

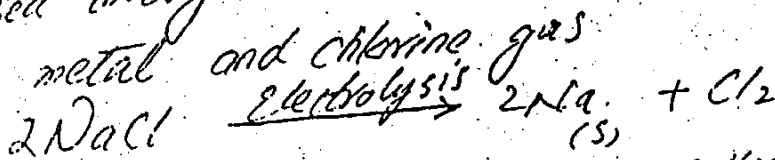
ELECTROCHEMISTRY

CHAPTER NO. 10

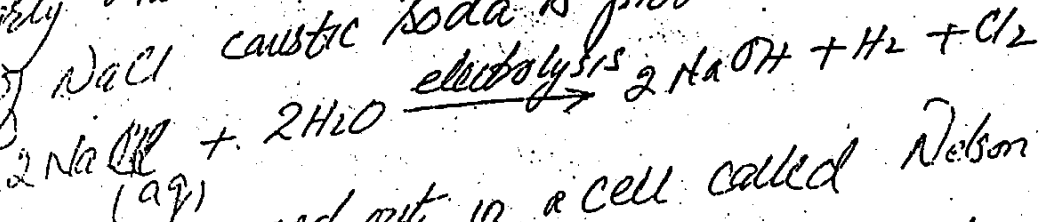
BOOK - I (1ST YEAR)

ELECTROCHEMISTRY :- The branch of chemistry which deals with :- (i) Conversion of electrical energy into chemical energy and (ii) ^{and} Conversion of chemical energy into electrical energy is called ELECTROCHEMISTRY.

ELECTROLYTIC CELL | The device in which electrical energy is used to carry out an otherwise non spontaneous process is called ELECTROLYTIC CELL. This process is called ELECTROLYSIS. For example when electric current is passed through molten NaCl it splits up into sodium metal and chlorine gas.



This process is carried out in a cell called Down's Cell. Similarly when electricity is passed through an aqueous soln. of NaCl caustic soda is produced.

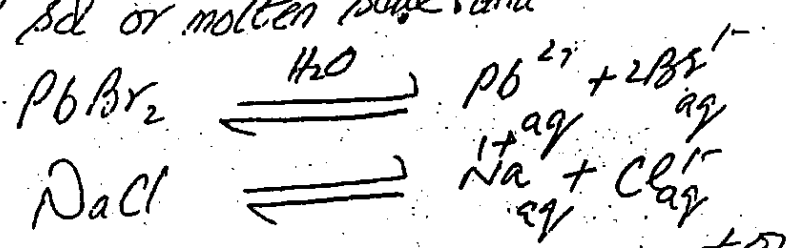


This process is carried out in a cell called Nelson Cell. GALVANIC CELL | The device in which steady current is produced by using a chemical reaction is called galvanic cell or Voltaic Cell. For example Daniell's Cell, Ni-Cd Cells, Fuel cells.

Both these cells are collectively called ELECTROCHEMICAL CELLS.

DIFFERENCE BETWEEN CONDUCTION OF ELECTRICITY BY METALS AND BY ELECTROLYTES.
Metals are conductors of electricity due to free

electrons. It is called electronic conduction or metallic conduction. On the other hand electrolytes are substances which ionize in aqueous sol or molten state.



They conduct electricity due to movement of ions to opposite electrodes.

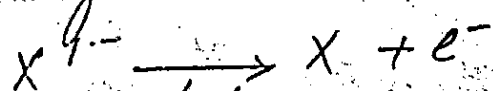
The conductivity of metals decreases with increase in temperature while conductivity of ~~non~~ electrolytes increases with temperature.

GENERAL INTRODUCTION OF ELECTROLYSIS.

During electrolysis metal plates are dipped in aqueous solution of electrolyte or molten electrolyte. When these plates are connected to D.C. source each electrode acquires and electric charge.

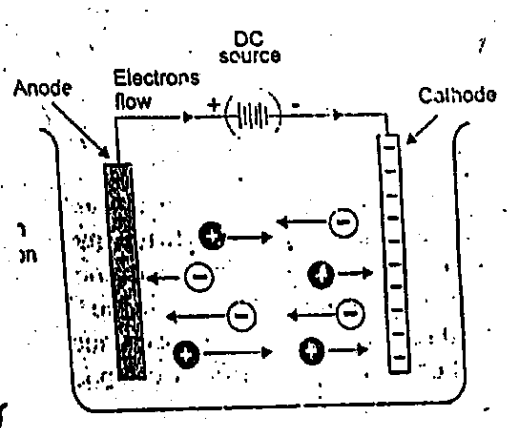
CATHODE | The -vely charged electrode is called cathode. The positive ions move to the cathode. These +ve ions are called CATIONS. These positive ions pick up e^{-} from cathode and get reduced. Thus REDUCTION TAKES place at Cathode.

ANODE | The positively charged electrode is called Anode. The negatively charged ions move to the anode and get ~~re~~ oxidized by giving electrons to anode.



This electrolysis is a redox reaction.

The sum of reactions taking place at electrodes is called Electrolysis.



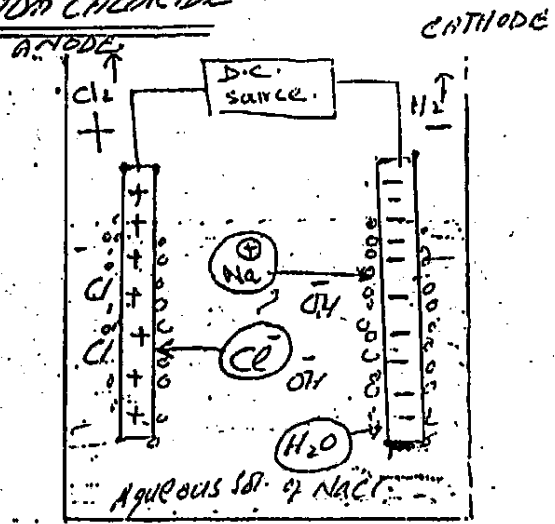
CONDUCTANCE OF ELECTRICITY THROUGH AN AQUEOUS SOLUTION OF AN ELECTROLYTE. (NaCl)

ELECTROLYSIS The process in which electric current is used to bring about chemical reactions that do not take place spontaneously is called ELECTROLYSIS.

FARADAY FIRST LAW OF ELECTROLYSIS It states that the amount of chemical change produced by an electric current is directly proportional to the quantity of electricity passed.

CONDUCTANCE OF ELECTRICITY THROUGH AN AQUEOUS SOLUTION OF SODIUM CHLORIDE

ELECTROLYTIC CELL A beaker containing an aqueous solution of an electrolyte (NaCl) and two inert electrodes dipped in it. These are connected to a source of electric potential (D.C. current). It is called electrolytic cell as shown in the fig.

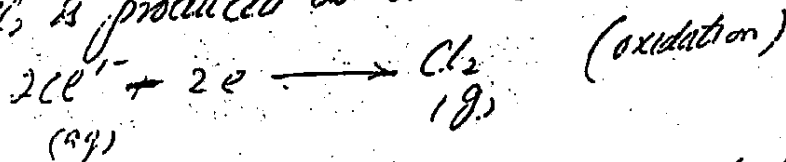


When solution of concentrated NaCl is placed in the cell and electrodes are connected to a source of D.C., H_2 gas is produced at cathode and Cl_2 is produced at anode. At the same time solution in the cell becomes alkaline. It can be explained as follows.

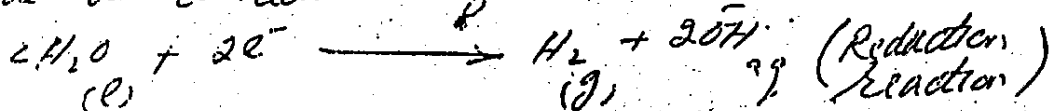
Solid sodium chloride When dissolved in water dissociates into ions

$$NaCl_{(s)} \rightleftharpoons Na^{+}_{(aq)} + Cl^{-}_{(aq)}$$

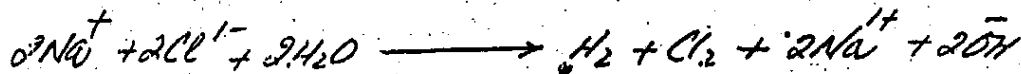
REACTION AT ANODE Oxidation of Cl^{-} ions takes place at anode. Thus Cl_2 is produced at anode



REDUCTION AT CATHODE Gaseous H_2 and OH^{-} ions are produced at cathode due to reduction of water



The net reaction in the cell can be written as



The above explanation indicates that two half reactions take place in electrolytic cell. Oxidation half reaction takes place at anode and reduction half reaction takes place at cathode. Oxidation involves removal of electrons and reduction involves addition of electrons.

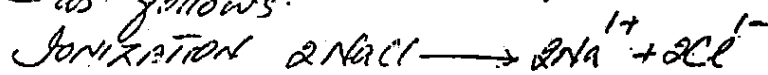
The net reaction is called REDOX REACTION.

Further it is also clear that water is reduced more easily than Na^+ the solution which remains in the cell is alkaline due to NaOH produced. Thus electrolysis of aqueous solution of sodium chloride is used to produce caustic soda on commercial scale.

ELECTROLYSIS OF FUSED SODIUM CHLORIDE:

When current is passed through fused sodium chloride Cl_2 is liberated at anode and "Na" metal (molten state) is produced at cathode.

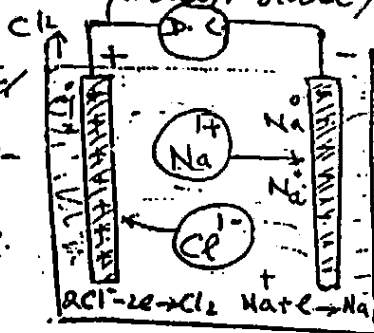
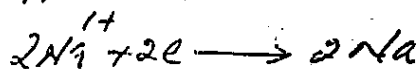
The reactions can be represented as follows.



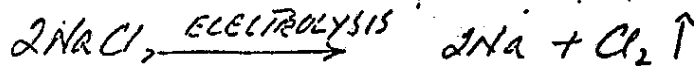
OXIDATION HALF REACTION AT ANODE.



REDUCTION HALF REACTION AT CATHODE



The net REDOX REACTION (BY ADDING ABOVE THREE)



AT CATHODE AT ANODE.

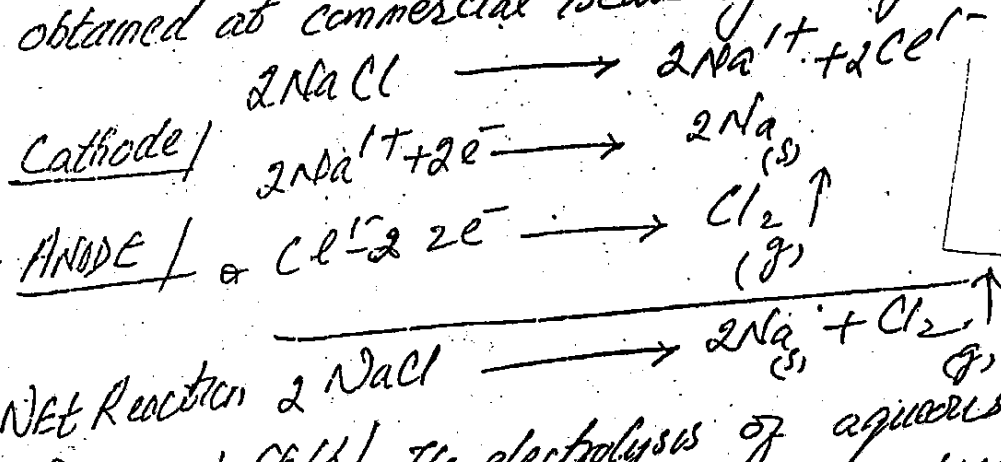
When molten salt is electrolyzed, the products are predictable. When an aqueous solution of salt is electrolyzed, H_2 and oxygen appear at cathode and anode in some cases.

See Table at p-341
(Table No. 10.1, 10.2)

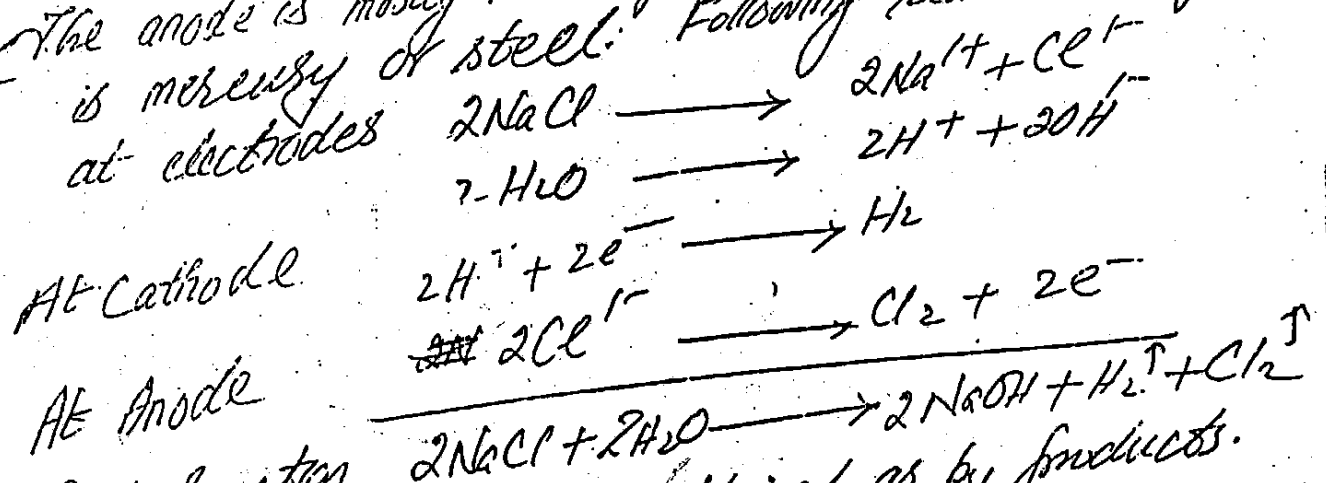
EXAMPLES OF ELECTROLYSIS:

Some important examples and applications of electrolysis are given below.

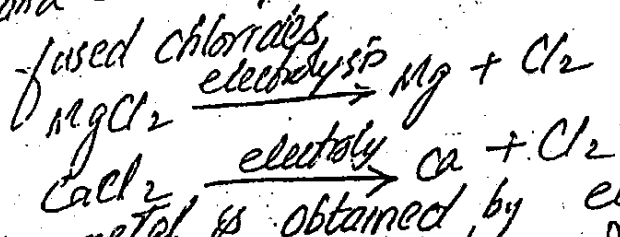
1. DOWN'S CELL / The electrolysis of molten NaCl is called DOWN'S CELL. Sodium metal is obtained at commercial scale by this process.



2. NELSON CELL / The electrolysis of aqueous solⁿ of NaCl is used to get caustic soda on commercial scale. The anode is mostly made up of Titanium and cathode is mercury or steel. Following reactions take place at electrodes



3. Hydrogen and chlorine are obtained as by products. Magnesium and Calcium metals are obtained by electrolysis of their ef fused chlorides



4. ALUMINIUM metal is obtained by electrolysis of fused Al_2O_3 Bauxite and Cryolite Na_3AlF_6 ($Al_2O_3 \cdot 2H_2O$)

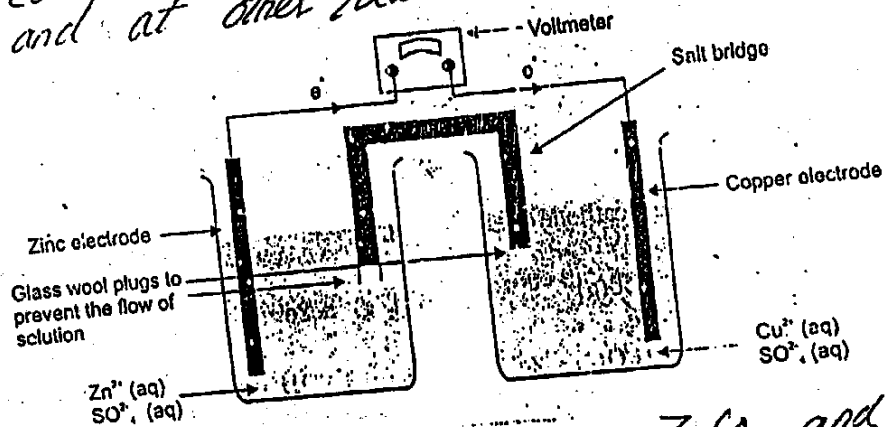
5. Copper, Nickel, silver Nickel plating is done by various types of electrolysis.

6. Anodized aluminium is prepared by electrolytic process. The electrolyte is H_2SO_4 or chromic acid. Aluminium is made anode. The thin layer of oxide deposited on aluminium acts as a protective covering and prevents attacks of corrosive agents. The freshly anodized aluminium is hydrated and it can absorb dyes.

7. Electrolytic cell can be used for purification of copper. Impure copper is made anode and thin sheet of pure copper is made cathode. The electrolyte is H_2SO_4 and copper sulphate solution.

WRITE A NOTE ON VOLTAGE CELL OR GALVANIC CELL.
The device by which a steady current could be produced by using a chemical reaction is called voltage cell or GALVANIC CELL.

A voltage cell consists of two half cells which are connected electrically. In one half cell oxidation takes place and at other reaction takes place.

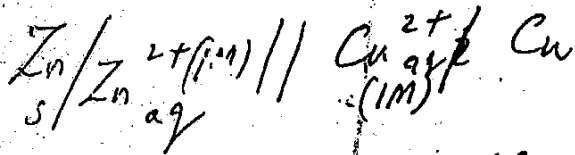
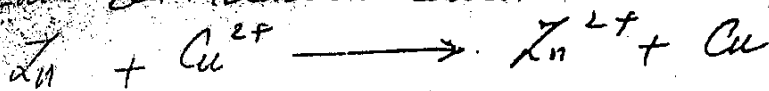


A zinc plate is dipped in a solution of $ZnSO_4$ and a copper plate is dipped in a solution of $CuSO_4$. The two solutions are connected by a salt bridge. Zinc electrode loses electrons more readily. Thus it acts as a source of e^- . These electrons flow from zinc to copper electrode through external circuit. The flow of electrons constitutes electric current.

AT ANODE $Zn \longrightarrow Zn^{2+} + 2e^-$

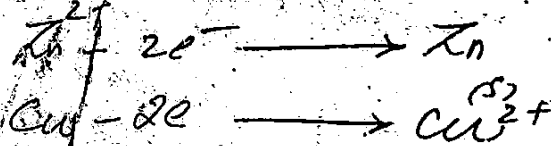
AT CATHODE $Cu^{2+} + 2e^- \longrightarrow Cu$

Overall cell reaction could be written as



In voltaic cell the electric current in external circuit can be used to light a bulb, drive a motor or for any other purpose.

The electrode reactions can be reversed by using a source of electricity which opposes the voltaic cell. Now external circuit pushes electrons in opposite direction the electrode reactions now become



Now oxidation takes place at copper and reduction at zinc. The electrical energy from an external source is used to bring about a chemical reaction which is otherwise not possible.

Important point in both electrolytic cell and Galvanic cell oxidation takes place at anode and reduction takes place at cathode.

WHAT ARE FUNCTIONS OF SALT BRIDGE:- A salt bridge is a U-shaped tube filled with an electrolyte such as KCl in gelatin. It serves three main purposes.

- 1) It allows electrical contact between two solutions.
- 2) It prevents mixing of two solutions.
- 3) It maintains electrical neutrality in each half cell.

A porous partition can also serve

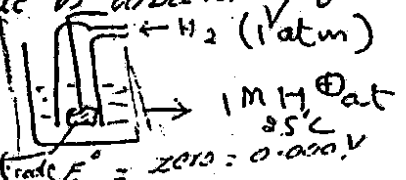
the same three purposes.

Q:- WRITE A NOTE ON STANDARD HYDROGEN ELECTRODE.

It is not possible to determine electrode potential of a single electrode. The potential of single electrode is determined by coupling it with a standard electrode.

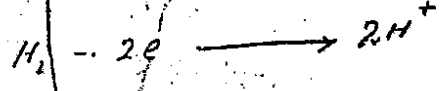
The electrode chosen as standard for determination of electrode potentials is "S.H.E"

A standard hydrogen electrode consists of a platinum foil coated with finely divided platinum. This is connected with a platinum wire and enclosed in a glass sleeve. Hydrogen gas is bubbled at this electrode at 1 atm pressure. This platinum electrode is immersed in 1M solution of HCl at 25°C. The electrode potential of such an electrode is arbitrarily fixed at zero at all temperatures.

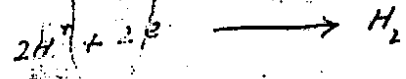


S.H.E. HALF REACTIONS

S.H.E ANODE



S.H.E CATHODE



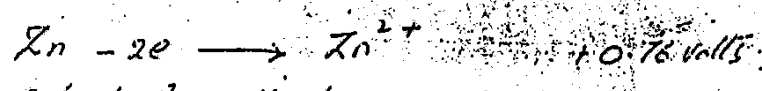
$$E^\circ = 0.000 V$$

Thus oxidation and reduction potentials of S.H.E are exactly 0.0.

DETERMINATION OF ELECTRODE POTENTIALS:-

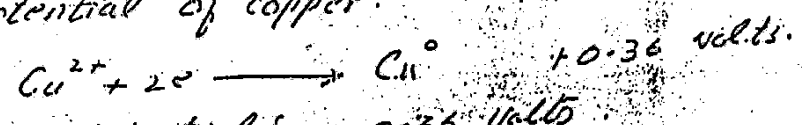
The electrode whose electrode potential is to be determined is connected to the S.H.E. The cell potential is determined from voltmeter, which shows deflection one way or the other. The cell potential is taken equal to potential of other electrode. If electrode under consideration act as anode when connected to SHE then its potential noted from voltmeter is its oxidation potential.

For example Dena zinc electrode is connected to SHE it acts as anode and shows cell potential 0.76. Thus its oxidation potential is +0.76.



Its reduction potential will be -0.76

On the other hand when copper is connected to S.H.E it act as cathode and cell potential is 0.36. Its reduction potential of copper.



Its oxidation potential is -0.36 volts

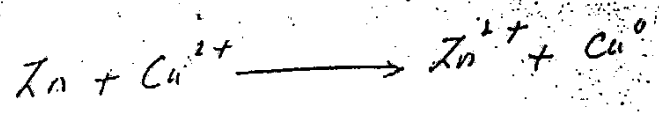
ELECTROCHEMICAL SERIES Different elements have been arranged according to increasing or decreasing values of oxidation or reduction potentials. This series of elements with respect to oxidation or reduction potentials is called electrochemical series. FOR APPLICATIONS OF ELECTROCHEMICAL SERIES SEE TEXT BOOK.

Q:- what is voltage of cell? Give its applications.

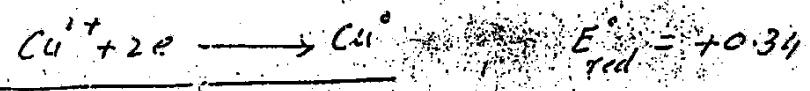
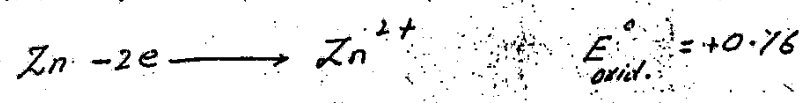
The algebraic sum of oxidation potential and reduction potentials of electrodes is called Cell potential.

$$E_{\text{cell}}^{\circ} = E_{\text{oxidation}}^{\circ} + E_{\text{reduction}}^{\circ}$$

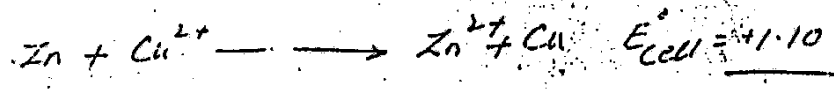
For example when zinc electrode is dipped in Zn^{2+}O_4 and copper electrode is dipped in CuSO_4 , the zinc acts as anode and copper as cathode. The cell reaction is



OXIDATION HALF REACTION:-



CELL REACTION



APPLICATION The voltage of cell can be used to determine whether a reaction will take place spontaneously or not. In other words it is used to determine whether a metal will displace another metal or not. For example consider following reactions

MODERN BATTERIES & FUEL CELLS FROM TEXT BOOK

Q. WHAT IS OXIDATION NUMBER? WRITE RULES OF ASSIGNING OXIDATION NUMBER?

Ans: Oxidation Number:- The apparent positive or negative charge which an atom would have, in an ion, radical or a molecule is called its oxidation number or oxidation state. The oxidation number can be assigned to any atom keeping in view following rules.

Rules:-

1. The oxidation number of elements in their elementary forms will always be zero.
2. The oxidation number of hydrogen in its binary compounds is +1 except in its hydrides. In hydrides oxidation no. of hydrogen is -1.
3. The oxidation number of oxygen in its binary compounds is -2 except in peroxides and superoxides. In peroxides its oxidation state is -1 and in superoxides it is -1/2. In F₂O its oxidation state is +2.
4. The oxidation number of alkali metals (Li, Na, K, Rb, Cs, Fr) is +1.
5. The oxidation number of alkaline earth metals is +2 (Ca, Mg, Be).
6. The oxidation number of 3rd group elements is +3.
7. The oxidation number of halogens is -1 in their binary comp.
8. The oxidation number of ion or radical is equal to charge on the ion or radical.
9. The sum of oxidation numbers of all elements present in a neutral molecule is always zero.
10. The same element can show different oxidation numbers in different compounds.

Calculate Oxidation Number of Each element in following compounds:-

DETERMINE OX. NO. OF FOLLOWING FOR PRACTICE

$KMnO_4, H_2CrO_4$
 $K_2Cr_2O_7, Na_3PO_4$
 $Cr_2(SO_4)_3, HNO_3$
 H_2SO_4

K_2CrO_4

$$2(+1) + Cr + (-2)4 = 0$$

$$K_2CrO_4$$

$$+2 + Cr - 8 = 0$$

$$Cr - 6 = 0$$

$$Cr = +6$$

$K_2Cr_2O_7$

$$2(+1) + 2Cr + (-2)7 = 0$$

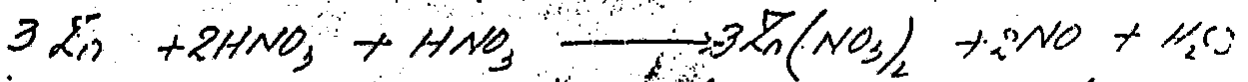
$$K_2Cr_2O_7$$

$$+2 + 2Cr - 14 = 0$$

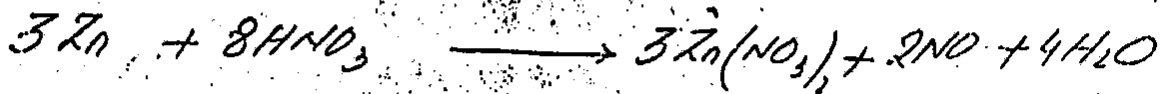
$$2Cr - 12 = 0$$

$$Cr = \frac{+12}{2}$$

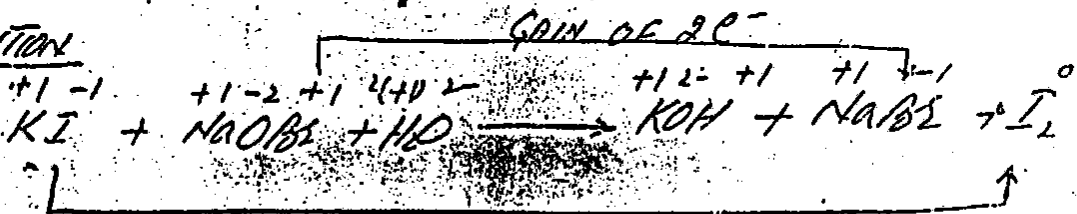
$$Cr = +6$$



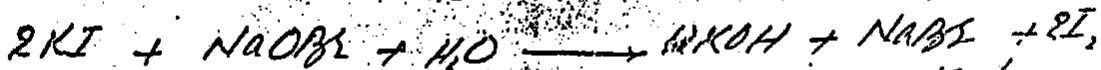
Now by inspection method balance other elements



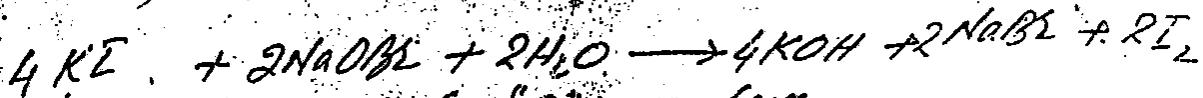
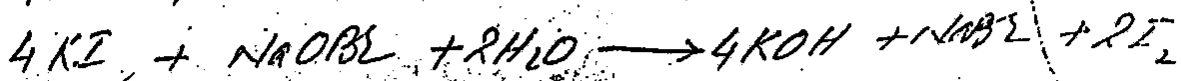
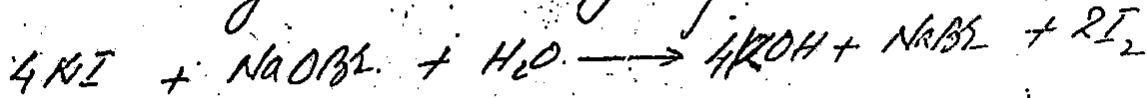
SOLUTION



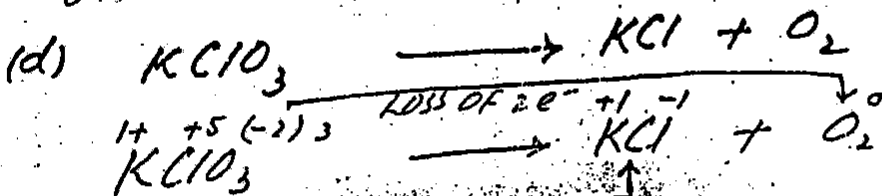
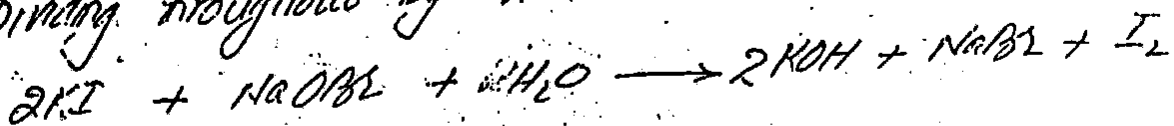
Loss of $1e^-$



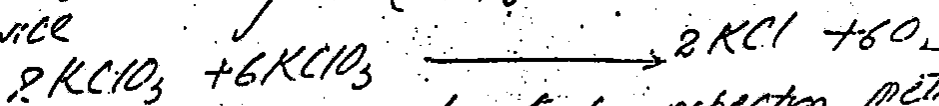
Now balancing other atoms by inspection method.



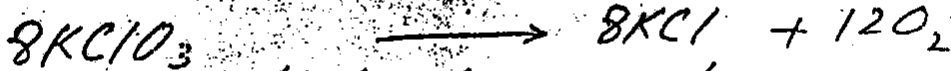
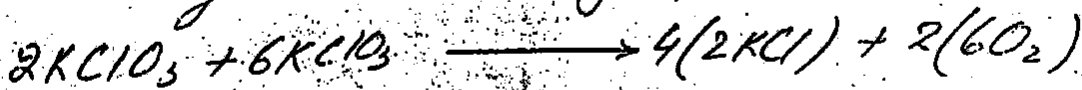
Dividing throughout by "2" we have



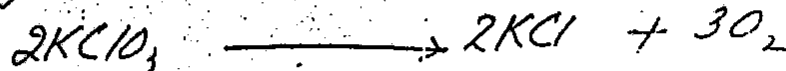
Since element undergoing oxidation and reduction are present in the same compound therefore this compound is written twice

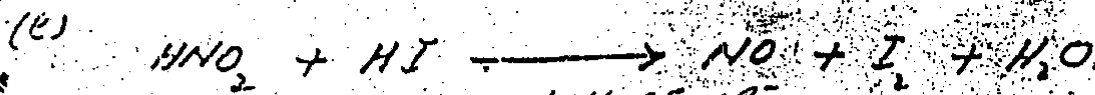


Now balancing other elements by inspection method

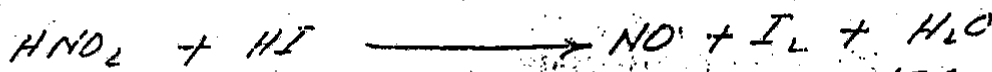
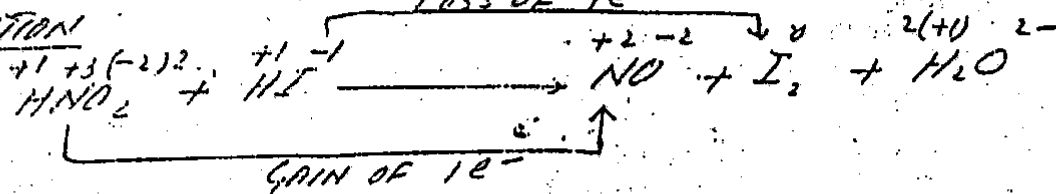


Dividing throughout by 4 we get

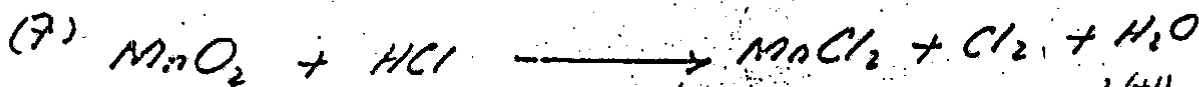
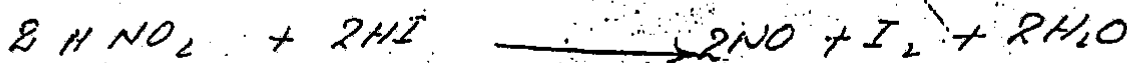




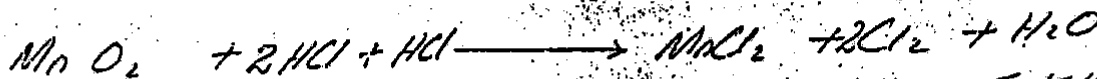
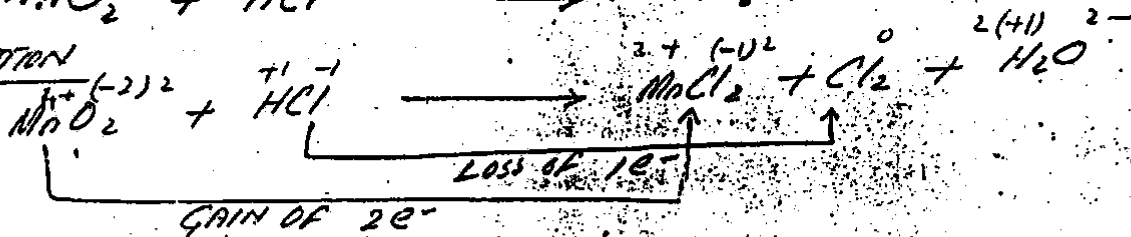
SOLUTION



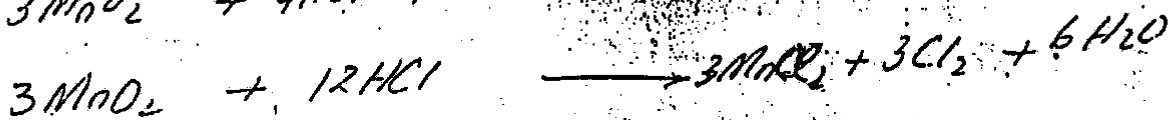
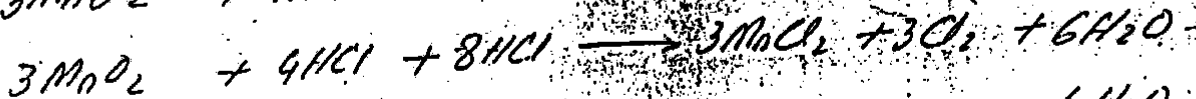
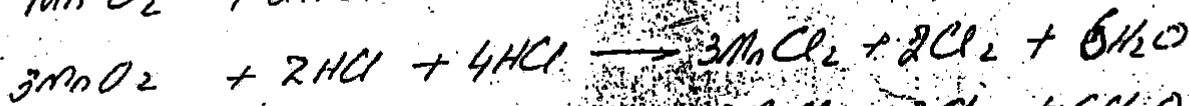
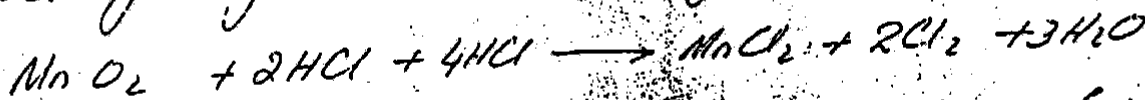
Now by inspection method balance other reactants & products



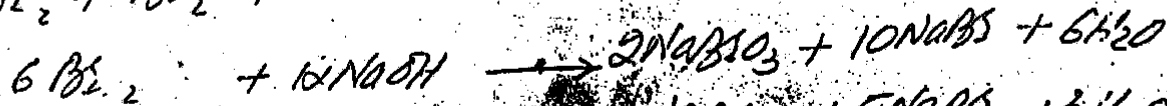
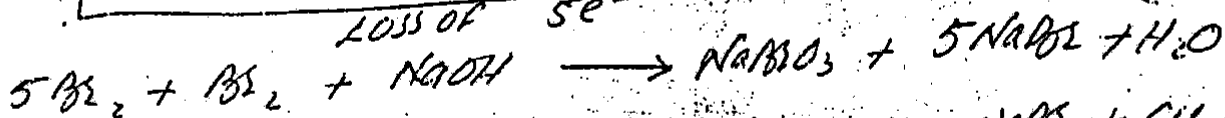
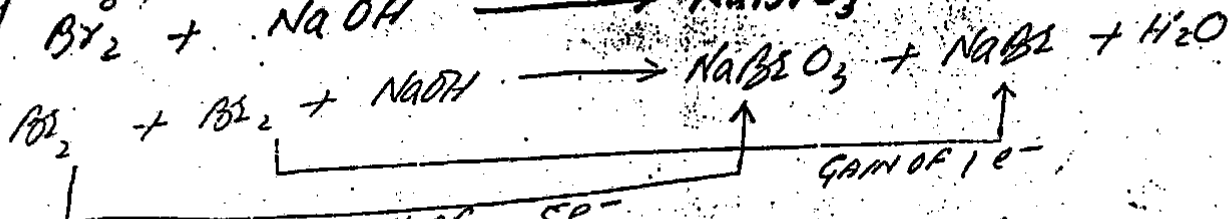
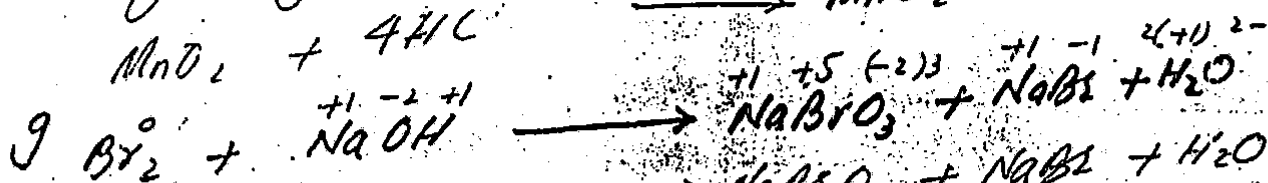
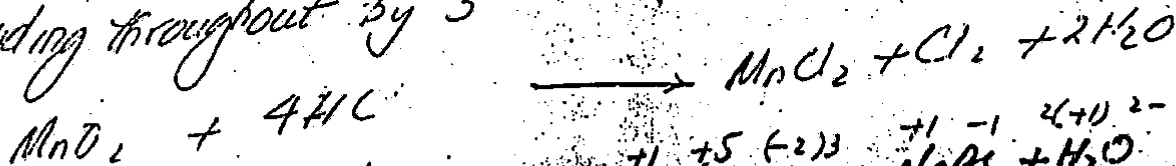
SOLUTION



Now by inspection method balancing other reactants & products



Dividing throughout by 3



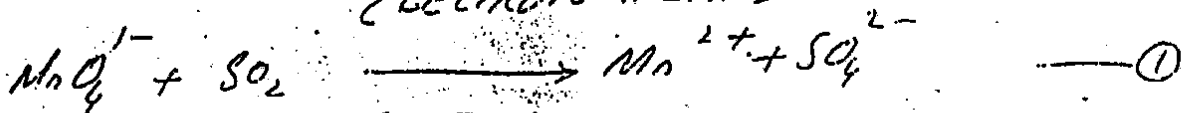
1.24 BALANCING OF EQUATIONS BY ION ELECTRON METHOD

PRINCIPLE The number of electrons lost by reducing agent must be equal to number of electrons gained by oxidizing agent

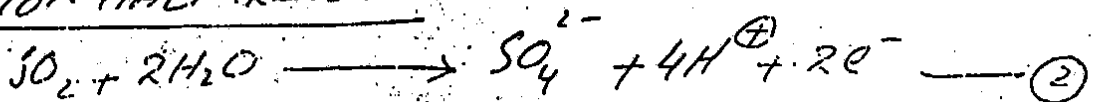
RULES FOR ION ELECTRON METHOD

1. Split the given equation into two half reactions. One is oxidation half reaction, other is reduction half reaction.
2. Balance each half reaction
3. In acidic medium, H⁺ is added to either side to balance oxygen and H⁺ are added to balance hydrogen
In basic medium OH⁻ is added to balance oxygen and H₂O is added to balance hydrogens
4. Electrons added to either side to balance charges
5. The oxidation half reaction is multiplied with the no. of electrons involved in reduction half reaction & vice versa
6. The two equations added to get net equation (the electrons are always cancelled out in final equation).

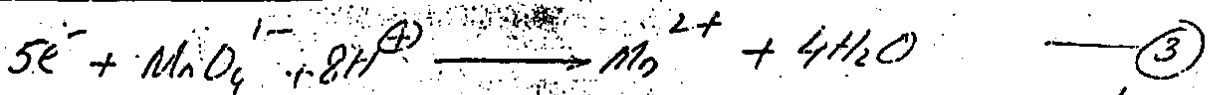
EXAMPLE NO. 6 Balance following equation by ION ELECTRON METHOD.



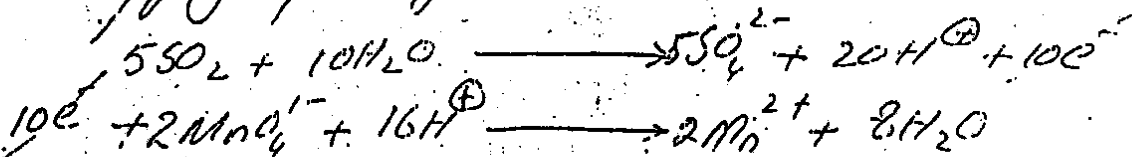
OXIDATION HALF REACTION



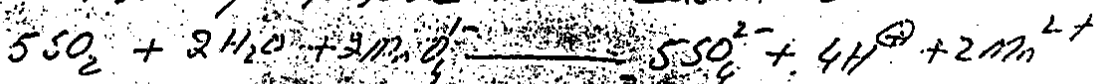
REDUCTION HALF REACTION



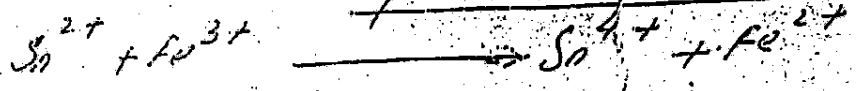
Multiplying eq. ② by 5 and eq. ③ by 2 we get



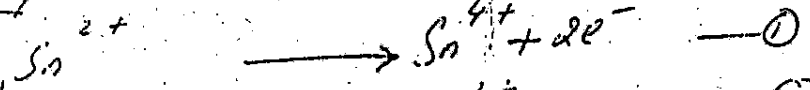
ON ADDING ABOVE TWO EQUATIONS



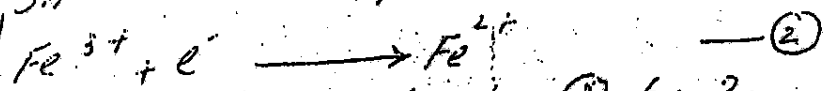
EXERCISE (Q. NO. 15) BALANCE THE FOLLOWING EQUATIONS BY ION ELECTRON METHOD



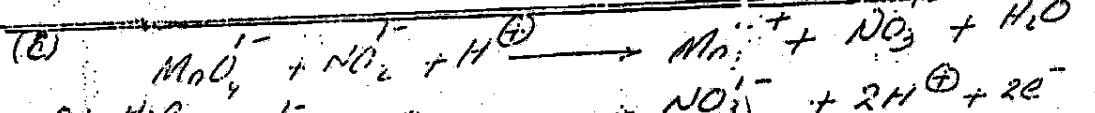
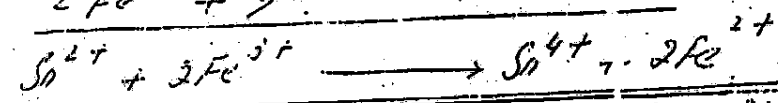
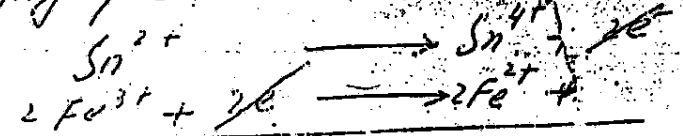
OX. H. R.



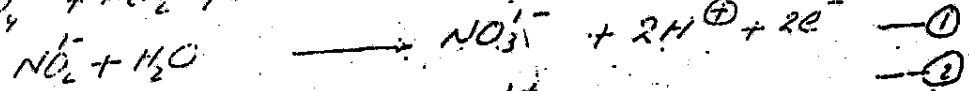
RED. H. R.



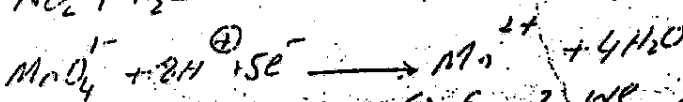
Multiplying eq. (1) with 1 and eq. (2) by 2.



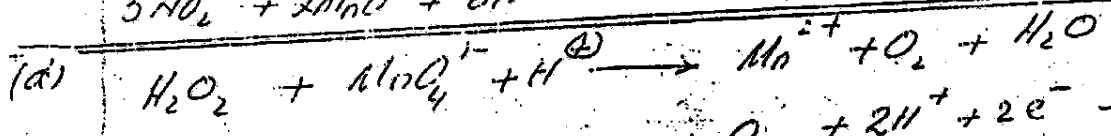
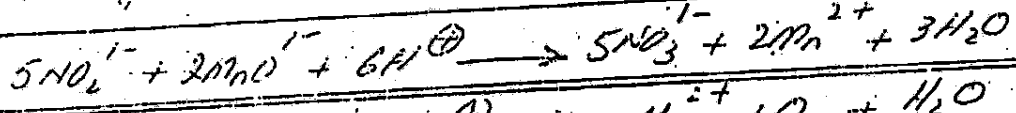
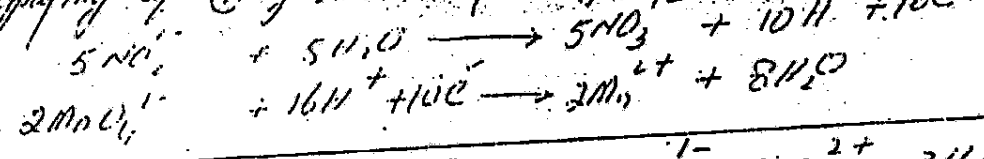
OX. H. R.



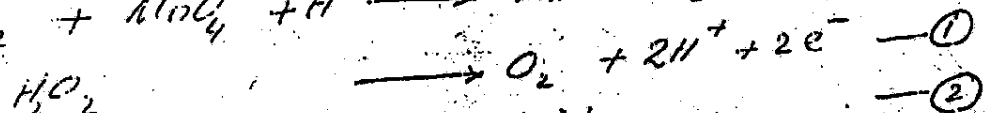
RED. H. R.



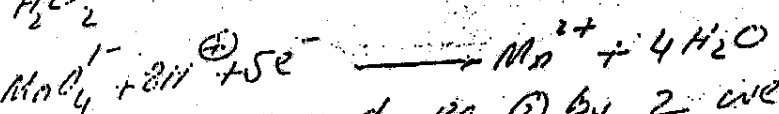
Multiplying eq. (1) by 5 and eq. (2) by 2 we get.



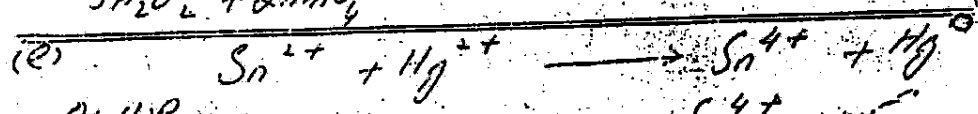
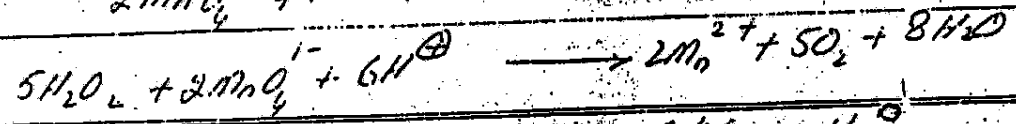
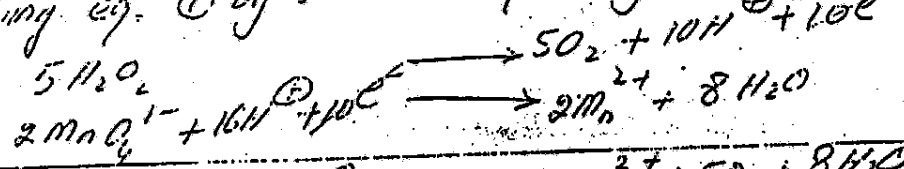
OX. H. R.



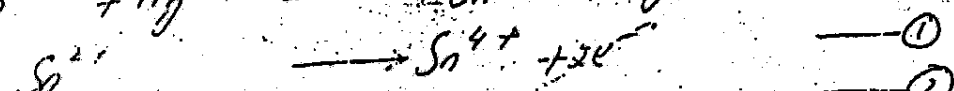
RED. H. R.



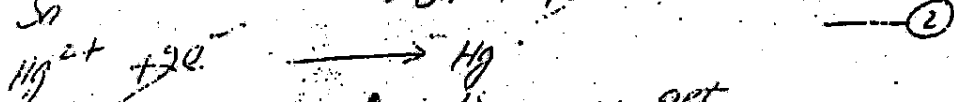
Multiplying eq. (1) by 5 and eq. (2) by 2 we get.



OX. H. R.

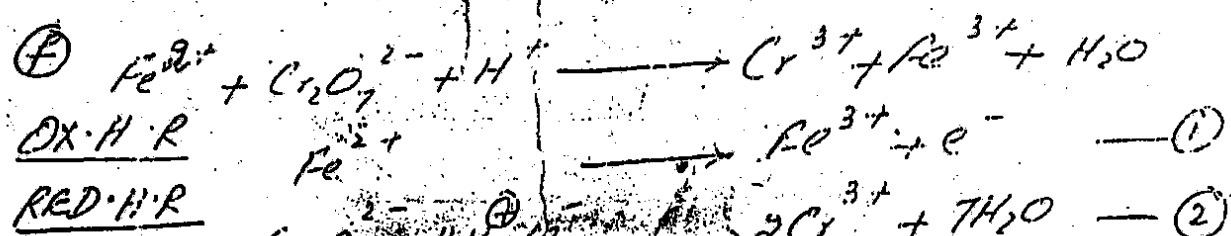


RED. H. R.

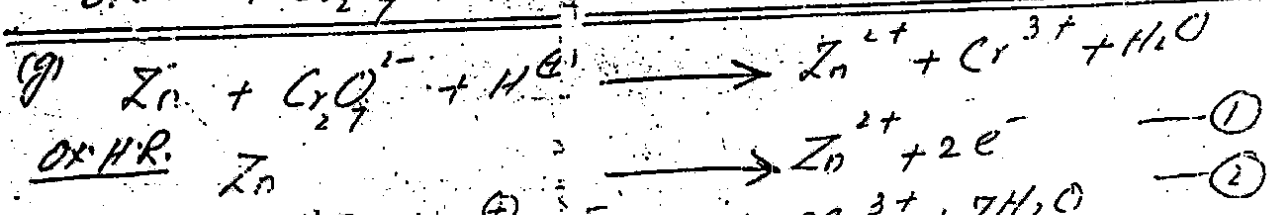
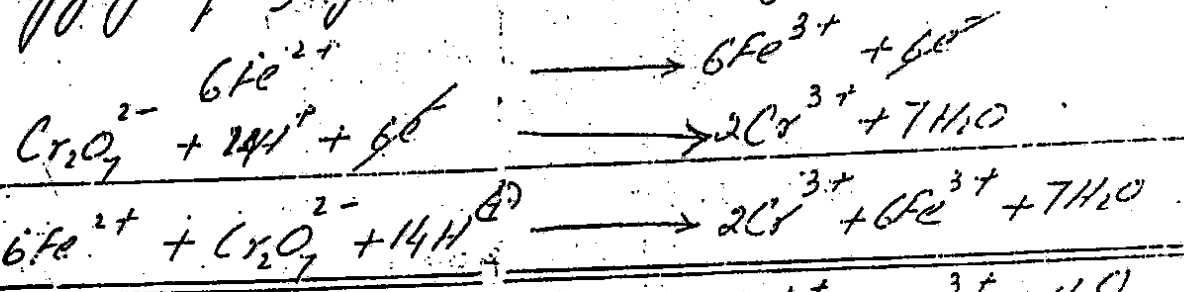


By adding above two equations we get

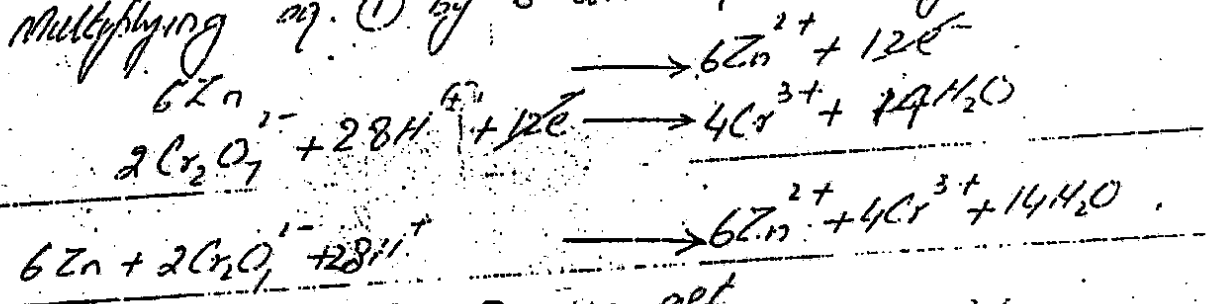




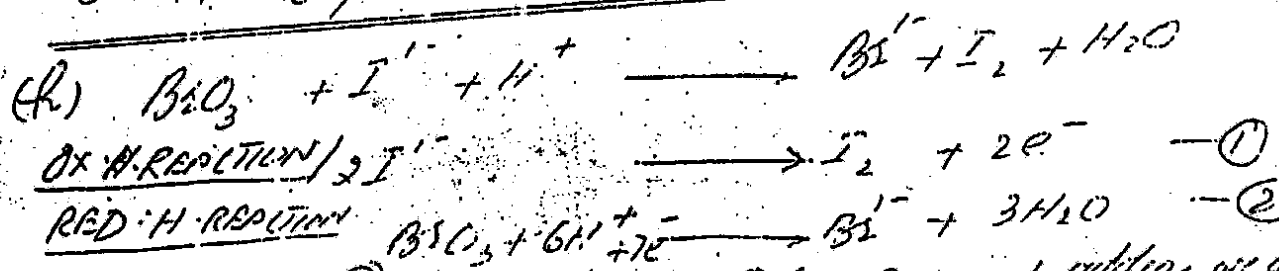
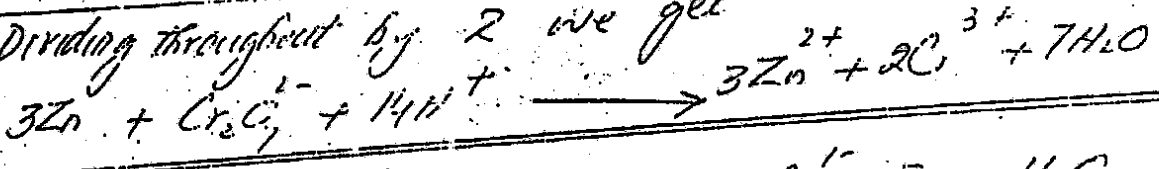
Multiplying eq (1) by 6 and eq (2) by 1 we get



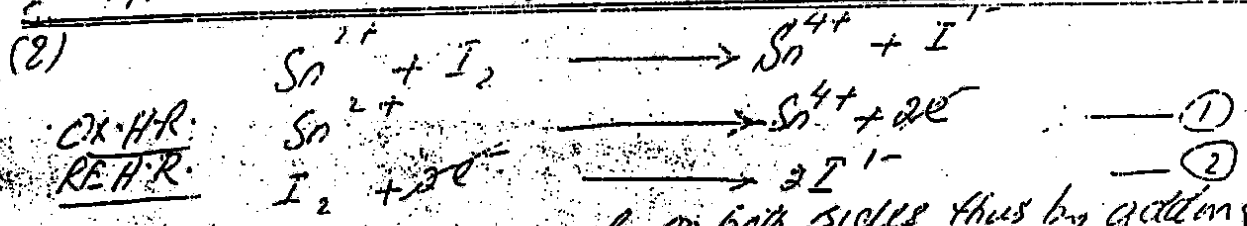
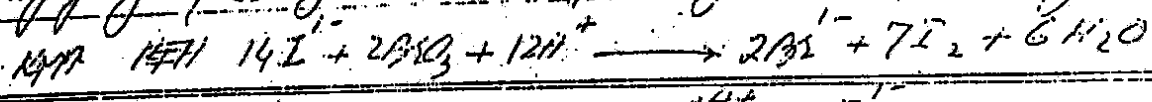
Multiplying eq. (1) by 6 and eq. (2) by 2 we get



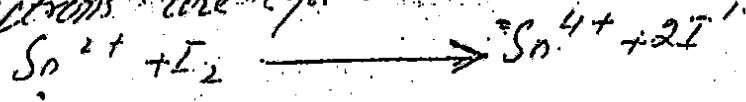
Dividing throughout by 2 we get



Multiplying eq (1) by 7 and eq. (2) by 2 and adding we get



Since electrons are equal on both sides thus by adding (1) & (2)



NOTE For eq. (b) SEE P.No. 38 of n.c.eo.