

Teacher: Sutapa Chakrabarty

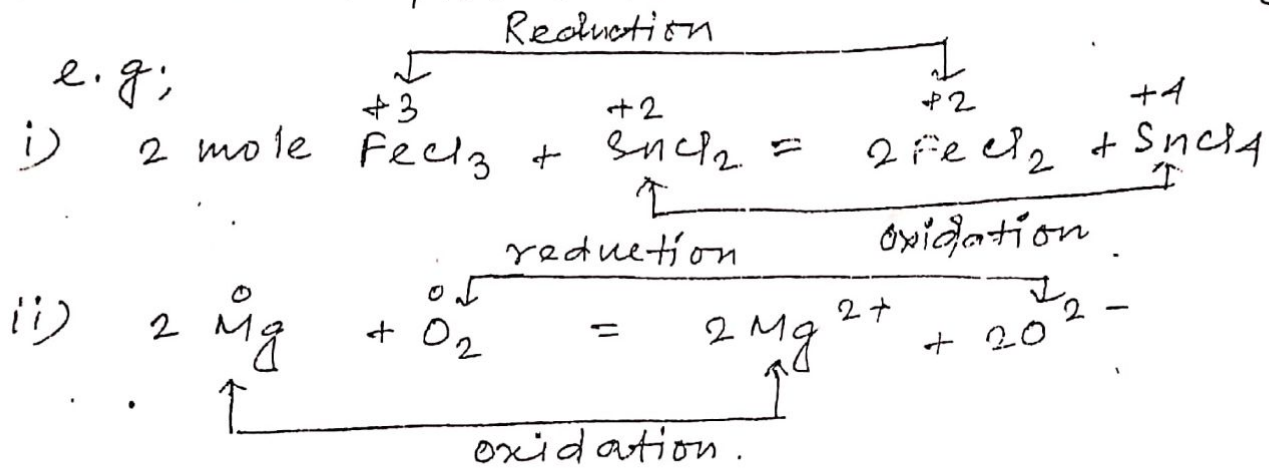
Class : Semester-2

Paper: C3T: Inorganic Chemistry

Topic : Redox Reaction and Precipitation
reaction

• Redox Rxn

An oxidation-reduction rxn is called Redox rxn. A redox rxn is that in which oxidation and reduction take place simultaneously i.e. in a redox rxn one substance is oxidise and the other substance is reduce and hence oxidation and reduction process occurs simultaneously.



• Oxidising Reagent and Reducing Reagent

An oxidising agent is one that gains electrons and is reduce to a lower oxidation state.

A reducing agent is one that losses electrons and is oxidise to a higher oxidation state.

e.g; In the above eqⁿ (i) FeCl₃ acts as an oxidising agent and SnCl₂ acts as a reducing agent.

• Oxidation no and Oxidation State

In most of the cases these two terms are used in the same sense. Oxidation no (O.N) of an atom is the apparent charge on the atom, in it's compound or in it's ion while oxidation state of an atom is the oxidation no. per atom of that element in a given compound or in an ion.

$K_2Cr_2O_7$ is +12, oxidation state of Cr atom in this molecule is $+12/2 = +6$.

Actually the O.N or valence no. of an element in a particular compound is a no. which denotes the extent of oxidation or reduction necessary to change the element from the free state into that in the compound.

The oxidation no is given a +ve sign if oxidation is required to effect the change and a -ve sign if reduction is necessary.

• General Rules for Calculating the oxidation no. and oxidation state.

Some general rules are given below which can be used to calculate the O.N of the elements.

i) O.N of an element in the free state (i.e elementary state) is zero. e.g; O.N of Cr in Cr_2 is zero.

ii) Oxidation no of an monoatomic ion (e.g; Al^{3+} , Cl^- etc) is equal to the number of positive or negative charges on the ion.

e.g; O.N of Al atom in Al^{3+} ion and of Cl in Cl^- ion are +3 and -1 respectively.

iii) The sum of the oxidation no of all the atoms in a given molecule is zero. This sum is equal to the sum of O.N's of individual atoms.

e.g; In Na_2SO_4 molecule, the sum of oxidation no = $2 \times (+1) + 1 \times (+6) + 4 \times (-2) = 0$

iv) In polyatomic ions (e.g SO_4^{2-} , NH_4^+ etc) the algebraic sum of O.N of all the constituent atoms is equal to the number of +ve or -ve charges on the polyatomic ion.

e.g; In $Cr_2O_7^{2-}$ ion, the algebraic sum of O.N = $2 \times (+6) + 7 \times (-2) = -2$ which is the charge on $Cr_2O_7^{2-}$ ion.

v) O.N of non metal is negative in it's compound with metals or with hydrogen.

e.g; O.N of N atom in both the molecules (Ca_3N_2 and NH_3) is -3.

vi) O.N of metals of group IA (alkali metals) or of group IIA (alkali earth metals) is +1 and +2 respectively.

e.g; The O.N of Na and Mg are +1 and +2 respectively.

vii) The O.N of an atom is a variable quantity. Since it may be different in different compounds. The fact is evident from following examples.

1) O.N of H atom is

a) zero in free H atom or H_2 molecule.

b) +1 in compounds like NH_3 , PH_3 , H_2O_2 etc.

c) -1 in metallic hydrides NaH , $LiAlH_4$ etc.

2) O.N of O atom is

a) -2 in H_2O , SO_2 , Cl_2O etc.

b) -1 in compounds containing peroxide ion e.g; Na_2O_2 , H_2O_2 , BaO_2 etc.

c) $-\frac{1}{2}$ in superoxide like KO_2 .

d) +1 in O_2F_2 .

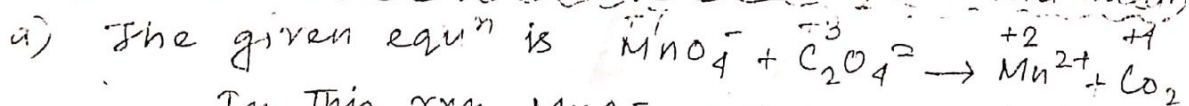
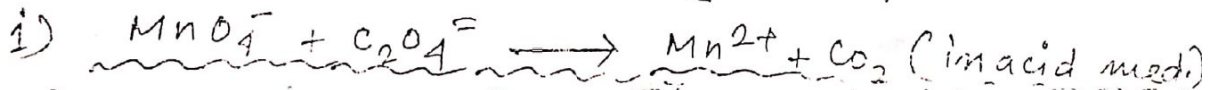
e) +2 in OF_2 .

viii) F is the most electronegative element and has an oxidation number of -1 in all its compounds.

ix) In all the halides (compounds of HX or MX type, where X is the halogen, M is the metal atom) the O.N of the halogen is -1.

Balancing of the Redox Rxn by O.N method

The use of this method can be understood by considering the following examples.



In this rxn MnO_4^- acts as an oxidising agent and $C_2O_4^{2-}$ as a reducing agent. This is decreased from +7 to +2 and that of Carbon is increased from +3 to +4.

The oxidation no of O remain same.

b) Increase in oxidation number of one carbon

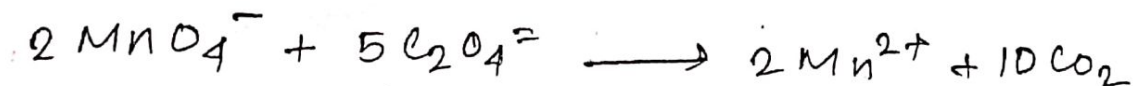
$$\text{atom} = (+4) - (+3) = +1$$

Increase in O.N. of two Carbon atoms $= (+1) \times 2 = +2$

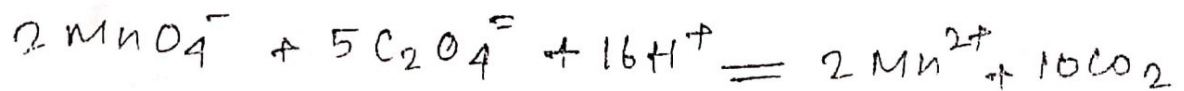
Decrease in O.N. of one Mn atom $= (+7) - (+2) = +5$

In order to make the total increase in O.N. the oxidising agent should be multiplied by 2 and the reducing agent should be multiplied by 5.

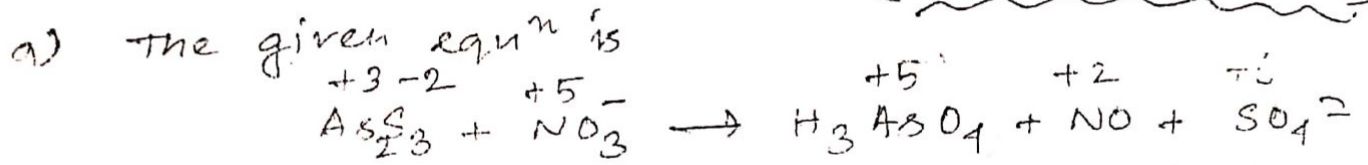
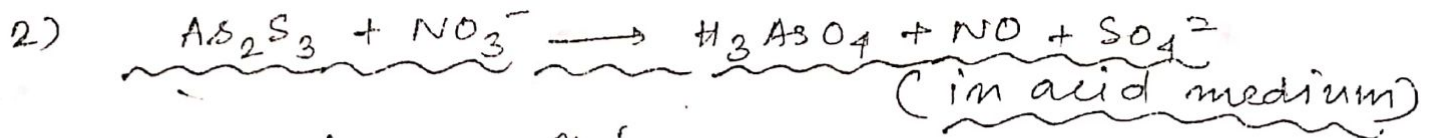
Thus the given equⁿ should be written as



c) In order to balance 'O' atoms, add 8H₂O mol-ecules to the R.H.S of the above equⁿ and the equⁿ becomes -



This is the balanced equⁿ, since electrical charges on both sides are equal. + 8H₂O



In the given equation NO_3^- acts as an oxidising agent. This is because of the fact that O.N per atom of N is decreased from +5 to +2 and that of As is increased from +3 to +5 and S is increased from -2 to +6. The O.N of 'O' atom remain same.

b) Increase in O.N of ^{one} As atom = $(+5) - (+3) = +2$

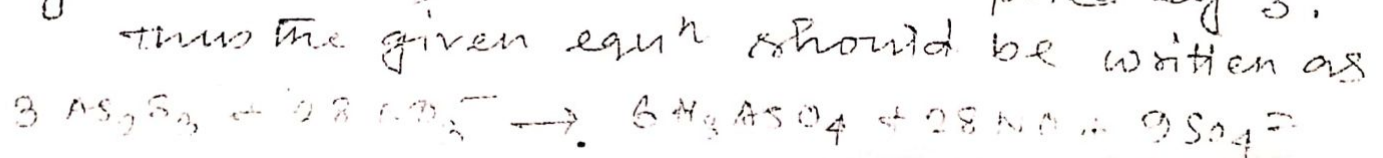
Increase in O.N of two As atom = $+2 \times 2 = +4$

Increase in O.N of S atom = $(+6) - (-2) = +8$

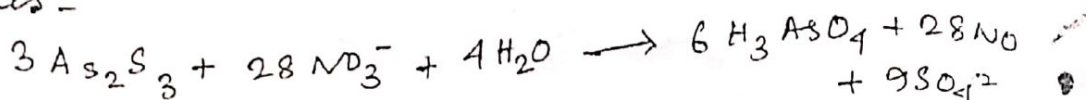
Increase in O.N of three S atom = $+8 \times 3 = +24$

Therefore total increase of oxidation no of two As atom and three S atom = $+4 + 24 = +28$

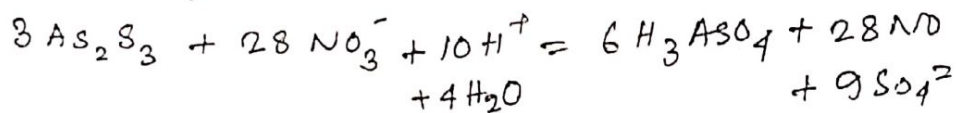
Decrease in O.N of one 'N' atom = $(+5) - (+2) = +3$
 equal to the total decrease in O.N, The oxidising agent (NO_3^-) should be multiplied by 28 and the reducing agent (As_2S_3) should be multiplied by 3.



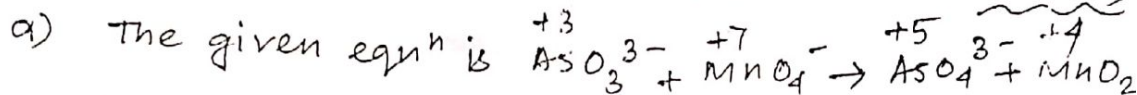
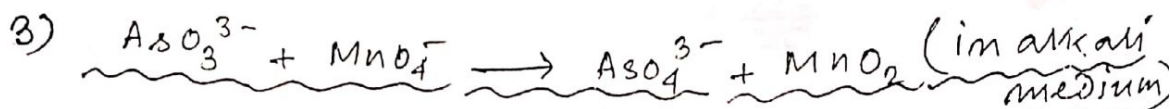
c) In order to balance 'O' atoms add $4H_2O$ molecules to the L.H.S of the above eqn and the becomes -



d) In order to show the acidic medium of the rxn and to balance H atom add $10H^+$ to the L.H.S of the above equation.



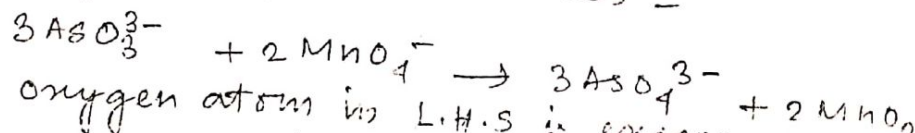
This is the balanced equation, since the electrical charges on both sides are same.



In the given eqn MnO_4^- acts as an oxidising agent and AsO_3^{3-} behave as a reducing agent. This is because of the fact that O.N of Mn is decreased from +7 to +4, and that of As is increased from +3 to +5. The O.N of 'O' atom remain the same.

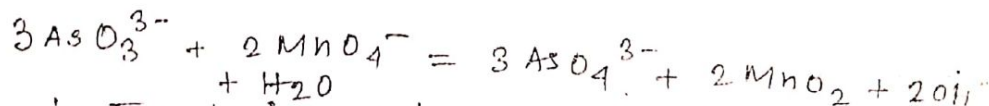
b) Increased in O.N of As atom = $(+5) - (+3) = +2$
Decreased in O.N of Mn atom = $(+7) - (+4) = +3$

In order to make the total increasing in O.N equal to the total decreasing of O.N; the oxidising agent MnO_4^- should be multiplied by 2 and the reducing agent (AsO_3^{3-}) should be multiplied by 3. Thus the given equation becomes -



c) One oxygen atom in L.H.S is excess. In order to show alkaline medium of the rxn and to balance O and H atom one H_2O is added L.H.S and two OH^- on R.H.S.

Hence the eqn becomes



This is the balanced equation. Since electrical charges on both sides are equal.

• Balancing of Redox Rxn by ion electron method

various steps involved in this method are given below —

i) Ascertain the reactants and products and their chemical formulae.

ii) If the unbalanced equation is in the molecular form convert into ionic form and then break this ionic equation into two half reactions (partial eqⁿ). These equations represent the reduction of oxidant and the oxidation of reductant.

iii) Balance both the partial equations in the following way;

a) Balance the no. of atoms other than H and O by multiplying the R.H.S or L.H.S of half rxns by a suitable multiple.

b) In order to balance O atoms, add the appropriate number of H₂O molecules to the side deficient in O atoms.

c) In order to balance H atoms and to show the acidic medium of the rxn add H⁺ ions to the side deficient to the H atoms.

d) If the rxn takes place in the basic medium, H⁺ ions used in step c) should be allowed to combine with the equal no of OH⁻ ion to product, same no of H₂O molecule. Now add the resulted equation, so that H⁺ ions are cancelled out from both the equation.

e) Balance the electrical charges on both sides by adding electrons to the side deficient in the negative charges.

f) Multiply one or both half reactions by a suitable number so that by adding the two half rxns the electrons are cancelled out.

iv) The above six steps give both the half rxns in a balanced state. Now add the balanced two half rxns and cancel out the terms which are common to both side.

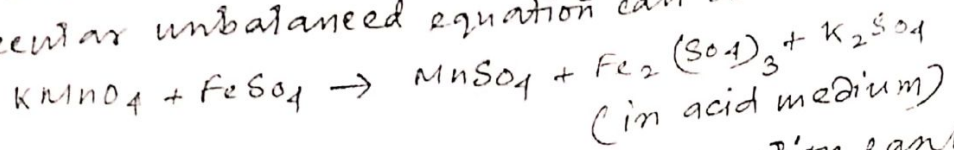
State what happens when

- i) KMnO₄ is treated with FeSO₄ in acid medium.
- ii) K₂Cr₂O₇ is treated with KI in acid medium.
- iii) KMnO₄ is treated with sodium stannite in alkali.
- iv) K₄[Fe(CN)₆] is treated with H₂O₂ in acid medium.

Give the balanced equation in each case.

i) $KMnO_4$ is treated with $FeSO_4$ in acid medium

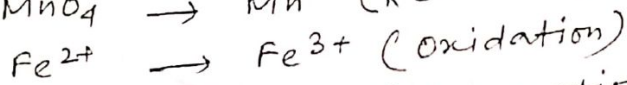
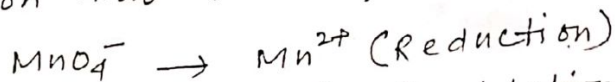
a) In aqueous acid medium $KMnO_4$ oxidises $FeSO_4$ to $Fe_2(SO_4)_3$ and it itself reduces to manganous salt. Hence the molecular unbalanced equation can be written as



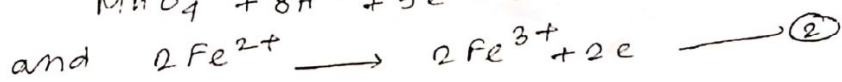
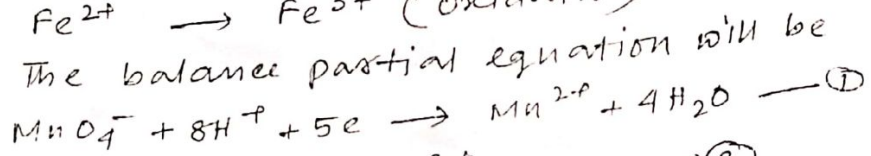
b) In the ionic form this molecular equation can be written as,



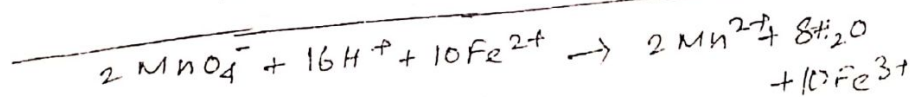
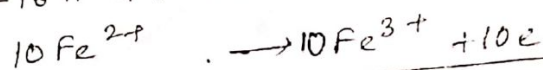
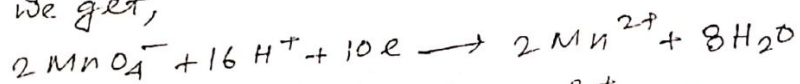
This ionic equation can be broken into oxidation and reduction half rxns as,



c) Hence the balanced partial equation will be

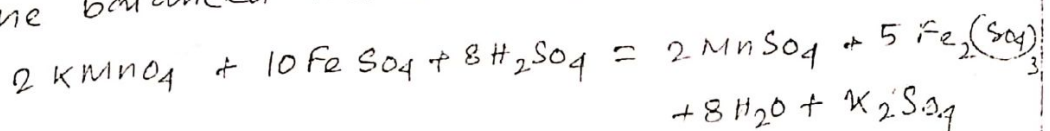


Multiplying eqⁿ (1) by 2 and eqⁿ (2) by 5 and adding them, we get,



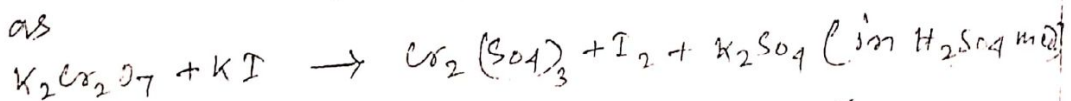
This is the balanced equation

d) The balanced molecular equation will be



ii) $K_2Cr_2O_7$ is treated with KI in dilute acid medium

a) In dilute acid medium $K_2Cr_2O_7$ oxidises KI to I_2 and it itself reduces to chromic salt [$Cr_2(SO_4)_3$]. Hence the molecular unbalanced equation can be written as



b) In the ionic form, this molecular equation can be written as -



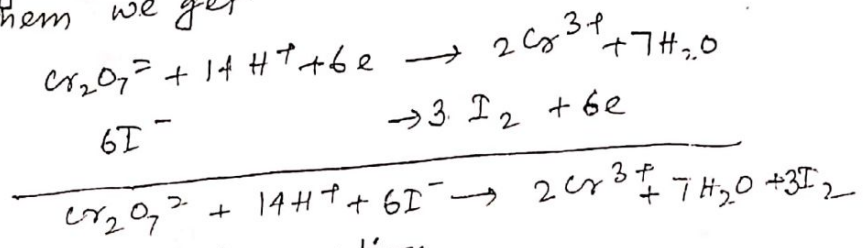
This ionic equation can be broken into oxidation

as to hence

and reduction half rxns as -
 $Cr_2O_7^{2-} \rightarrow Cr^{3+}$ (Reduction)
 $I^- \rightarrow I_2$ (Oxidation)

c) Hence the balanced partial equation will be
 $Cr_2O_7^{2-} + 14H^+ + 6e \rightarrow 2Cr^{3+} + 7H_2O$ — (1)
 and $2I^- \rightarrow I_2 + 2e$ — (2)

Multiplying equation (1) by 1 and equation (2) by 3 and adding them we get



This is the balanced equation.

d) The balanced molecular equation will be
 $K_2Cr_2O_7 + 7H_2SO_4 + 6KI = Cr_2(SO_4)_3 + 7H_2O + 3I_2 + 4K_2SO_4$

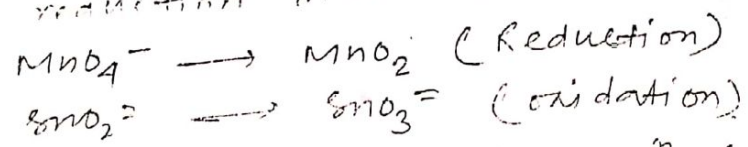
iii) $KMnO_4$ is treated with sodium stannite (Na_2SnO_2) in alkaline medium.

In alkaline medium $KMnO_4$ oxidises Na_2SnO_2 to Na_2SnO_3 and itself reduced to MnO_2 . Hence the molecular unbalanced equation will be
 $KMnO_4 + Na_2SnO_2 \rightarrow MnO_2 + Na_2SnO_3$ (in KOH medium)

b) In the ionic form, This molecular equation can be written as



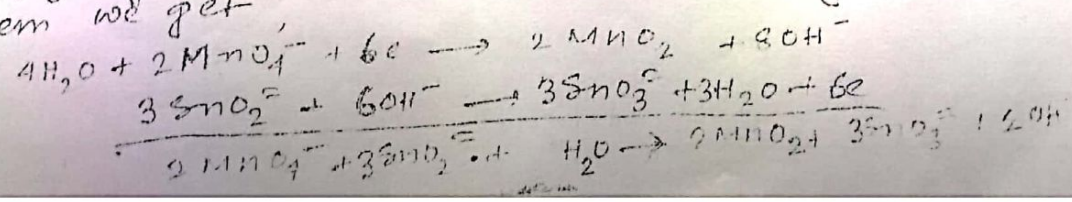
This ionic equation can be broken into oxidation and reduction half reactions as



c) Hence the balanced partial eqnⁿ will be
 $2H_2O + MnO_4^- + 3e \rightarrow MnO_2 + 4OH^-$ — (1)

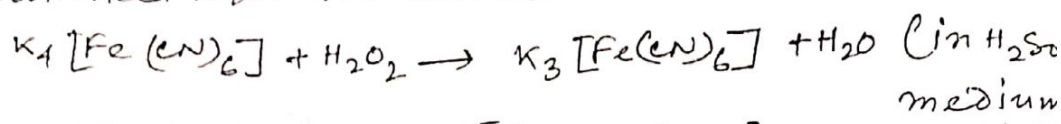
and $SnO_2^{2-} + 2OH^- \rightarrow SnO_3^{2-} + H_2O + 2e$ — (2)

Multiplying eqnⁿ (1) by 2 and eqnⁿ (2) by 3 and adding them we get

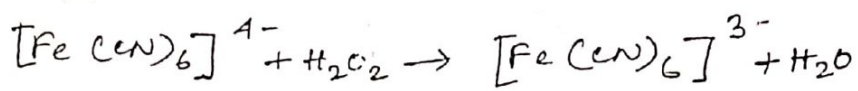


iv) $K_4[Fe(CN)_6]$ is treated with H_2O_2 in acid medium

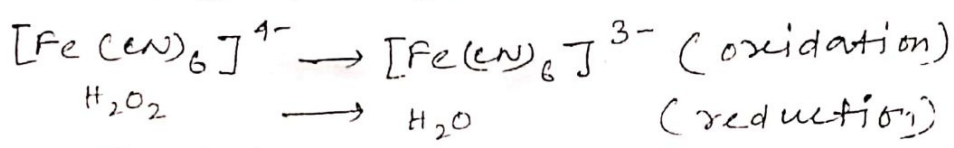
a) In acid medium $K_4[Fe(CN)_6]$ reduces H_2O_2 to H_2O and itself oxidises to $K_3[Fe(CN)_6]$. Hence the molecular unbalanced equation can be written as,



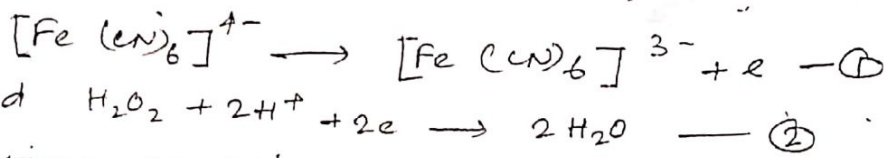
b) In the ionic form, this molecular equation can be written as



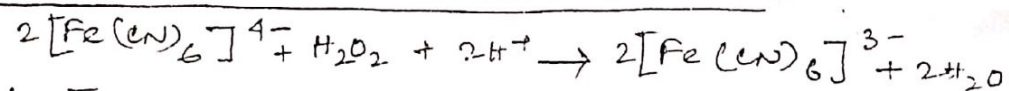
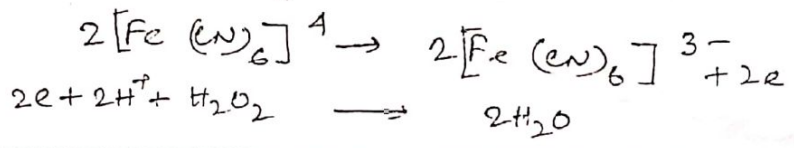
This ionic equation can be broken into oxidation and reduction half rxns as -



c) Hence the balanced partial eqnⁿ will be

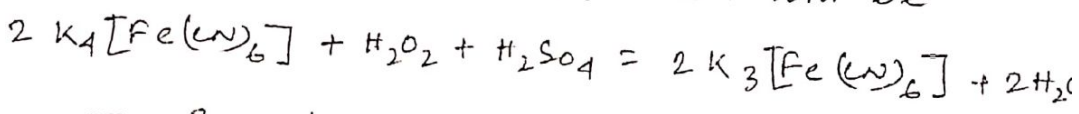


Multiplying equation (1) by 2 and eqnⁿ (2) by 1 and adding them we get

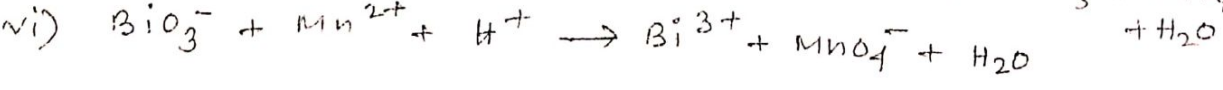
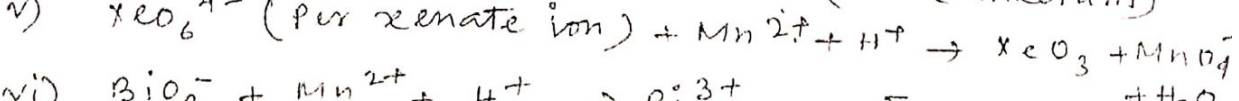
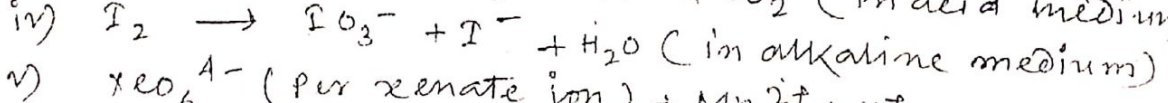
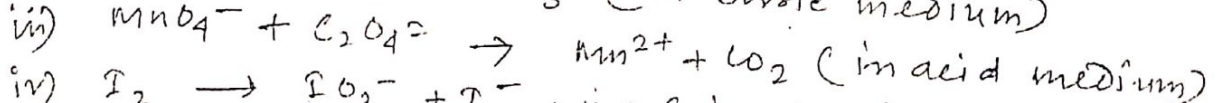
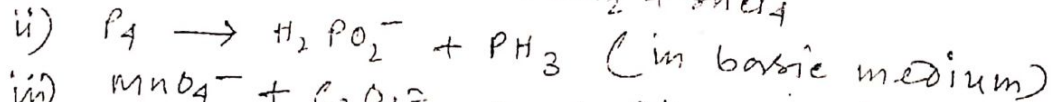
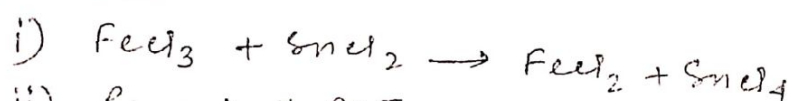


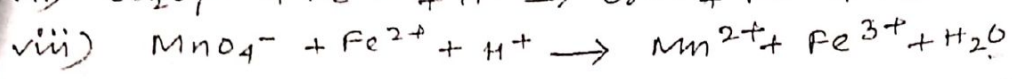
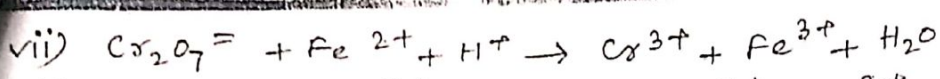
This is the balanced equation.

d) The balanced molecular equation will be



• Balance the following equations by ion electron method.

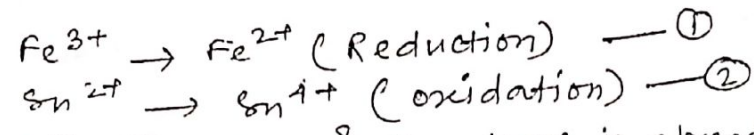




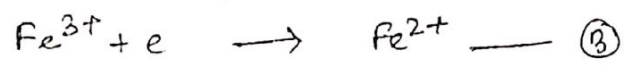
i) The given equation is $\text{FeCl}_3 + \text{SnCl}_2 \rightarrow \text{FeCl}_2 + \text{SnCl}_4$
 This is the unbalanced molecular equation.

a) In the ionic form, The above equation can be written as
 $\text{Fe}^{3+} + \text{Sn}^{2+} \rightarrow \text{Fe}^{2+} + \text{Sn}^{4+}$

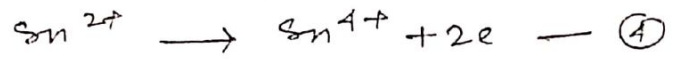
This ionic equation can be broken into two partial equations as



b) In equation ① The no. of Fe atoms is already balanced. In order to balance the electrical charge adding one electron to the L.H.S of eqn ① we get



c) In equation ② The no. of Sn atoms is already balanced. In order to balance the electrical charge adding two electrons to the R.H.S of eqn ②, we get

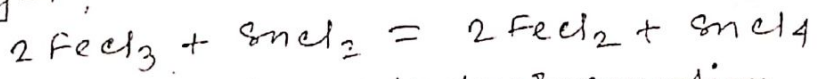


d) Multiplying equation ③ by 2 and eqn ④ by 1 and adding them we get



This is the balanced ionic equation.

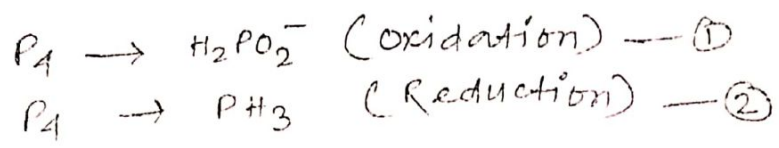
e) Converting the above ionic eqn into the molecular form we get,



This is the balanced molecular equation.

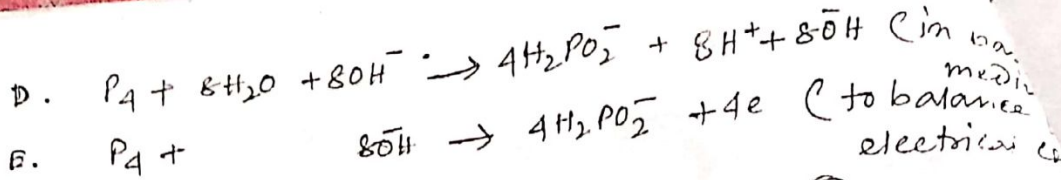
ii) The given eqn is $\text{P}_4 \rightarrow \text{H}_2\text{PO}_2^- + \text{PH}_3$ (in basic med.)

a) This eqn is in the ionic form. In this equation P_4 is oxidised to H_2PO_2^- as well as reduced to PH_3 . Thus the given eqn can be broken into the following partial equations,



b) To balance all the atoms and electrical charge in eqn ① the following steps are required.

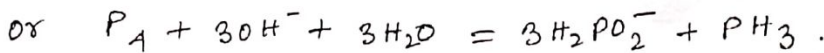
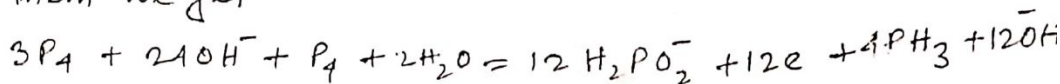
- A. $\text{P}_4 \rightarrow 4\text{H}_2\text{PO}_2^-$ (to balance P atom)
- B. $\text{P}_4 + 8\text{H}_2\text{O} \rightarrow 4\text{H}_2\text{PO}_2^-$ (to balance O atom)
- C. $\text{P}_4 + 8\text{H}_2\text{O} \rightarrow 4\text{H}_2\text{PO}_2^- + 8\text{H}^+$ (to balance H atom)



c) To balance all the atoms and electrical charge, the following steps are required;

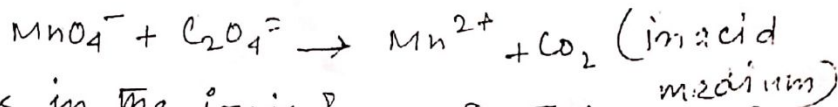
- $P_4 \rightarrow 4PH_3$ (to balance P atom)
- $P_4 + 12H^+ \rightarrow 4PH_3$ (to balance H atom)
- $P_4 + 12H^+ + 12OH^- \rightarrow 4PH_3 + 12OH^-$ (in alkaline medium)
- $P_4 + 12H_2O + 12e^- \rightarrow 4PH_3 + 12OH^-$ (to balance electrical charges)

d) Multiplying eqnⁿ ③ by 3 and eqnⁿ ④ by 1 and adding them we get

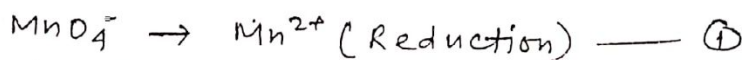


this is the balanced ionic equation.

iii) The given eqnⁿ is



a) This eqnⁿ is in the ionic form. In this equation MnO_4^- is reduced to Mn^{2+} and $C_2O_4^{2-}$ is oxidised to CO_2 . Thus the given eqnⁿ can be broken into two partial equations.



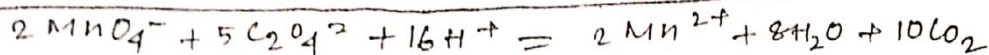
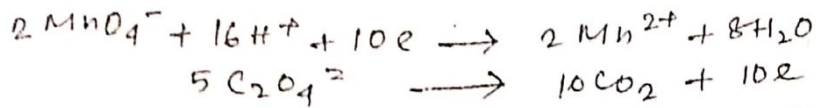
b) The eqnⁿ ① can be balanced by using the following steps.

- $MnO_4^- \rightarrow Mn^{2+} + 4H_2O$ (to balance O atom)
- $MnO_4^- + 8H^+ \rightarrow Mn^{2+} + 4H_2O$ (to balance H atom)
- $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (to balance electrical charge)

c) The eqnⁿ ② can be balanced by using the following steps.

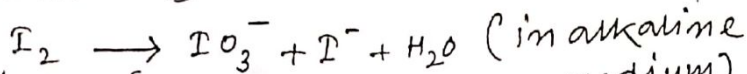
- $C_2O_4^{2-} \rightarrow 2CO_2$ (to balance C atom)
- $C_2O_4^{2-} \rightarrow 2CO_2 + 2e^-$ (to balance electrical charge)

d) Multiplying eqnⁿ ③ by 2 and eqnⁿ ④ by 5 and adding them we get,

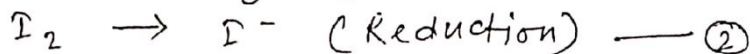
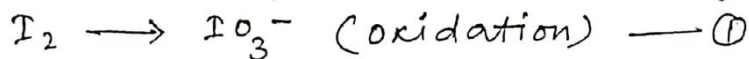


This is the balanced eqn. Since the electrical charges on both side are equal.

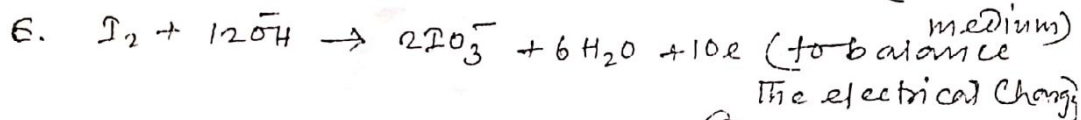
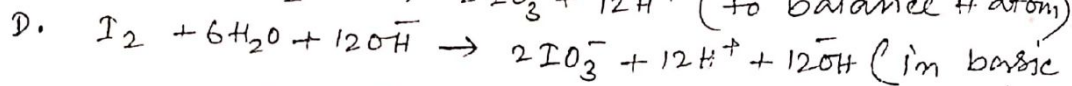
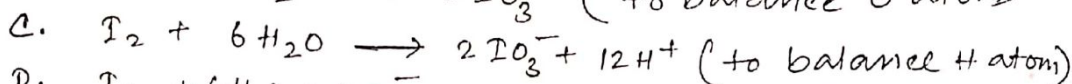
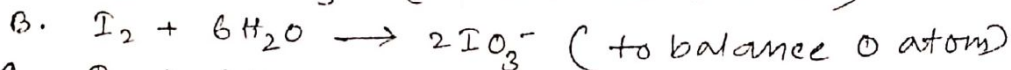
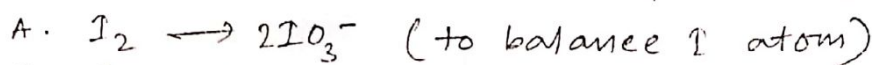
(iv) The given equation is



a) This eqn is in the ionic form. In this eqn I_2 is oxidised to IO_3^- as well as reduced to I^- . Thus the given eqn can be broken into the following partial eqn.

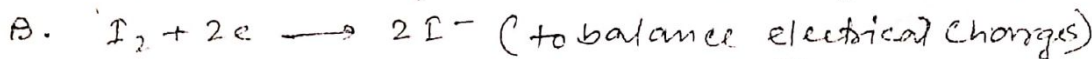
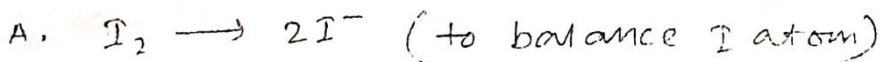


b) The eqn (1) can be balanced by following steps.



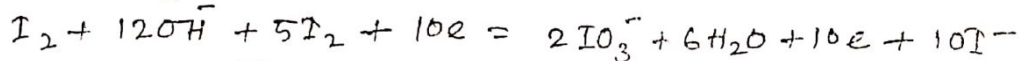
..... (3)

c) The eqn (2) can be balanced by using following steps.

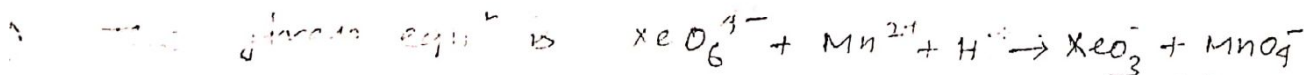


..... (4)

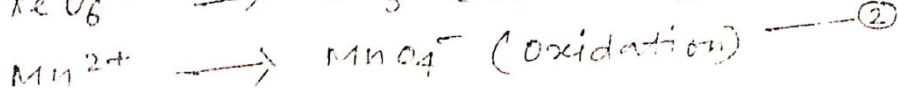
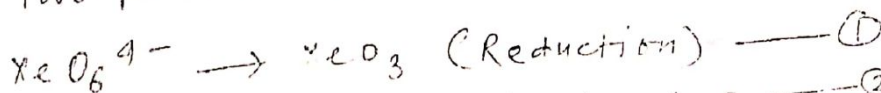
d) Multiplying eqn (3) by 1 and eqn (4) by 5 and adding them we get



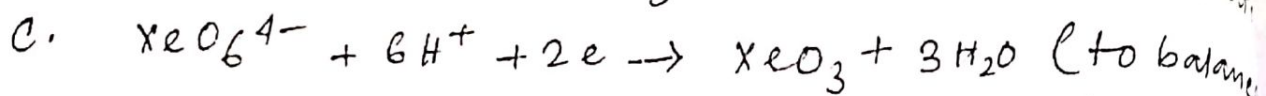
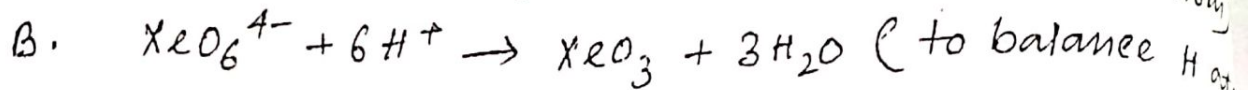
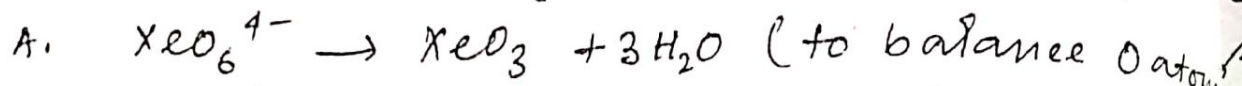
This is the balanced ionic equation.



a) This eqn is in the ionic form. Since H^+ ions are involved in this eqn hence this rxn occurs in acid medium. In this eqn XeO_6^{4-} is reduced to XeO_3 and Mn^{2+} is oxidised to MnO_4^- ion. Thus the given eqn is broken into two partial eqns.

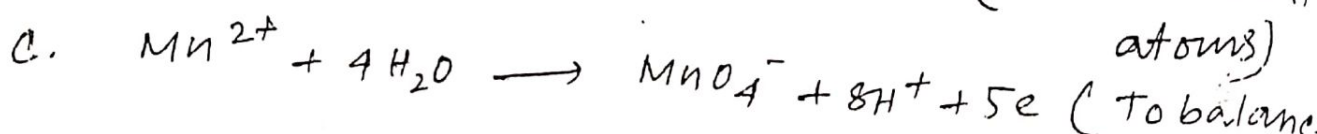
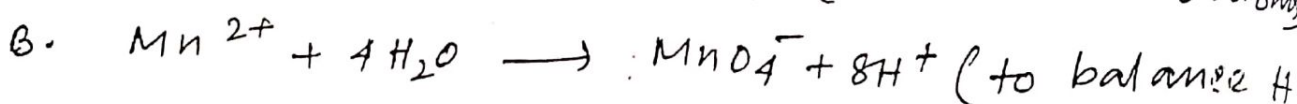
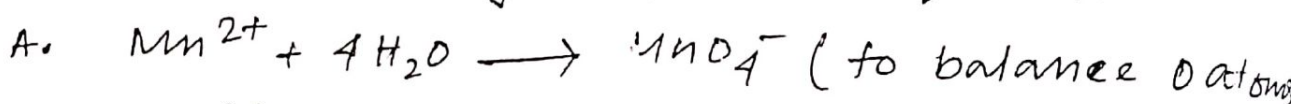


b) To balance all the atoms and electrical charge in equation ① the following steps are required.



The electrical charge

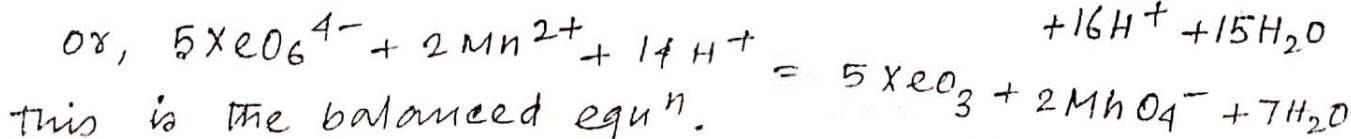
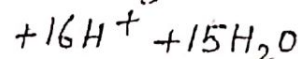
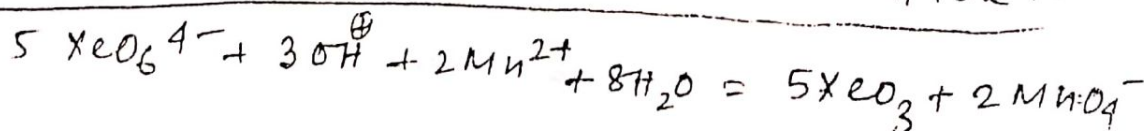
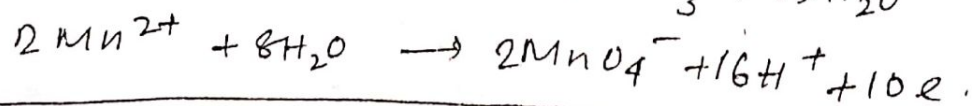
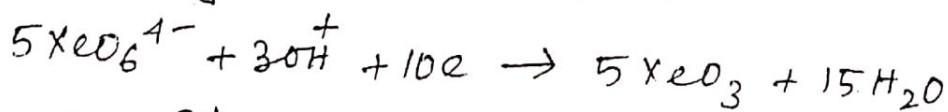
c) To balance all the atoms and electrical charge in equation ② the following steps are required.



The electrical charge

..... ④

d) Multiplying equation ③ by 5 and equation ② by 2 and adding them we get



this is the balanced equation.