(q) $\text{FeSO}_4 \cdot (\text{NH}_4)_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$: Ox. no. of Fe = a

$$\text{Sum of ox. no. for } (\text{NH}_4)_2\text{SO}_4 = 0$$

$$\text{Sum of ox. no. for } \text{H}_2\text{O} = 0$$

$$\text{Sum of ox. no. for } \text{SO}_4^{2-} = -2$$

$$\therefore a + (-2) + 0 + 6 \times (0) = 0$$

$$\therefore a = +2$$

(r) NOCl : $\text{Cl}-\text{N}=\text{O}$ or use NO^+Cl^-

$$\text{Ox. no. of N} = +1 \quad (\text{for covalent bond with Cl})$$

$$\text{Ox. no. of N} = +2 \quad (\text{for two covalent bonds with O})$$

$$\therefore \text{Total ox. no. of N in NOCl} = +3$$

(s) NOClO_4 : The compound may be written as $\text{NO}^+\text{ClO}_4^-$ for ClO_4^- .

$$\text{For } \text{ClO}_4^-, \text{ let Ox. no. of Cl} = a$$

$$a + 4 \times (-2) = -1$$

$$a = +7$$

(t) $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$: NO in iron complex has NO^+ nature.

$$\therefore 2 \times 1 + [a + 5 \times (-1) + (+1)] = 0$$

$$\therefore a = +2$$

(u) $[\text{Fe}(\text{NO})(\text{H}_2\text{O})_5]\text{SO}_4$:

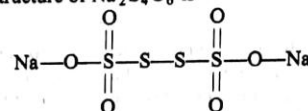
$$a + 1 + 5 \times 0 + (-2) = 0$$

$$a = +1$$

(v) $\text{Na}_2\text{S}_4\text{O}_6$: $2 \times (+1) + 4a + 6 \times (-2) = 0$

$$\therefore a = +\frac{5}{2}$$

Here also this value is the average oxidation no. of S.

The structure of $\text{Na}_2\text{S}_4\text{O}_6$ is

Thus, ox. no. of each S-atom forming double bond is +5 whereas, ox. no. of each S-atom involved in pure covalent bonding is zero.

$$\therefore \text{Average ox. no.} = \frac{+5 + 5 + 0 + 0}{4} = +\frac{5}{2}$$

(w) Dimethyl sulphoxide or $(\text{CH}_3)_2\text{SO}$:

$$\text{Ox. no. of CH}_3 = +1; \quad \text{Ox. no. of O} = -2$$

$$\therefore 2 \times (+1) + a + (-2) = 0$$

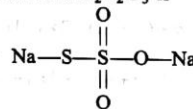
$$a = 0$$

(x) $\text{Na}_2\text{S}_2\text{O}_3$:

$$2 \times 1 + 2 \times a + 3 \times (-2) = 0$$

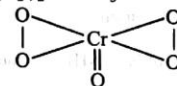
$$\therefore a = +2$$

Here too it is the average ox. no.

The structure of $\text{Na}_2\text{S}_2\text{O}_3$ is

The ox. no. of S involved in double bond is +5.

The ox. no. of other S-atom is -1

(y) CrO_5 or $\text{CrO}(\text{O}_2)_2$: CrO_5 has butterfly structure as:

i.e., two peroxide bonds and thus four oxygen atoms

have ox. no. = -1 and one oxygen atom has ox. no. -2

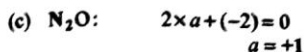
$$\text{Thus, } a + 4 \times (-1) + 1 \times (-2) = 0 \quad \therefore a = +6$$

(z) CaOCl_2 : In bleaching powder two Cl-atoms are as $\text{Ca}(\text{OCl})\text{Cl}$, i.e., one as Cl^- having ox. no. -1 and other as OCl^- having ox. no. +1.2. (a) CuH : $a + 1 = 0$

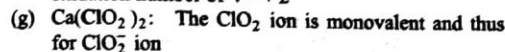
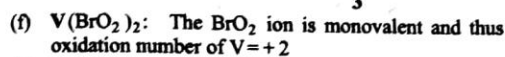
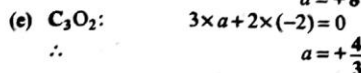
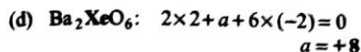
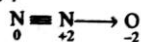
$$\therefore a = -1 \quad (\because \text{H in CuH has } +1 \text{ oxidation number})$$

(b) $\text{Na}_2\text{S}_3\text{O}_6$: $2 \times 1 + 3 \times a + 6 \times (-2) = 0$

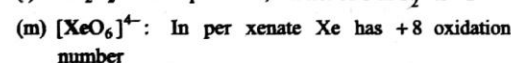
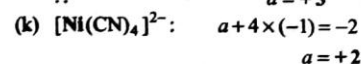
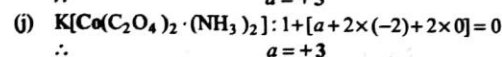
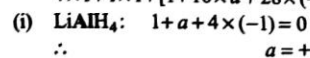
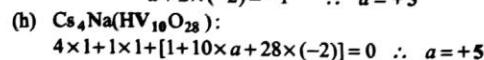
$$\therefore a = +\frac{10}{3}$$



Although it is average of two oxidation numbers as shown below:



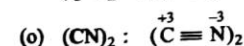
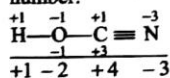
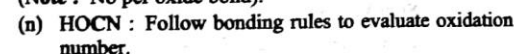
$$a + 2 \times (-2) = -1 \quad \therefore a = +3$$



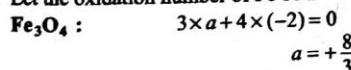
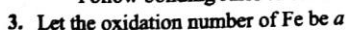
$$a + 6 \times (-2) = -4$$

$$a = +8$$

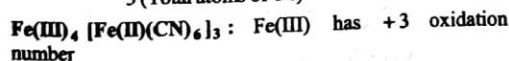
(Note: No per oxide bond).



Follow bonding rules to evaluate oxidation number.



Actually this is average oxidation number of Fe in Fe_3O_4 . It exist in $\text{FeO} \cdot \text{Fe}_2\text{O}_3$ having oxidation number of Fe +2 in FeO and +3 in Fe_2O_3 . Thus, average oxidation number

$$= \frac{2 \times \text{atom of Fe (in FeO)} + 3 \times 2 \text{ atoms of Fe (in Fe}_2\text{O}_3)}{3 \text{ (Total atoms of Fe)}} = +\frac{8}{3}$$


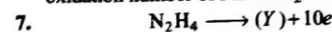
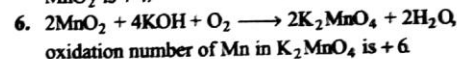
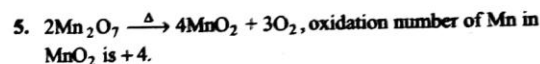
Also, average oxidation number

$$= \frac{4 \times (+3) + 3 \times (+2)}{7} = +\frac{18}{7}$$

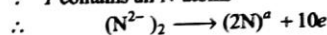


$$(-1) + 8 + (-n) = +2$$

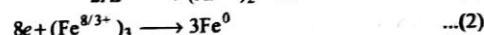
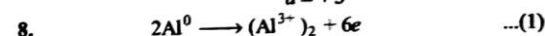
$$n = 5$$



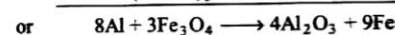
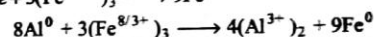
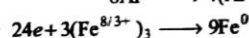
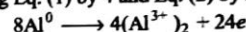
$\therefore$ Y contains all N-atoms



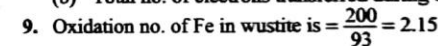
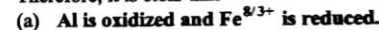
Therefore, $2a - (-4) = 10$
 $a = +3$



Multiplying Eq. (1) by 4 and Eq. (2) by 3, then adding



Therefore, it is clear that

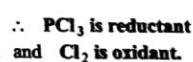
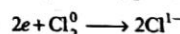
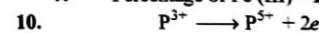
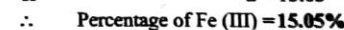


It is an intermediate value in between two oxidation state of Fe as, Fe (II) and (III).

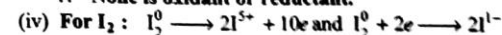
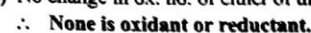
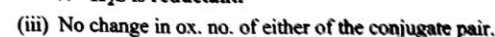
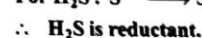
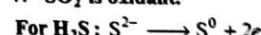
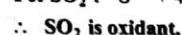
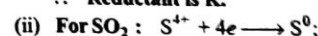
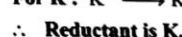
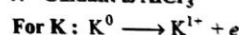
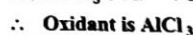
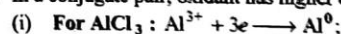
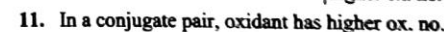
Let percentage of Fe (III) be a , then

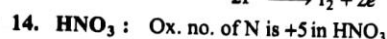
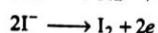
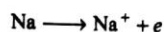
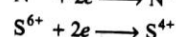
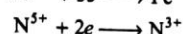
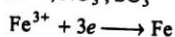
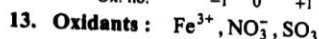
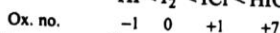
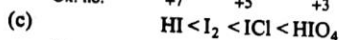
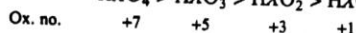
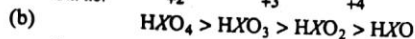
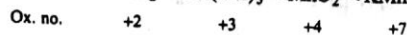
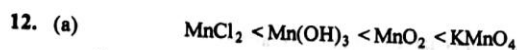
$$2 \times (100 - a) + 3 \times a = 2.15 \times 100$$

or $a = 15.05$



$\therefore$ In a conjugate pair of redox the one having higher ox. no. is oxidant.

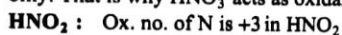




Maximum ox. no. of N is +5

Minimum ox. no. of N is -3

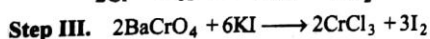
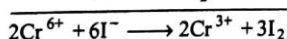
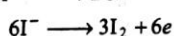
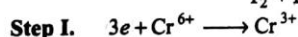
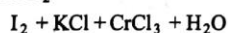
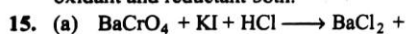
Thus, ox. no. of N in HNO_3 is maximum and it can decrease only. That is why HNO_3 acts as oxidant only.



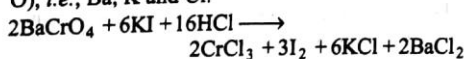
Maximum ox. no. of N is +5

Minimum ox. no. of N is -3

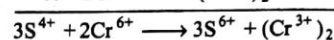
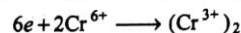
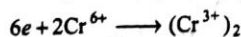
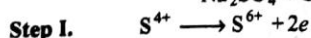
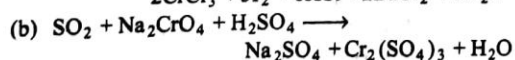
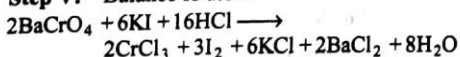
Thus, ox. no. of N (in HNO_2) can show an increase or decrease as the case may be. That is why HNO_2 acts as oxidant and reductant both.



Step IV. Balancing of other atoms except (H and O), i.e., Ba, K and Cl.

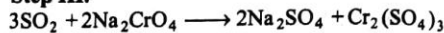


Step V. Balance H-atom

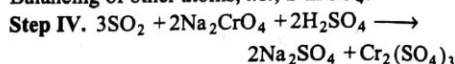


Three S^{6+} atoms are distributed in $2\text{Na}_2\text{SO}_4$ and $1\text{Cr}_2(\text{SO}_4)_3$

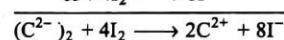
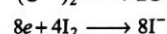
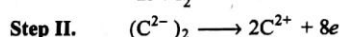
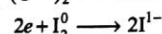
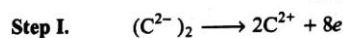
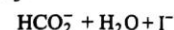
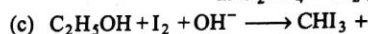
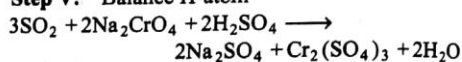
Step III.



Balancing of other atoms, i.e., S in SO_4 .

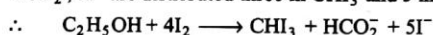


Step V. Balance H-atom



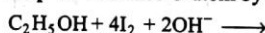
Step III. 2C^{2+} are distributed one each in CHI_3 and

HCO_2^- , 8I^- are distributed three in CHI_3 and 5 in I^-

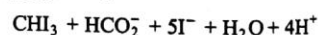
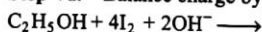


Step IV. Balancing other atoms no need since no other (except H and O) atoms are unbalanced.

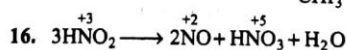
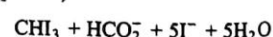
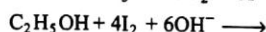
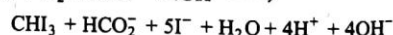
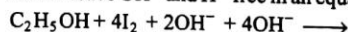
Step V. Balance O-atom by OH^- and H_2O



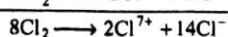
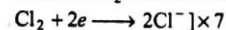
Step VI. Balance charge by H^+



Do not leave OH^- and H^+ free in an equation and thus,



17. Cl_2 can undergo only in Cl^- state to show loss of electron. Since loss and gain of 14 electrons occurs between Cl_2 and thus 7 mole show oxidation.



● SINGLE INTEGER ANSWER PROBLEMS ●

- The positive oxidation no. of Xe in perxenate ion is:
- The value of n in the reaction :

$$\text{Cr}_2\text{O}_7^{2-} + ne + 14\text{H}^+ \longrightarrow 2\text{Cr}^{3+} + 7\text{H}_2\text{O}$$
- Total number of electrons involved in change:

$$2\text{Al} + \text{Fe}_2\text{O}_3 \longrightarrow \text{Al}_2\text{O}_3 + 2\text{Fe}$$
- If four mole of Br_2 undergo a loss and gain of six mole electrons to form two new oxidation state of Br. How much Br_2 mole acts as reductant?
- The total number of electrons involved in redox change:

$$3\text{Fe} + 4\text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$$
- The stoichiometric coefficient n in the reaction is:

$$n\text{H}_2\text{CO}_2 + 2\text{KMnO}_4 \longrightarrow n\text{CO}_2 + \text{K}_2\text{O} + \text{MnO} + \text{H}_2\text{O}$$
- Intramolecular redox

$$(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \longrightarrow \text{N}_2 + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O}$$
 shows a loss and gain of how much electron?
- The stoichiometric coefficient of blue perchromate in its reaction with H_2SO_4 is
- The tailing of mercury on exposure to air shows a change in oxidation number by
- Total number of electrons involved per molecule oxidation of FeC_2O_4 to Fe^{3+} and CO_2 .
- No. of peroxide bonds in blue perchromate is
- In the reaction $\text{P}_4 + \text{NaOH} \longrightarrow \text{PH}_3 + \text{NaH}_2\text{PO}_2$, mole ratio of NaH_2PO_2 and PH_3 is
- In the reaction : $\text{Mn}^{2+} + \text{S}_2\text{O}_8^{2-} \longrightarrow \text{SO}_4^{2-} + \text{MnO}_4^-$ (acid med.) the number of mole of $\text{S}_2\text{O}_8^{2-}$ required to oxidise 2 mole Mn^{2+} .
- The ratio of oxygen atom having -2 and -1 oxidation numbers in $\text{S}_2\text{O}_8^{2-}$ is
- Five mole of Ferric oxalate are oxidised by how much mole of KMnO_4 in acid medium?
- 1 mole of Cu_2S reduces how many mole of KMnO_4 ? If the redox reaction is

$$\text{Cu}_2\text{S} + \text{KMnO}_4 + \text{H}_2\text{SO}_4 \longrightarrow \text{CuSO}_4 + \text{MnSO}_4 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O}$$
- Number of electrons lost per molecule of Fe_3O_4 during its oxidation to Fe_2O_3 is
- Number of H_2O_2 mole needed to convert two mole of $\text{Cr}(\text{OH})_3$ in alkaline medium into sodium chromate are
- Number of mole of KO_2 required to absorb one mole of CO are
- Six mole of I_2 undergoes disproportionation involving 10 electrons, what is the oxidation number of oxidised iodine atom?
- The ratio of oxidation numbers of carbon in hydrocyanic acid and isocyanic acid is:
- Oxidation number of Xe in Barium perxenate is:
- The number of electrons involved in the change :

$$\text{Cu}_2\text{S} \longrightarrow \text{Cu}^{2+} + \text{SO}_2$$
 is:
- On heating FeCr_2O_4 with Na_2CO_3 in presence of KClO_3 , the total number of electrons lost by one Cr atom are:
- The oxidation number of Cr in the product formed on heating $\text{K}_2\text{Cr}_2\text{O}_7$ with KOH is:
- On combustion of CH_4 to CO_2 and H_2O , the oxidation number of carbon changes by:
- Oxidation no. of carbon in NaCNS is:
- On passing NO to $\text{FeSO}_4(\text{aq})$ brown ring formation takes place, the oxidation number of Fe changes by:
- The most common oxidation state of an element is -2 . The number of electrons present in its outer most shell is:
- The difference in oxidation number of two nitrogen atoms in NH_4NO_3 is
- The difference in oxidation number of Cl atoms in CaOCl_2 is
- How much of the following have per oxide bonds? Blue per chromate, Barium per xenate, Barium per oxide, H_2SO_5 , PbO_2 , $\text{H}_2\text{S}_2\text{O}_8$, Permanganic acid, Perchloric acid.
- The sum of the oxidation numbers of two different oxidation states of Fe atoms in Fe_3O_4 is
- Number of electrons involved in the redox change : $2\text{Fe} + \text{O}_2 + 4\text{H}^+ \longrightarrow 2\text{Fe}^{2+} + 2\text{H}_2\text{O}$, are
- Oxidation number of Na in Na-Hg amalgam is
- In the reaction, $\text{VO} + \text{Fe}_2\text{O}_3 \longrightarrow \text{FeO} + \text{V}_2\text{O}_5$, the number of electrons used in redox reaction are
- Number of O—O bonds in K_3CrO_8 is
- 4 mole of Cl_2 undergoes disproportionation involving six electrons in change. How much Cl_2 molecules are oxidised?
- Number of pi bonds in Br_3O_8 are
- Among the following, the number of elements showing only one non zero oxidation state is (IIT 2010)
O, Cl, F, N, P, Sn, Tl, Na, Ti
- The value of n in the molecular formula $\text{Be}_n\text{Al}_2\text{Si}_6\text{O}_{18}$ is (IIT 2010)
- The difference in the oxidation number of the two types of sulphur atoms in $\text{Na}_2\text{S}_4\text{O}_6$ is (IIT 2011)

ANSWERS

- | | | | | | | | | | | | |
|----------|-----------|-----------|---------|-----------|-----------|---------|----------|----------|-----------|-----------|-----------|
| 1. Eight | 2. Six | 3. Six | 4. One | 5. Eight | 6. Five | 7. Six | 8. Four | 9. One | 10. Three | 11. Two | 12. Three |
| 13. Five | 14. Three | 15. Six | 16. Two | 17. One | 18. Three | 19. Two | 20. Five | 21. One | 22. Eight | 23. Eight | 24. Zero |
| 25. Six | 26. Eight | 27. Four | 28. One | 29. Six | 30. Eight | 31. Two | 32. Four | 33. Five | 34. Four | 35. Zero | 36. Six |
| 37. Four | 38. One | 39. Eight | 40. Two | 41. Three | 42. Five | | | | | | |

OBJECTIVE PROBLEMS (One Answer Correct)

- In which of the following highest oxidation state is not possible:
 - $[\text{XeO}_6]^{4-}$
 - XeF_8
 - OsO_4
 - RuO_4
- Number of per oxide bonds in per xenate ion $[\text{XeO}_6]^{4-}$ is:
 - 0
 - 2
 - 3
 - 1
- Oxidation number of Pr in Pr_6O_{11} is:
 - $\frac{22}{6}$
 - $\frac{20}{6}$
 - 3
 - 4
- Oxidation number of S in H_2SO_5 is:
 - +8
 - +6
 - +4
 - +2
- Which one is not correct about the change given below?

$$\text{K}_4\text{Fe}(\text{CN})_6 \xrightarrow{\text{oxi}} \text{Fe}^{3+} + \text{CO}_2 + \text{NO}_3^-$$
 - Fe is oxidised Fe^{2+} to Fe^{3+}
 - Carbon is oxidised from C^{2+} to C^{4+}
 - N is oxidised from N^{3-} to N^{5+}
 - Carbon is not oxidised
- Which of the following is not a intramolecular redox?
 - $\text{NH}_4\text{NO}_2 \longrightarrow \text{N}_2 + 2\text{H}_2\text{O}$
 - $2\text{Mn}_2\text{O}_7 \longrightarrow 4\text{MnO}_2 + 3\text{O}_2$
 - $2\text{KClO}_3 \longrightarrow 2\text{KCl} + 3\text{O}_2$
 - $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$
- Which of the following is not disproportionation?
 - $\text{P}_4 + 5\text{OH}^- \longrightarrow \text{H}_2\text{PO}_4^- + \text{PH}_3$
 - $\text{Cl}_2 + \text{OH}^- \longrightarrow \text{ClO}^- + \text{ClO}_2^-$
 - $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$
 - $\text{PbO}_2 + \text{H}_2\text{O} \longrightarrow \text{PbO} + \text{H}_2\text{O}_2$
- Which of the following is intermolecular redox reaction?
 - $$\begin{array}{c} \text{CHO} \\ | \\ \text{CHO} \end{array} \xrightarrow{\text{OH}^-} \begin{array}{c} \text{CH}_2\text{OH} \\ | \\ \text{COOH} \end{array}$$
 - $2\text{C}_6\text{H}_5\text{CHO} \xrightarrow{\text{Al}(\text{OC}_2\text{H}_5)_3} \text{C}_6\text{H}_5\text{COOH} + \text{C}_6\text{H}_5\text{CH}_2\text{OH}$
 - $4\text{CrO}_3 + 6\text{H}_2\text{SO}_4 \longrightarrow 2\text{Cr}_2(\text{SO}_4)_3 + 6\text{H}_2\text{O} + 7\text{O}_2$
 - $\text{As}_2\text{S}_3 + \text{HNO}_3 \longrightarrow \text{H}_3\text{AsO}_4 + \text{H}_2\text{SO}_4 + \text{NO}$
- The number of electrons lost in the change are:

$$\text{Fe} + \text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + \text{H}_2$$
 - 2
 - 4
 - 6
 - 8
- The oxidation state of A, B and C in a compound are +2, +5 and -2 respectively. The compound is:
 - $\text{A}_2(\text{BC})_2$
 - $\text{A}_2(\text{BC})_3$
 - $\text{A}_3(\text{BC}_4)_2$
 - $\text{A}_2(\text{BC}_4)_3$
- In the equation : $\text{NO}_2^- + \text{H}_2\text{O} \longrightarrow \text{NO}_3^- + 2\text{H}^+ + ne$, n stands for:
 - 1
 - 2
 - 3
 - 4
- The oxidation number of sulphur in S_8 , S_2F_2 and H_2S are:
 - 0, +1 and -2
 - +2, +1 and -2
 - 0, +1 and +2
 - 2, +1 and -2
- In a reaction, 4 mole of electrons are transferred to 1 mole of HNO_3 , the possible product obtained due to reduction is:
 - 0.5 mole of N_2
 - 0.5 mole of N_2O
 - 1 mole of NO_2
 - 1 mole of NH_3
- The colour of $\text{K}_2\text{Cr}_2\text{O}_7$ changes from red-orange to lemon-yellow on treatment with $\text{KOH}(\text{aq.})$ because of:
 - Reduction of Cr (VI) to Cr (III)
 - Formation of chromium hydroxide
 - Conversion of dichromate into chromate ion
 - Oxidation of potassium hydroxide to potassium peroxide
- During developing of an exposed camera film, one step involves in the following reaction,

$$\text{HO} \text{---} \text{C}_6\text{H}_4 \text{---} \text{OH} + 2\text{AgBr} + 2\text{OH}^- \longrightarrow \text{O} \text{---} \text{C}_6\text{H}_4 \text{---} \text{O} + 2\text{Ag} + 2\text{H}_2\text{O} + 2\text{Br}^-$$

(Hydroquinol)

 which of the following best describes the role of hydroquinol :
 - It acts as an acid
 - It act as reducing agent
 - It acts as oxidant
 - It act as a base
- Which of the following is not correct for the reaction,

$$(\text{CN})_2 + 2\text{OH}^- \longrightarrow \text{CNO}^- + \text{CN}^- + \text{H}_2\text{O}$$
 - It is a disproportionation reaction
 - N atom disproportionates and oxidation number of N are -3 in $(\text{CN})_2$, -2 in CN^- and -5 in CNO^-
 - C atom disproportionate and oxidation number carbon are +3 in $(\text{CN})_2$, +4 in CNO^- and +2 in CN^-
 - $(\text{CN})_2$ undergoes auto redox
- One mole of N_2H_4 loses 10 mole of electrons to form a new compound y. Assuming that all the nitrogen appears in the new compound, what is the oxidation state of N in y. (There is no change in the oxidation state of H.)
 - 1
 - 3
 - +3
 - +5
- The oxidation number of carbon in CH_2O is :
 - 2
 - +2
 - 0
 - +4

19. The brown ring complex is formulated as $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]\text{SO}_4$. The oxidation number of Fe is :
 (a) +1 (b) +2
 (c) +3 (d) 0
20. The oxidation number of phosphorus in $\text{Ba}(\text{H}_2\text{PO}_2)_2$ is :
 (a) +3 (b) +2
 (c) +1 (d) -1
21. The oxidation state of the most electronegative element in the products of the reaction, BaO_2 with dil H_2SO_4 are :
 (a) 0 and -1 (b) -1 and -2
 (c) -2 and 0 (d) -2 and +1
22. For the redox reaction,

$$\text{MnO}_4^- + \text{C}_2\text{O}_4^{2-} + \text{H}^+ \longrightarrow \text{Mn}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$$
 The correct coefficients of the reactants for the balanced reaction are :

MnO_4^-	$\text{C}_2\text{O}_4^{2-}$	H^+
(a) 2	5	16
(b) 16	5	2
(c) 5	16	2
(d) 2	16	5
23. Oxidation number of carbon in C_3O_2 and Mg_2C_3 are respectively:
 (a) $+\frac{2}{3}, -\frac{2}{3}$ (b) $+\frac{4}{3}, -\frac{4}{3}$
 (c) $-\frac{4}{3}, +\frac{4}{3}$ (d) $-\frac{2}{3}, +\frac{2}{3}$
24. In the reaction : $\text{NaH} + \text{H}_2\text{O} \longrightarrow \text{NaOH} + \text{H}_2$, which one is not correct :
 (a) H-atom undergoes oxidation
 (b) H-atom undergoes reduction
 (c) It is a redox change
 (d) It is disproportionation reaction
25. Ozone tails mercury due to :
 (a) oxidation of Hg
 (b) reduction of Hg
 (c) adsorption of O_3 on Hg
 (d) none of these
26. The tailing of mercury is removed by :
 (a) O_2 (b) H_2O_2
 (c) SO_2 (d) O_3
27. Iodine has +7 oxidation state in :
 (a) HIO_4 (b) H_3IO_5
 (c) H_5IO_6 (d) all of these
28. Which of the following compound is not possible for +7 oxidation state of iodine ?
 (a) IF_7 (b) I_2O_7
 (c) ICl_7 (d) None of these
29. Amongst the following identify the species with an atom in +6 oxidation state: (IIT 2000)
 (a) MnO_4^- (b) $\text{Cr}(\text{CN})_6^{3-}$
 (c) NiF_6^{2-} (d) CrO_2Cl_2
30. In the standardisation of $\text{Na}_2\text{S}_2\text{O}_3$ using $\text{K}_2\text{Cr}_2\text{O}_7$ by iodometry, the equivalent mass of $\text{K}_2\text{Cr}_2\text{O}_7$ is: (IIT 2001)
 (a) $M/2$ (b) $M/6$
 (c) $M/3$ (d) M
31. The reaction;

$$3\text{ClO}^- (\text{aq.}) \longrightarrow \text{ClO}_3^- (\text{aq.}) + 2\text{Cl}^- (\text{aq.})$$
 is an example of: (IIT 2001)
 (a) oxidation reaction (b) reduction reaction
 (c) disproportion (d) decomposition
32. Maximum oxidation state is present in: (IIT 2004)
 (a) CrO_2Cl_2 and MnO_4^-
 (b) MnO_2
 (c) $[\text{Fe}(\text{CN})_6]^{3-}$ and $[\text{Co}(\text{CN})_6]^{3-}$
 (d) MnO
33. The reaction of white phosphorus with aqueous NaOH gives phosphine along with another phosphorus containing compound. The reaction type; the oxidation states of phosphorus in phosphine and the other product are respectively : (IIT 2012)
 (a) redox reaction; -3 and -5
 (b) redox reaction; +3 and +5
 (c) disproportionation reaction; -3 and +1
 (d) disproportionation reaction; -3 and +3
34. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen? (IIT 2012)
 (a) $\text{HNO}_3, \text{NO}, \text{NH}_4\text{Cl}, \text{N}_2$
 (b) $\text{HNO}_3, \text{NO}, \text{N}_2, \text{NH}_4\text{Cl}$
 (c) $\text{HNO}_3, \text{NH}_4\text{Cl}, \text{NO}, \text{N}_2$
 (d) $\text{NO}, \text{HNO}_3, \text{NH}_4\text{Cl}, \text{N}_2$
35. Consider the following reaction :

$$x\text{MnO}_4^- + y\text{C}_2\text{O}_4^{2-} + z\text{H}^+ \longrightarrow x\text{Mn}^{2+} + 2y\text{CO}_2 + \frac{z}{2}\text{H}_2\text{O}$$
 The values of x, y and z in the reaction are, respectively : (JEE (Main) 2013)
 (a) 2, 5 and 16 (b) 5, 2 and 8
 (c) 5, 2 and 16 (d) 2, 5 and 8
36. Experimentally it was found that a metal oxide has formula $\text{M}_{0.98}\text{O}$. Metal M, is present as M^{2+} and M^{3+} in its oxide. Fraction of the metal which exists as M^{3+} would be : (JEE (Main) 2013)
 (a) 6.05% (b) 5.08%
 (c) 7.01% (d) 4.08%

SOLUTIONS (One Answer Correct)

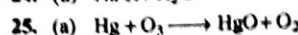
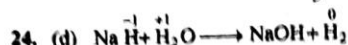
1. (b) No doubt Xe shows +8 oxidation state XeF_8 does not exist because of crowding of 8 F-atoms.
2. (a) Oxidation no. of Xe in $[\text{XeO}_6]^{4-}$ is +8
3. (a) Pr_6O_{11} , $6 \times a + (11 \times -2) = 0$ (No O—O bond),
 $a = +\frac{22}{6}$
4. (b) H_2SO_5 is $\text{HO}-\overset{\text{O}}{\underset{\text{O}}{\parallel}}\text{S}-\text{O}-\text{O}-\text{H}$
i.e., one peroxide bond.
5. (d) Carbon is also oxidised.
6. (d) Intramolecular redox change involve oxidation of one atom and reduction of other atom within a molecule.
7. (d) Disproportionation involves oxidation reduction of same atom in a molecule.
8. (d) Intermolecular redox change involves oxidation of one molecule and reduction of other molecule.
9. (d) $3\text{Fe}^0 + 8e^- \longrightarrow (\text{Fe}^{+8/3})_3$
 $[(\text{H}^+) \longrightarrow (\text{H}^0)_2 + 2e^-] \times 4$
 $3\text{Fe} + 4\text{H}_2\text{O} \longrightarrow \text{Fe}_3\text{O}_4 + 4\text{H}_2$
10. (c) $\text{A}_3(\text{BC}_4)_2$, $3 \times 2 + [5 + 4 \times (-2)] \times 2 = 0$
11. (b) Balance charge on two sides.
12. (a) $\text{S}_8 : a \times 8 = 0 \quad \therefore a = 0$
 $\text{S}_2\text{F}_2 : a \times 2 + 2 \times (-1) = 0 \quad \therefore a = +1$
 $\text{H}_2\text{S} : 2 \times 1 + a = 0 \quad \therefore a = -2$
13. (b) $2\text{N}^{5+} \longrightarrow (\text{N}^+)_2 + 8e^-$
 2 mole HNO_3 gives one mole of N_2O .
14. (c) $\text{K}_2\text{Cr}_2\text{O}_7 + 2\text{KOH} \longrightarrow 2\text{K}_2\text{CrO}_4 + \text{H}_2\text{O}$
15. (b) $\text{Ag}^+ + e^- \longrightarrow \text{Ag}$; hydroquinol reduces Ag^+ to Ag
16. (b) Rest all are true
17. (c) $(\text{N}^{2-})_2 \longrightarrow (\text{N}^{+a})_2 + 10e^-$
 $\therefore 2a - (-4) = 10$
 $a = +3$
18. (c) $a + 2 \times (+1) - 2 \times 1 = 0$
19. (a) NO in iron complex has +1 oxidation state.
20. (c) $2 \times 1 + 2[2 \times 1 + a + 2 \times (-2)] = 0$
 $\therefore a = +1$
21. (b) Products are BaSO_4 and H_2C_2 .
22. (a) $2\text{MnO}_4^- + 5\text{C}_2\text{O}_4^{2-} + 16\text{H}^+ \longrightarrow 2\text{Mn}^{2+} + 10\text{CO}_2 + 8\text{H}_2\text{O}$

$$23. (b) \text{C}_3\text{O}_2 : 3 \times a + 2(-2) = 0$$

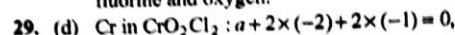
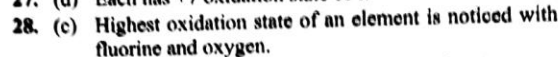
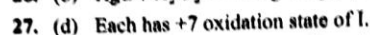
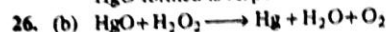
$$a = +\frac{4}{3}$$

$$\text{Mg}_2\text{C}_3 : 2 \times 2 + 3 \times a = 0$$

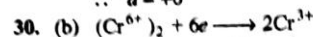
$$a = -\frac{4}{3}$$



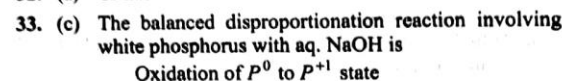
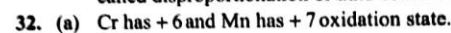
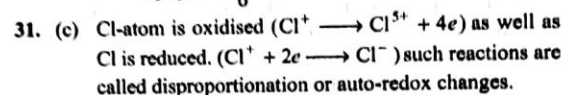
HgO formed is responsible for talling



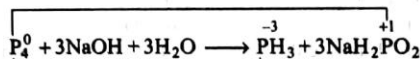
$$\therefore a = +6$$



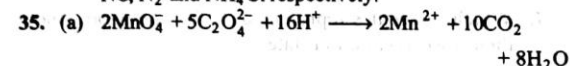
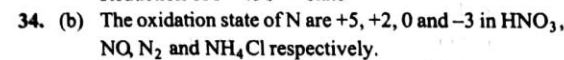
$$\therefore E_{\text{K}_2\text{Cr}_2\text{O}_7} = \frac{M}{6}$$



Oxidation of P^0 to P^{+1} state



Reduction of P^0 to P^{-3} state



(lies between 2 and 3)

Let % of M^{2+} be a and of M^{3+} be b

$$\text{or } \frac{2 \times a + (100 - a) \times 3}{100} = 2.04 (\because a + b = 100)$$

$$\therefore 2a + 300 - 3a = \frac{200}{98}$$

$$\therefore +a = 300 - 2.04 \times 100$$

$$= 300 - 204$$

$$= 96$$

$$\text{Thus } M^{2+} = 96\%$$

$$M^{3+} = 4\%$$

OBJECTIVE PROBLEMS (More Than One Answer Correct)

- Which of the following are disproportionation redox changes?
 - $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \longrightarrow \text{N}_2 + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O}$
 - $5\text{H}_2\text{O}_2 + 2\text{ClO}_2 + 2\text{OH}^- \longrightarrow 2\text{Cl}^- + 5\text{O}_2 + 6\text{H}_2\text{O}$
 - $3\text{ClO}^- \longrightarrow \text{ClO}_3^- + \text{Cl}^-$
 - $2\text{HCuCl}_2 \xrightarrow[\text{water}]{\text{Dilution with}} \text{Cu} + \text{Cu}^{2+} + 4\text{Cl}^- + 2\text{H}^+$
- Which one are correct about the reaction?

$$\text{HgS} + \text{HCl} + \text{HNO}_3 \longrightarrow \text{H}_2\text{HgCl}_4 + \text{NO} + \text{S} + \text{H}_2\text{O}$$
 - Hg is reduced
 - Sulphide is oxidised
 - N is reduced
 - HNO_3 is oxidant
- Which of the followings are disproportionation reactions?
 - $2\text{O}_3 \longrightarrow 3\text{O}_2$
 - $4\text{KClO}_3 \longrightarrow 3\text{KClO}_4 + \text{KCl}$
 - $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$
 - $2\text{KO}_2 + 2\text{H}_2\text{O} \longrightarrow 4\text{KOH} + 3\text{O}_2$
- For the reaction,

$$\text{KO}_2 + \text{H}_2\text{O} + \text{CO}_2 \longrightarrow \text{KHCO}_3 + \text{O}_2$$
 the mechanism of reaction suggests that:
 - acid-base reaction
 - disproportionation reaction
 - hydrolysis
 - redox change
- Which of the following can be used as oxidant and reductant both?
 - HNO_2
 - SO_2
 - O_2
 - CO
- Which molecules represented by the bold atoms show their highest oxidation state?
 - $\text{H}_2\text{S}_2\text{O}_8$
 - P_4O_{10}
 - F_2O
 - Mn_2O_7
- Which molecules represented by the bold atoms show their lowest oxidation state?
 - F_2O
 - H_2S
 - PH_3
 - N_2H_4
- Which one are not correct about $\text{CH}_2 = \text{CCl}_2$?
 - Both carbon are in +2 oxidation state
 - Both carbon are in -2 oxidation state
 - One carbon has +2 and other has -2 oxidation state
 - The average oxidation number of carbon is zero
- Which is correct about tailing of Hg?
 - it is due to Hg_2O
 - it is due to HgO
 - it is removed by H_2O_2
 - it is removed by O_3
- Thermal decomposition of $(\text{NH}_4)_2\text{Cr}_2\text{O}_7$ involves :
 - Oxidation of N
 - Reduction of Cr
 - Intramolecular redox
 - Disproportionation
- LiAlH_4 is used as :
 - an oxidant
 - a reductant
 - a mordant
 - water softner
- Which of the following are disproportionation reaction :
 - $\text{F}_2 + \text{H}_2\text{O} \longrightarrow \text{HOF} + \text{HF}$
 - $2\text{HCHO} + \text{NaOH} \longrightarrow \text{HCOONa} + \text{CH}_3\text{OH}$
 - $\text{P}_{4(s)} + 3\text{NaOH} + 3\text{H}_2\text{O} \longrightarrow \text{PH}_3 + 3\text{NaH}_2\text{PO}_2$
 - $2\text{NO}_2 + 2\text{KOH} \longrightarrow \text{KNO}_2 + \text{KNO}_3 + \text{H}_2\text{O}$
- In which of the following oxidation no. of nitrogen atom is correctly matched :

(a) HCN	-3
(b) HNC	-3
(c) HOCN	-3
(d) $(\text{CN})_2$	-2
- Select the correct statements :
 - Oxidation number of oxygen in O_2^+ is $+\frac{1}{2}$
 - Oxidation number of oxygen in O_2^- is $-\frac{1}{2}$
 - Oxidation number of Cr in K_3CrO_8 is +5
 - Average oxidation number of Br in tribromooxide (Br_3O_8) is $+\frac{18}{3}$

SOLUTIONS (More Than One Answer Correct)

- (c,d) $e + \text{Cl}^+ \longrightarrow \text{Cl}^-$ $\text{Cu}^+ \longrightarrow \text{Cu}^{2+} + e$
 $\text{Cl}^+ \longrightarrow \text{Cl}^{5+} + 4e$ $\text{Cu}^+ + e \longrightarrow \text{Cu}$
- (b,c,d) $\text{S}^{2-} \longrightarrow \text{S}^0 + 2e$, $3e + \text{N}^{5+} \longrightarrow \text{N}^{2+}$
- (b,c,d) $\text{Cl}^{+5} \longrightarrow \text{Cl}^{+7} + \text{Cl}^-$
 $\text{O}^- \longrightarrow \text{O}^{-2} + \text{O}_2^0$
 $\text{O}_2^{-1/2} \longrightarrow \text{O}^{-2} + \text{O}_2^0$
- (a,b,c,d) $4\text{KOH} + 2\text{H}_2\text{O} \longrightarrow 4\text{KOH} + 3\text{O}_2$
 (Hydrolysis and disproportionation)
 $4\text{KOH} + 4\text{CO}_2 \longrightarrow 4\text{KHCO}_3$ (Acid-base reaction)
- (a,b,c,d) The element (in a molecule) having its oxidation state in the middle (i.e., > minimum and < maximum) can be used as reductant and oxidant both.
- (a,b,d) The highest oxidation state is given by the gp. number (except O, F).
- (b,c) The lowest oxidation state is given by (gp. number - 8) except metals.
- (a,b) Average is zero.
- (a,c) Hg gets oxidised by O_3 to give sticking nature on glass
 $2\text{Hg} + \text{O}_3 \longrightarrow \text{Hg}_2\text{O} + \text{O}_2$
 $\text{Hg}_2\text{O} + \text{H}_2\text{O}_2 \longrightarrow \text{Hg}_2 + \text{H}_2\text{O} + \text{O}_2$
- (a,b,c) $(\text{NH}_4)_2\text{Cr}_2\text{O}_7 \longrightarrow \text{N}_2 + \text{Cr}_2\text{O}_3 + 4\text{H}_2\text{O}$
- (b) It is a fact.
- (b,c,d) $\text{F}_2 + \text{H}_2\text{O} \longrightarrow \text{HOF} + \text{HF}$
 $2\text{HCHO} + \text{NaOH} \longrightarrow \text{HCOONa} + \text{CH}_3\text{OH}$
 $\text{P}_{4(s)} + 3\text{NaOH} + 3\text{H}_2\text{O} \longrightarrow \text{PH}_3 + 3\text{NaH}_2\text{PO}_2$
 $2\text{NO}_2 + 2\text{KOH} \longrightarrow \text{KNO}_2 + \text{KNO}_3 + \text{H}_2\text{O}$
- (a,b,c) Oxidation no. of N in $(\text{CN})_2$ is -3.
- (a,b,c) In Br_3O_8 two Br atoms have +6 oxidation number and one has +4. The average oxidation no. is $+\frac{16}{3}$.

$$\begin{array}{ccccc} \text{O} & & \text{O} & & \text{O} \\ || & & || & & || \\ \text{O}=\text{Br}^{+6}- & \text{Br}^{+4}- & \text{Br}^{+6}=\text{O} \end{array}$$

COMPREHENSION BASED PROBLEMS

Comprehension 1 : In the chemical change:
 $a\text{N}_2\text{H}_4 + b\text{BrO}_3^- \longrightarrow a\text{N}_2 + b\text{Br}^- + 6\text{H}_2\text{O}$, answer the following questions:

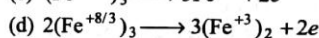
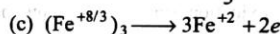
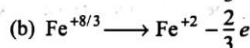
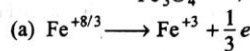
- The element oxidised and reduced in the reaction are respectively:
 (a) N_2H_4 , BrO_3^- (b) N, Br
 (c) H, Br (d) BrO_3^- , N_2H_4
- The number of electrons lost or gained during the redox change are:
 (a) 8 (b) 10
 (c) 12 (d) 6
- The equivalent mass of N_2H_4 in the above reaction is:
 (a) 8 (b) 10.6
 (c) 16 (d) 6.4
- The equivalent mass of KBrO_3 in the above reaction is:
 (a) 167 (b) 27.83
 (c) 55.67 (d) 83.5
- The values of a and b in the reaction are respectively:
 (a) 3, 2 (b) 2, 3
 (c) 4, 6 (d) 6, 4
- The species acting as oxidant and reductant respectively are:
 (a) BrO_3^- , N_2H_4 (b) N_2H_4 , BrO_3^-
 (c) N_2 , BrO_3^- (d) Br^- , N_2H_4
- The conjugate pair of oxidant-reductant is:
 (a) BrO_3^- , Br^- (b) N_2H_4 , BrO_3^-
 (c) Br^- , N_2 (d) Br^- , BrO_3^-

[8] The reaction shows:

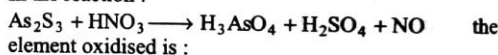
- (a) intermolecular redox (b) auto redox
 (c) intramolecular redox (d) either of these

Comprehension 2 : A redox reaction involves oxidation of reductant liberating electrons, which are then consumed by an oxidant. The sum of two half reactions give rise to net redox change. In half reaction charge and atoms are always conserved.

[1] Which of the following half reaction is correct for the redox change :



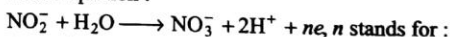
[2] In the reaction :



the element oxidised is :

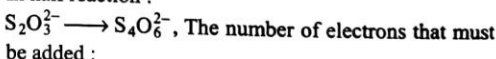
- (a) As only (b) S only
 (c) N only (d) As and S both

[3] In the equation :



- (a) 1 (b) 2
 (c) 3 (d) 4

[4] In half reaction :

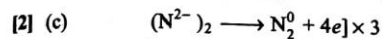
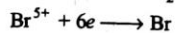
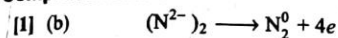


The number of electrons that must be added :

- (a) 2, on right side (b) 2, on left side
 (c) 3, on right side (d) 4, on left side

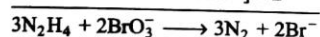
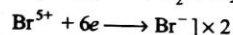
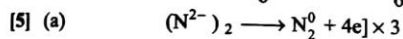
SOLUTIONS

Comprehension 1

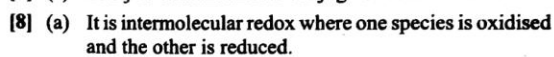
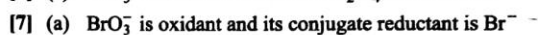
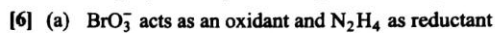
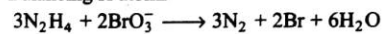


[3] (a) $E_{\text{N}_2\text{H}_4} = \frac{\text{Molar mass of N}_2\text{H}_4}{\text{No. of } e \text{ lost by 1 molecule}} = \frac{32}{4} = 8$

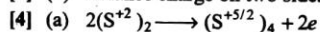
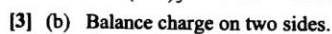
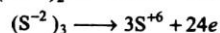
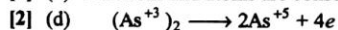
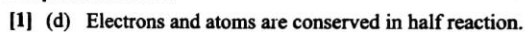
[4] (b) $E_{\text{KBrO}_3} = \frac{\text{Molar mass of KBrO}_3}{6} = \frac{167}{6} = 27.83$



Balancing H atoms



Comprehension 2



STATEMENT EXPLANATION PROBLEMS

Read the statement (S) and explanation (E) given below. Choose the correct choices (a), (b), (c) from (d) the options:

- (a) S is correct but E is wrong
 (b) S is wrong but E is correct
 (c) Both S and E are correct and E is correct explanation of S
 (d) Both S and E are correct but E is not correct explanation for S
- S** : Reaction of white phosphorus with NaOH(aq) gives PH_3 .
E : The reaction is disproportionation of P in alkaline medium.
 - S** : Na_2SO_3 solution is oxidised by air but Na_3AsO_3 not. However Na_3AsO_3 is oxidised in presence of Na_2SO_3 by air.
E : The reaction is called induced oxidation.
 - S** : Copper forms complexes $[\text{CuCl}_4]^{2-}$ but not $[\text{CuI}_4]^{2-}$.
E : $[\text{CuI}_4]^{2-}$ is not stable because Cu^{2+} is oxidant and I^- is reductant.
 - S** : The passage of H_2S through aqueous solution of SO_2 gives yellow turbidity of S in solution.
E : The yellow turbidity of S is in colloidal state due to oxidation of H_2S by SO_2 aq.
 - S** : Bleaching action of SO_2 is temporary whereas bleaching action of Cl_2 is permanent.
E : Bleaching by SO_2 and Cl_2 is due to oxidation.
 - S** : Conversion of black lead painting is made to white by the action of H_2O_2 .
E : Sulphur is oxidised to SO_4^{2-} .
 - S** : CrO_5 on decomposition undergoes disproportionation.
E : CrO_5 undergoes intermolecular redox reaction.
 - S** : NH_4NO_3 on heating gives N_2O .
E : NH_4NO_3 on heating shows disproportionation.
 - S** : In azide ion average oxidation number of N is $-1/3$.
E : In azide ion two N atoms have zero oxidation number and one has oxidation number -1 .
 - S** : $\text{K}_2[\text{CuCl}_4]$ exists but $\text{K}_2[\text{CuI}_4]$ does not exist.
E : I^- is strong oxidant.
 - S** : Oxidation number of Cu in CuH is -1 .
E : Cu is placed below H in electrochemical series.
 - S** : Oxidation state of H is $+1$ in CuH and -1 in CaH_2 .
E : Ca is strong electropositive metal.
 - S** : Oxygen atom in both O_2 and O_3 has oxidation number zero.
E : In F_2O , oxidation number of O is $+2$.
 - S** : N atom has two different oxidation states in NH_4NO_2 .
E : One N atom has $-ve$ oxidation number as it is attached with less electronegative H atom and other has $+ve$ oxidation number as it is attached with more electronegative atom.
 - S** : $2\text{H}_2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{O}_2$ is a auto redox change.
E : One oxygen atom is oxidised and one oxygen atom is reduced.
 - S** : Oxidation number of metals in metal carbonyls is zero.
E : The oxidation number of CO has been taken to be zero.
 - S** : SO_2 can be used as reductant as well as oxidant.
E : The oxidation number of S is $+4$ in SO_2 which lies in between its minimum (-2) and maximum ($+6$) values.
 - S** : KMnO_4 is strong oxidant whereas Mn^{2+} is weaker reductant.
E : Stronger is the oxidant weaker is its conjugate reductant.
 - S** : VO_2^+ and VO^{2+} both are called vanadyl ions.
E : VO_2^+ is dioxovanadium (V) ion and VO^{2+} is oxovanadium (IV) ion.
 - S** : In the reaction,

$$3\text{As}_2\text{S}_3 + 28\text{HNO}_3 + 4\text{H}_2\text{O} \longrightarrow 6\text{H}_3\text{AsO}_4 + 9\text{H}_2\text{SO}_4 + 28\text{NO}$$
electrons transferred are 84.
E : As is oxidised from $+3$ to $+5$ and sulphur from -2 to $+6$.
 - S** : If a strong acid is added to a solution of potassium chromate it changes its colour from yellow to orange.
E : The colour change is due to the oxidation of potassium chromate.

ANSWERS (Statement Explanation Problems)

1. (c) $4\text{P} + 3\text{NaOH} + 3\text{H}_2\text{O} \longrightarrow 3\text{NaH}_2\text{PO}_2 + \text{PH}_3$
2. (c) Explanation is correct reason for statement.
3. (c) Explanation is correct reason for statement.
4. (c) $2\text{H}_2\text{S} + \text{SO}_2 \longrightarrow 2\text{H}_2\text{O} + 3\text{S}$
5. (a) $\text{Cl}_2 + \text{H}_2\text{O} \longrightarrow 2\text{HCl} + \text{O}_2$
 $\text{SO}_2 + 2\text{H}_2\text{O} \longrightarrow \text{H}_2\text{SO}_4 + 2\text{H}$
6. (c) $\text{PbS} + 4\text{H}_2\text{O}_2 \longrightarrow \text{PbSO}_4 + 4\text{H}_2\text{O}$
7. (a) $\text{CrO}_5 \xrightarrow{\Delta} \text{CrO}_3 + \text{O}_2$ (Disproportionation of O^-)
8. (a) $\text{NH}_4\text{NO}_3 \longrightarrow \text{N}_2\text{O} + 2\text{H}_2\text{O}$ (intermolecular redox)
9. (c) $\begin{array}{c} 0 \\ \text{N} \\ || \\ \text{N} \end{array} \begin{array}{c} -1 \\ \text{N} \\ -\text{H} \end{array}$, Explanation is correct reason for statement.
10. (c) Explanation is correct reason for statement.
11. (c) The explanation is correct reason for statement.
12. (c) The explanation is correct reason for statement.
13. (d) The reason is that the sum of oxidation number of elements in a molecule is equal to zero.
14. (c) N in NH_4^+ is in -3 oxidation state and in NO_2^- it is in $+3$ oxidation state.
15. (c) The explanation is correct reason.

$$\begin{array}{l} 2\text{O}^- \longrightarrow \text{O}_2^0 + 2e \\ \text{O}^- + e \longrightarrow \text{O}^{2-} \end{array}$$
16. (c) The explanation is correct reason for statement.
17. (c) The explanation is correct reason for statement.
18. (c) The explanation is correct reason for statement.
19. (d) Both statement and explanation are correct but explanation is not reason for statement.
20. (c) $(\text{As}^{3+})_2 \longrightarrow 2\text{As}^{5+} + 4e$
 $(\text{S}^{2-})_3 \longrightarrow 3\text{S}^{6+} + 24e$
 $[\text{As}_2\text{S}_3 \longrightarrow 2\text{As}^{5+} + 3\text{S}^{6+} + 28e] \times 3$
 $[3e + \text{N}^{5+} \longrightarrow \text{N}^{2+}] \times 28$
21. (a) $2\text{CrO}_4^{2-} \xrightarrow{\text{H}^+} \text{Cr}_2\text{O}_7^{2-}$
yellow orange
 Cr in $+6$ state.

MATCHING TYPE PROBLEMS

Type I : Only One Match Is Possible

1. Match the following :

- | List A | List B |
|---------------------------------|--|
| (a) Intermolecular redox change | (i) $\text{CO}_2 + \text{C} \longrightarrow 2\text{CO}$ |
| (b) Intramolecular redox change | (ii) $\text{As}_2\text{O}_3 + 3\text{H}_2\text{S} \longrightarrow \text{As}_2\text{S}_3 + 3\text{H}_2\text{O}$ |
| (c) Auto-redox change | (iii) $\text{KClO}_4 \longrightarrow \text{KCl} + 2\text{O}_2$ |
| (d) Precipitation | (iv) $\text{C}_3\text{O}_2 \longrightarrow \text{CO}_2 + 2\text{C}$ |

Type II : More Than One Match Are Possible

2. Match the following with their minimum and maximum oxidation number if any as well as with respective variable oxidation number if any.
- | List A | List B |
|---------------------------------|------------------------|
| (a) HNO_2 | (i) Oxidant |
| (b) HCN | (ii) Reductant |
| (c) CO | (iii) Complexing agent |
| (d) NaOCl | (iv) Acid |
| (e) $\text{C}_2\text{O}_4^{2-}$ | (v) Base |

- | List A | List B |
|--------|---------------------|
| (a) N | (i) zero |
| (b) P | (ii) $-\frac{1}{3}$ |
| (c) Mn | (iii) +3 |
| | (iv) +5 |
| (d) C | (v) +7 |
| (e) Bi | (vi) +4 |
| (f) Cl | (vii) -4 |

4. Column-I

- (a) $\text{O}_2^- \rightarrow \text{O}_2 + \text{O}_2^{2-}$
 (b) $\text{CrO}_4^{2-} + \text{H}^+ \rightarrow$
 (c) $\text{MnO}_4^- + \text{NO}_2^- + \text{H}^+ \rightarrow$
 (d) $\text{NO}_3^- + \text{H}_2\text{SO}_4 + \text{Fe}^{2+} \rightarrow$

Column-II

- (i) Redox reaction
 (ii) One of the products has trigonal planar structure
 (iii) Dimeric bridged tetra-hedral metal ion
 (iv) Disproportionation

Type III : Only One Match From Each List

- | List-A | List-B | List-C |
|---------------------------------|------------------------|---|
| (a) CH_4 | (i) E. mass = $M/8$ | (A) $\text{C}^{2+} \longrightarrow \text{C}^{4+}$ |
| (b) CO | (ii) E. mass = $M/2$ | (B) $\text{C}^{-4} \longrightarrow \text{C}^{4+}$ |
| (c) $\text{C}_2\text{O}_4^{2-}$ | (iii) E. mass = $M/12$ | (C) $\text{C}^{3+} \longrightarrow \text{C}^{4+}$ |
| (d) C_2H_4 | | (D) $\text{C}^{-2} \longrightarrow \text{C}^{4+}$ |

ANSWERS

1. a-i; b-iii; c-iv; d-ii
 2. a-i, ii, iv; b-ii, iii, iv; c-i, iii; d-i, ii; e-ii, iii, v
 3. a-i, ii, iii, iv; b-i, iii, iv; c-i, iii, iv, v, vi;
 d-i, vi, vii; e-i, iii, iv; f-i, iii, iv, v, vi

4. a-i, iv; b-iii; c-i, ii; d-i
 5. a-i-B; b-ii-A; c-ii-C; d-iii-D