Chapter Ten

Oxidation-Reduction Titrations

10 Oxidation-Reduction Titrations

10.1 Some definitions:

Oxidation-Reduction reactions (redox):

They are processes involving transfer of electrons between the reactants. Volumetric methods based on electron transfer are more numerous and more variant than those for any other reaction type.

Oxidation : The loss of electrons by substance which terminates with an increase in oxidation number.

Reduction : The gain or acceptance of electrons which terminates with decrease in oxidation number.

In any oxidation-reduction reaction, the number of electrons lost by species is equal to the number of electrons gained by the other. This fact should be taken into account when balancing of oxidation-reduction reactions equations.

Oxidising agent (or oxidant) : The material which has high affinity to electrons i.e. it is the material which accepts the electrons given by reducing agent, thus the oxidant is reduced.

Reducing agent (or reductant) : The material which has the affinity to donate electrons to oxidising agent, thus the reductant is oxidised.

Therefore, the oxidation-reduction reactions involve the transfer of electrons from reducing agent to oxidising agent. The oxidising agents and reducing agents are varied from each other in their strength, i.e. their chemical activity. So, the strong oxidising agent have high ability to accept the electrons. They have the capability to remove or gain the electrons from reducing agents even they are weak. On other hand, the weak oxidising agents have not the ability to gain the electrons unless the corresponding

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reducing agents are strong enough. The process of loss or gaining electrons by an atom depends on its ionisation potential and its electron affinity.

10.2 Oxidation number.

It is defined as the number which refers to the atom or the element valence whether it is free or combined in a compound. The oxidation number may be positive or negative or equal zero. The oxidation number may be not representing the actual valence of the atom or element.

There are some rules which should be followed to calculate the oxidation number:

1- The oxidation number of the free atom or element equals zero, such as Na, Mg, Ba, H_2, and Cl_2, all their oxidation numbers = 0.

2- The oxidation number for simple ion equals its charge whether it is negative or positive. Therefore, the oxidation number of Fe^{3+} = +3, Zn^{2+} = +2, $Br^- = -1$, $Sn^{+4} = +4$, $S^{2-} = -2$, $H^+ = +1$ and $I^- = -1$ .....etc.

3- The oxidation number of oxygen in its compounds = -2 except for peroxides, the oxidation number = -1 and in fluoride compounds equals +2 such as OF_2 .

4- Oxidation number of hydrogen ion= +1 except in hydrides where the oxidation number equals -1 such as NaH and CaH_2 .

5- The algebric summation of the oxidation numbers of all atoms of the compound equals zero, such as $KMnO_4$: +1+7-8=0 and $K_2Cr_2O_7$: +2+12-14=0 .

6- The algebric summation of the oxidation numbers of all atoms of the ion equals the charge of the ions such as SO_4^{2-}: +6 -8 = -2 and MnO_4^- : +7 -8 = -1 .
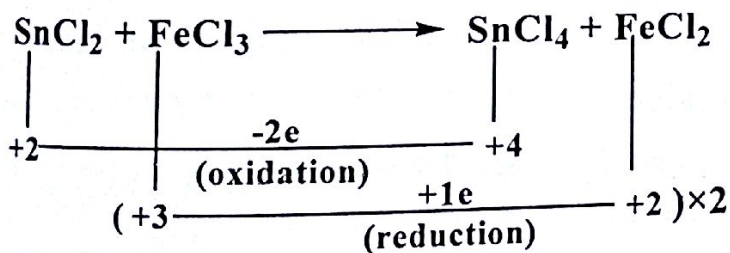
10.3 Balancing of oxidation-reduction equations.

Equations of oxidation-reduction reactions are clearly different from other equations. Therefore, two methods are available to balance these equations. Each equation contains oxidising and reducing agents and other species such as the neutral or acidic or basic medium and the water molecules.

10.3.1: Oxidation number method:

It involves writing the complete equation which contains all the reactants and products. The elements which are reduced and oxidised are identified. The change in oxidation number for each element is calculated in both sides of the equation.
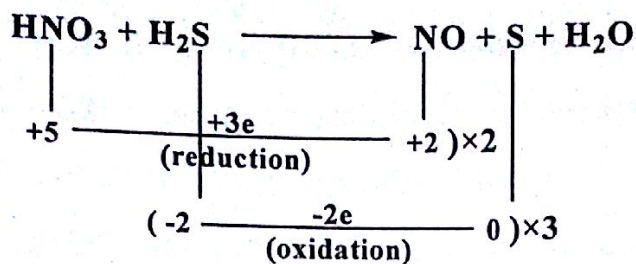
The number of accepted electrons is balanced with the number of donated electrons and finally the equation is balanced relative to the other atoms on both sides of the equation.
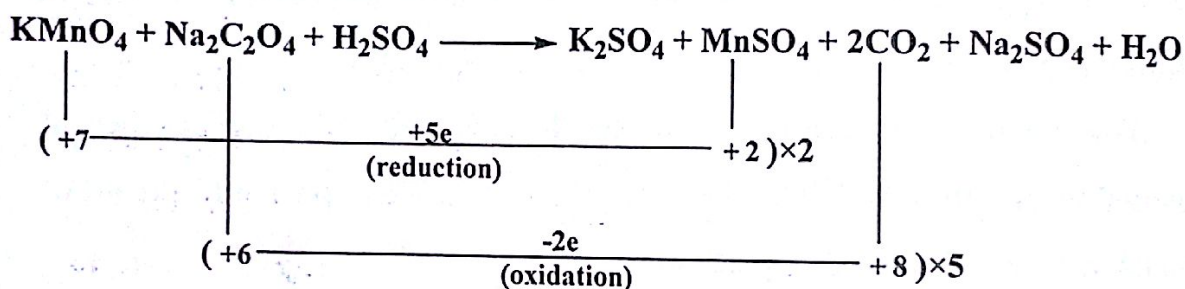
<u>Example(1)</u>: Reduction of $FeCl_3$ by $SnCl_2$:

$$SnCl_2 + FeCl_3 \longrightarrow SnCl_4 + FeCl_2$$

$+2$ $\underset{\text{(oxidation)}}{\overset{-2e}{\rule{4cm}{0.4pt}}}$ $+4$

$(+3 \underset{\text{(reduction)}}{\overset{+1e}{\rule{3cm}{0.4pt}}} +2)\times 2$

The one mole of reducing agent ($SnCl_2$) donates two electrons while one mole of $FeCl_3$ (oxidising agent) accepts one electron. The accepted electrons should equal the donated electrons, therefore, the change in oxidising number of Fe should be multiplied by 2 to balance the equation as follows:
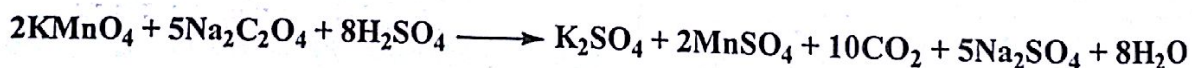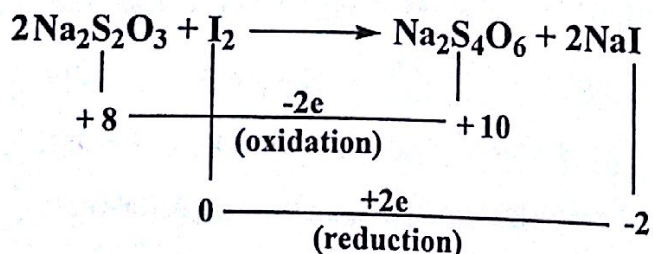
$$SnCl_2 + 2FeCl_3 \longrightarrow SnCl_4 + 2FeCl_2$$

Example(2):

$$HNO_3 + H_2S \longrightarrow NO + S + H_2O$$

$$+5 \xrightarrow[\text{(reduction)}]{+3e} +2 \;)\times 2$$

$$(-2 \xrightarrow[\text{(oxidation)}]{-2e} 0\;)\times 3$$

$$2HNO_3 + 3H_2S \longrightarrow 2NO + 3S + H_2O$$

The final equation takes into consideration the number of molecules of water:

$$2HNO_3 + 3H_2S \longrightarrow 2NO + 3S + 4H_2O$$

Example(3):

$$KMnO_4 + Na_2C_2O_4 + H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + 2CO_2 + Na_2SO_4 + H_2O$$

$$(+7 \xrightarrow[\text{(reduction)}]{+5e} +2\;)\times 2$$

$$(+6 \xrightarrow[\text{(oxidation)}]{-2e} +8\;)\times 5$$

$$2KMnO_4 + 10Na_2C_2O_4 + H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + Na_2SO_4 + H_2O$$

The final equation should consider the number of SO_4^{2-} groups on both sides and the number of water molecules:

$$2KMnO_4 + 5Na_2C_2O_4 + 8H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 10CO_2 + 5Na_2SO_4 + 8H_2O$$

Example(4):

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$

$$+8 \xrightarrow[\text{(oxidation)}]{-2e} +10$$

$$0 \xrightarrow[\text{(reduction)}]{+2e} -2$$

The donated electrons equal the accepted electrons. The other atoms should be balanced to write the equation in its final form:

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2NaI$$
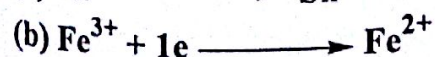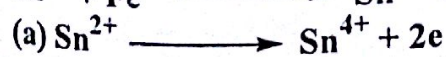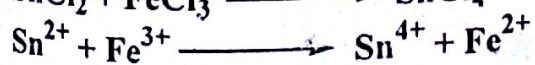
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10.3.2: Ion-electron method:

This method involves writing the complete equation into two half equations: one of them includes the oxidising agent and the other includes the reducing agent. So, in order to balance the equation according to this method, the following steps should be considered:

1- Writing the half equation which includes the reactants and products.

2- Each element should be balanced on both sides (except hydrogen and oxygen).

3- The oxygen is balanced by addition one water molecule for each oxygen atom on the opposite side. Hydrogen ions are used to balance hydrogen atoms in the neutral and acidic medium. In basic medium, oxygen atom is balanced by addition water molecule to the same side of the equation and $2OH^-$ to the other side. If there is unbalance in hydrogen atoms, hydroxyl group (OH^-) is added for each hydrogen atom in the same side and one molecule of water to the other side.

4- Charges on both side are balanced by addition integral number to one side of the equation.

5- Each half of the equation is multiplied by a suitable factor to balance the accepted electrons with the donated electrons.

6- The half equations are summated and the similar elements are summarised and the electrons are cancelled.

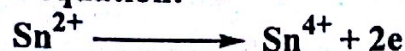7- The final equation is accurately inspected to balance each element atom on both sides.

Example(1): Reduction of $FeCl_3$ by $SnCl_2$:

$$SnCl_2 + FeCl_3 \longrightarrow SnCl_4 + FeCl_2$$
$$Sn^{2+} + Fe^{3+} \longrightarrow Sn^{4+} + Fe^{2+}$$

(a) $Sn^{2+} \longrightarrow Sn^{4+} + 2e$ oxidation equation

(b) $Fe^{3+} + 1e \longrightarrow Fe^{2+}$ reduction equation

Equation (b) is multiplied by 2 and added to equation (a) to get the final equation:

$$Sn^{2+} \longrightarrow Sn^{4+} + 2e$$

$$\underline{2Fe^{3+} + 2e \longrightarrow 2Fe^{2+} \qquad \text{Summation}}$$

$$Sn^{2+} + 2Fe^{3+} \longrightarrow Sn^{4+} + 2Fe^{2+}$$

Example(2):

$$HNO_3 + H_2S \longrightarrow NO + S + H_2O$$
(a) $H_2S \longrightarrow S$ oxidation equation
(b) $NO_3^- \longrightarrow NO$ reduction equation

Hydrogen atoms in oxidation equation is balanced:

$$H_2S \longrightarrow S + 2H^+ \qquad \text{oxidation equation}$$

Hydrogen and oxygen atoms in reduction equation are balanced:

$$NO_3^- + 4H^+ \longrightarrow NO + 2H_2O \qquad \text{reduction equation}$$
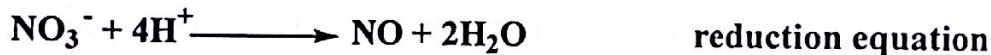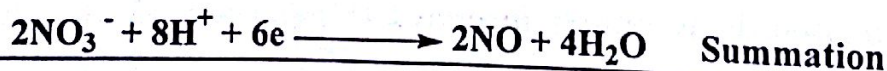
Charges on both sides of the equations are balanced by addition a certain number of electrons:

$$H_2S \longrightarrow S + 2H^+ + 2e$$

$$NO_3^- + 4H^+ + 3e \longrightarrow NO + 2H_2O$$
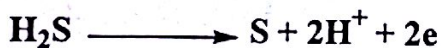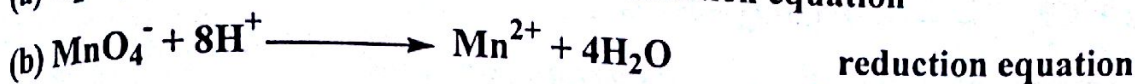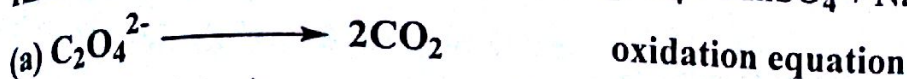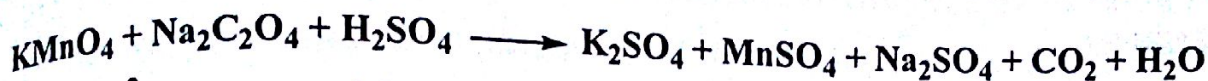
Oxidation equation is multiplied by 3, and reduction equation is multiplied by 2, and the half equation are added:

$$3H_2S \longrightarrow 3S + 6H^+ + 26$$
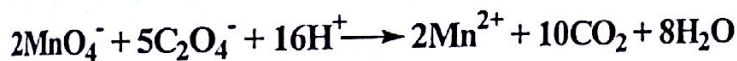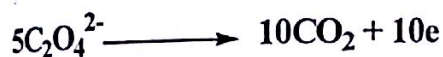
$$\underline{2NO_3^- + 8H^+ + 6e \longrightarrow 2NO + 4H_2O \qquad \text{Summation}}$$

$$3H_2S + 2NO_3^- + 2H^+ \longrightarrow 3S + 2NO + 4H_2O$$

The final equation is:

$$3H_2S + 2HNO_3 \longrightarrow 3S + 2NO + 4H_2O$$

Example(3):

$$KMnO_4 + Na_2C_2O_4 + H_2SO_4 \longrightarrow K_2SO_4 + MnSO_4 + Na_2SO_4 + CO_2 + H_2O$$

(a) $C_2O_4^{2-} \longrightarrow 2CO_2$ oxidation equation

(b) $MnO_4^- + 8H^+ \longrightarrow Mn^{2+} + 4H_2O$ reduction equation

Charges are balanced on both sides by addition suitable number of

electrons:

$$C_2O_4^{2-} \longrightarrow 2CO_2 + 2e$$
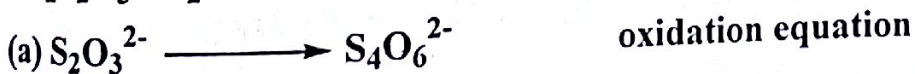
$$MnO_4^- + 8H^+ + 5e \longrightarrow Mn^{2+} + 4H_2O$$

The number of electrons are balanced in both equations and

summated:

$$5C_2O_4^{2-} \longrightarrow 10CO_2 + 10e$$

$$2MnO_4^- + 16H^+ + 10e \longrightarrow 2Mn^{2+} + 8H_2O$$
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$$2MnO_4^- + 5C_2O_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

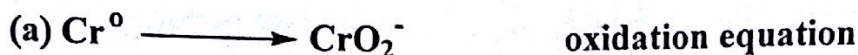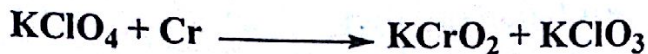The final equation is:

$$2KMnO_4 + 5Na_2C_2O_4 + 8H_2SO_4 \longrightarrow 2MnSO_4 + K_2SO_4 + 5Na_2SO_4 + 10CO_2 + 8H_2O$$

Example(4):

$$Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + NaI$$

(a) $S_2O_3^{2-} \longrightarrow S_4O_6^{2-}$ oxidation equation

(b) $I_2 \longrightarrow 2I^-$ reduction equation

$$2S_2O_3^{2-} \longrightarrow S_4O_6^{2-} + 2e$$

$$I_2 + 2e \longrightarrow 2I^-$$
_____

$$2S_2O_3^{2-} + I_2 \longrightarrow S_4O_6^{2-} + 2I^-$$

The final equation is:

$$2Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2I^-$$
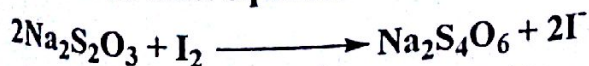
10.3.3: Balancing of oxidation-reduction equations in basic media.

Example:

$$KClO_4 + Cr \longrightarrow KCrO_2 + KClO_3$$

(a) $Cr^o \longrightarrow CrO_2^-$ oxidation equation

(b) $ClO_4^- \longrightarrow ClO_3^-$ reduction equation
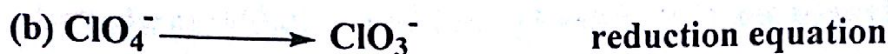
$2H_2O$ is added to the right side of the oxidation equation and $4OH^-$ to the left.

$2OH^-$ is added to the right side of the reduction equation and H_2O to the left side.

$$Cr^o + 4OH^- \longrightarrow CrO_2^- + 2H_2O$$

$$ClO_4^- + H_2O \longrightarrow ClO_3^- + 2OH^-$$

Charges are balanced on both sides:

$$Cr^o + 4OH^- \longrightarrow CrO_2^- + 2H_2O + 3e$$

$$ClO_4^- + H_2O + 2e \longrightarrow ClO_3^- + 2OH^-$$
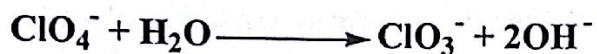
The number of accepted and donated electrons are balanced:

$$2Cr^o + 8OH^- \longrightarrow 2CrO_2^- + 4H_2O + 6e$$

$$3ClO_4^- + 3H_2O + 6e \longrightarrow 3ClO_3^- + 6OH^- \qquad \text{summation}$$

$$3ClO_4^- + 2Cr^o + 2OH^- \longrightarrow 3ClO_3^- + 2CrO_2^- + H_2O$$
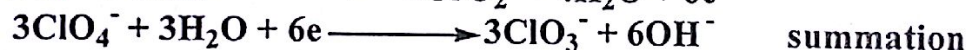
The final equation is written as following:

$$3KClO_4 + 2Cr + 2KOH^- \longrightarrow 3KClO_3 + 2KCrO_2 + H_2O$$

The equation is balanced by oxidation number as following:

$$KClO_4 + Cr + KOH^- \longrightarrow KClO_3 + KCrO_2 + H_2O$$

$$(+7 \underset{\text{reduction}}{\overset{+2e}{\rule{3cm}{0.4pt}}} +7) \times 3$$

$$(0 \underset{\text{oxidation}}{\overset{-3e}{\rule{3cm}{0.4pt}}} +3) \times 2$$
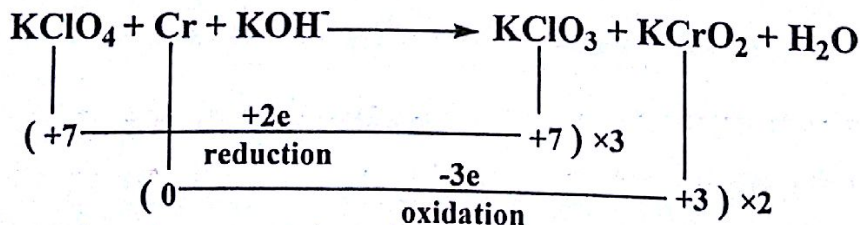
The final equation becomes:

$$3KClO_4 + 2Cr + 2KOH^- \longrightarrow 3KClO_3 + 2KCrO_2 + H_2O$$

10.4 Electrochemical cells:

The electrical current is defined as a flow of electrons or transition of electrons. Therefore, the oxidation-reduction reactions are reactions at which the electrical current is generated and transferred from the reducing agent into the oxidising agent.
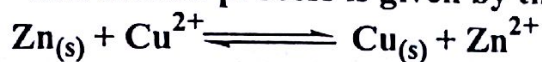
If a strip of copper is partially immersed in a copper sulphate solution, the copper ions migrate and are reduced at the surface of copper.

$$Cu^{2+} + 2e \rightleftharpoons Cu_{(s)}$$
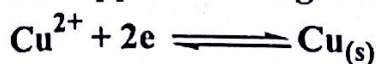
Meanwhile, an equivalent quantity of zinc is oxidised and dissolved in the solution.

$$Zn_{(s)} \rightleftharpoons Zn^{2+} + 2e$$
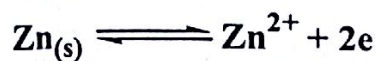
The overall process is given by the sum of these half reactions:

$$Zn_{(s)} + Cu^{2+} \rightleftharpoons Cu_{(s)} + Zn^{2+}$$

or $Zn_{(s)} + CuSO_4 \rightleftharpoons ZnSO_4 + Cu_{(s)}$

The reduction of ferric chloride ($FeCl_3$) by stannous chloride ($SnCl_2$) can be expressed by the following reaction:

$$2FeCl_3 + SnCl_2 \rightleftharpoons 2FeCl_2 + SnCl_4$$

or $2Fe^{3+} + Sn^{2+} \rightleftharpoons 2Fe^{2+} + Sn^{4+}$

Therefore, one gram atom of Fe(III) (55.85g) requires 96500 coulombs (or faraday) in order to be reduced to Fe(II). Also, one gram atom of Sn(II) requires 2X96500 coulombs to be oxidised to Sn(IV).

Figure (10-1) shows two beakers, one of them contains $SnCl_2$ solution and the other contains $FeCl_3$ solution. Both solutions are acidified with dilute hydrochloric acid to increase their conductivities.

In each solution, a thin plate of platinum is immersed to behave as metalic electrodes which are connected externally by a cable involving millimeter and internally by saltbridge which is glass tube in the form of inverse U and it contains gel or gelatin saturated with KCl.

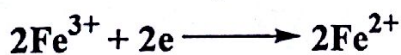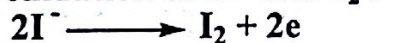The advantage of this salt bridge is to connect the two solutions without mixing them.

When this cell is closed, the current is clearly transferred from $SnCl_2$ solution to $FeCl_3$ solution as shown in figure (1).

$$Pt \, (A) \, Sn^{2+}, Sn^{4+} \, || \, (B) \, Fe^{3+}, Fe^{2+} \, / \, Pt$$
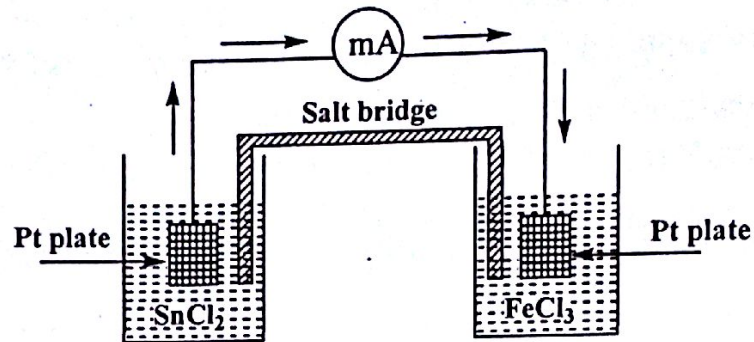
Fig(10-1): Schematic diagram of an oxidation-reduction cell which involves the transition of electrons from $SnCl_2$ to $FeCl_3$ solution.

After a while, Sn^{4+} ions can be detected in beaker A and Fe^{2+} ions in beaker B. If KI in beaker A is used instead of $SnCl_2$ as a reducing agent, the current is also transferred and the solution becomes yellow indicating the oxidation of $2I^-$ into I_2 .

$$2I^- \longrightarrow I_2 + 2e$$

$$2Fe^{3+} + 2e \longrightarrow 2Fe^{2+}$$

$$\overline{\phantom{2Fe^{3+} + 2I^- \rightleftharpoons I_2 + 2Fe^{2+}}}$$

$$2Fe^{3+} + 2I^- \rightleftharpoons I_2 + 2Fe^{2+}$$
$$\text{yellow}$$

The platinum plate in beaker A is called the anode and that in beaker B is called the cathode. The current is transferred in the above electrical cell as a result of the electromotive force (EMF) which is generated as a result of the chemical change of oxidation-reduction reaction (or as a result of the difference potential between the electrodes).

10.5 Types of electrochemical cells:

10.5.1 Galvanic cells (Voltaic cells):

They are cells at which a chemical reactions take place where the chemical energy is changed into electrical energy.

Galvanic cell is due to Luigi Galvani and voltaic cell is due to Alessandro Volta who had discovered this type of cells.

The reader finds the following group of galvanic cells:

10.5.1.1 Daniel Cell

This cell consists of two electrodes; one of them is a rod of zinc immersed partially in zinc sulphate solution. The second electrode is a rod of copper immersed partially in copper sulphate solution (Fig 10.2). The electrodes are connected by a conductive wire such as copper wire connected to milliameter or millivoltmeter. Both solutions are connected by a salt bridge made of potassium chloride. When the circuit is closed, the following reactions occur:

The zinc rod is oxidised to give zinc ions which transfer into the solution and the emitted electrons are transferred across the copper wire

$$Zn_{(s)} \longrightarrow Zn^{2+} + 2e$$
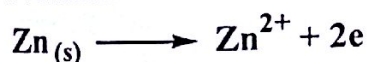
The Zinc rod becomes the positive electrode. On other electrode, the copper ions in the solution are reduced and precipitated on the electrode.

$$Cu^{2+} + 2e \longrightarrow Cu_{(s)}$$

The copper electrode becomes the negative electrode. The total reaction is:

$$Zn_{(s)} + Cu^{2+} \longrightarrow Zn^{2+} + Cu_{(s)}$$

The cell continues in its work (oxidation-reduction reaction) until all Zn is consumed and dissolved in the solution and all Cu^{2+} is deposited on the electrode and then the cell has consumed all its energy.

ZnSO₄ Solution (1M)

$$Zn_{(s)} + Cu^{2+} \longrightarrow Zn^{2+} + Cu_{(s)}$$
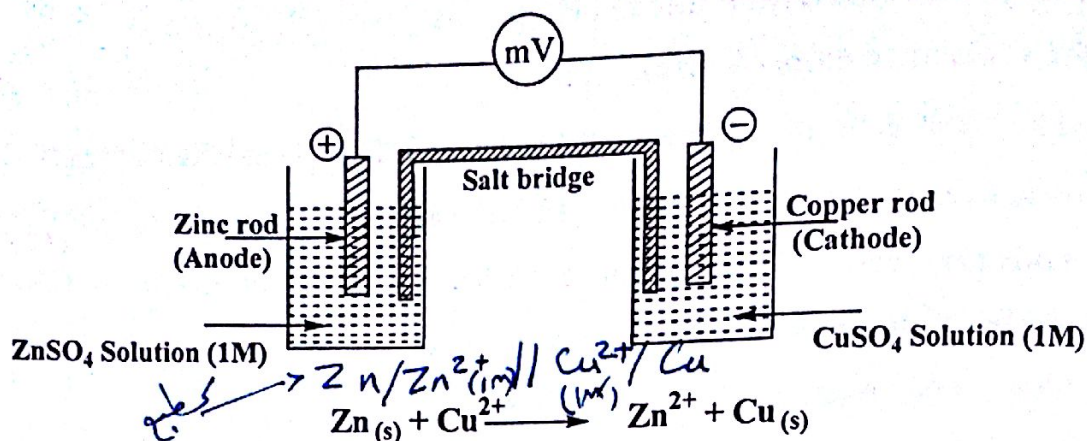
Fig(10-2): Daniel Galvanic cell

10.5.1.2 Wetson standard cell

The negative electrode consists of two phases of cadmium amalgam (about 12.5% Cd W/W).

Saturated cadmium sulphate is in contact with excess of its solid crystal to insure saturation in different temperatures. It is saturated also with Hg_2SO_4. The cell is designed as glass device in H form (Fig 10.3).

The activities of the participated materials on the electrode reactions are constant in any given temperature. Therefore, the voltage difference is constant since all the solutions are saturated.
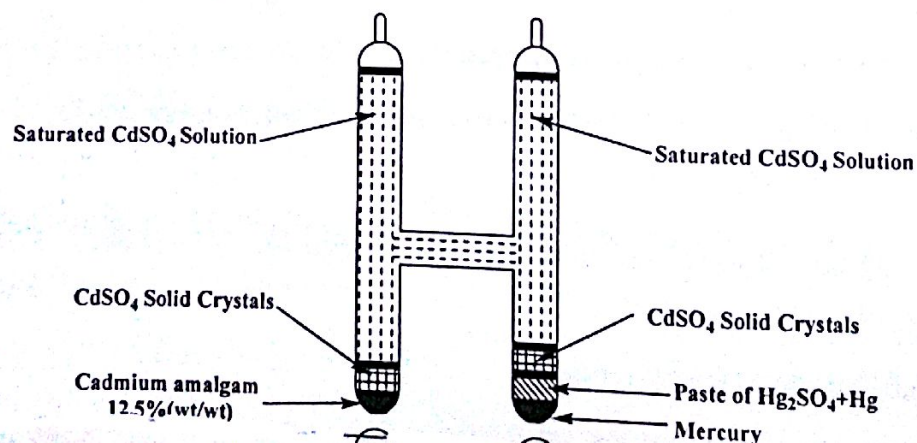

Fig (10-3): Weston standard cell (Galvanic cell).

When Weston cell is in use, some of its current is lost, therefore, the chemical species activities are lowered with a following little decrease of its electromotive force. But the cell retains its electromotive force gradually by several solubility equilibria. The cell should be kept from high change in temperatures especially the sudden changes.

10.4.1.3 The lead accumulator:

It is called also lead battery (or car battery). It is galvanic or voltaic liquid cell. It consists of two groups of plates or hollow plates. The first group is filled with PbO_2 and the second group is filled with spongeous lead. Both groups are immersed in sulphuric acid (30% W/W). When both groups are connected by suitable circuit, the electrons are flowing from lead plate to PbO_2 plate. The following changes are occurred in this cell in order to keep the potential variance at 12 volts.
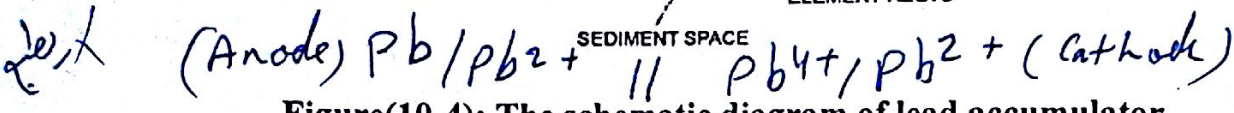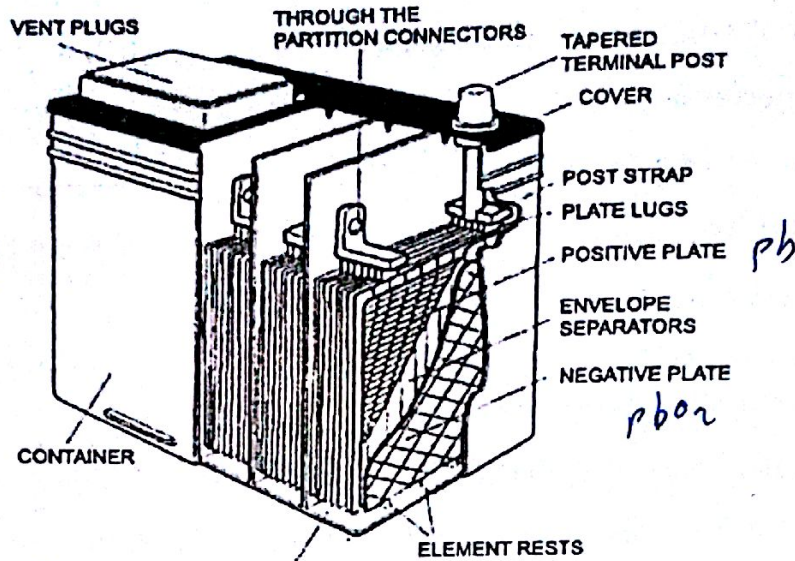
On the cathode (PbO_2 electrode):

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e \longrightarrow PbSO_4 + 2H_2O$$

Or $Pb^{4+} + 2e \longrightarrow Pb^{2+}$
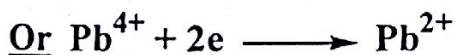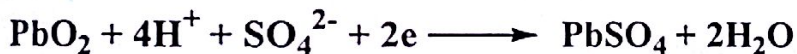
On the anode (Pb electrode):

$$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e$$

Or $Pb \longrightarrow Pb^{2+} + 2e$

As a result of this variations, the plates will be covered with $PbSO_4$ and the concentration of H_2SO_4 will be lowered in addition to its specific gravity. These changes are occurred gradually depending on frequent use of the cell. Fig (10.4) is a schematic diagram of lead accumulator involving of six plates.

VENT PLUGS

THROUGH THE
PARTITION CONNECTORS

TAPERED
TERMINAL POST

COVER

POST STRAP

PLATE LUGS

POSITIVE PLATE pb

ENVELOPE
SEPARATORS

NEGATIVE PLATE pbO_2

CONTAINER

ELEMENT RESTS

SEDIMENT SPACE

$(Anode) \; Pb / Pb^{2+} \; || \; Pb^{4+} / Pb^{2+} \; (Cathode)$

Figure(10-4): The schematic diagram of lead accumulator.

If a sufficient voltage difference is used in opposite directions for the current flowing, the former reactions can be reversed.

The charging process of this battery should be done periodically if it is wanted for the battery to continue in its electrical energy. The electrical energy is then stored into chemical energy:

$$Pb + PbO_2 + 2H_2SO_4 \underset{\text{charging}}{\overset{\text{discharging}}{\rightleftharpoons}} PbSO_4 + 2H_2O$$
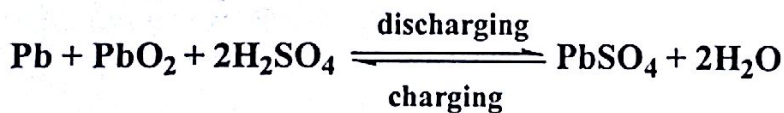
Every pair of plates (one of them is Pb and the second is PbO_2) produces potential equals 2 volts. Most of cars use batteries of 6 volts or 12 volts.

10.5.1.4 The dry cell

It is called also Leclanch's cell. It is consisted of graphite cathode surrounded with paste of NH_4Cl, $ZnCl_2$, carbon black, starch and MnO_2 (to forbid polarization). The whole components of the cell is covered with zinc cover which behaves as anode.

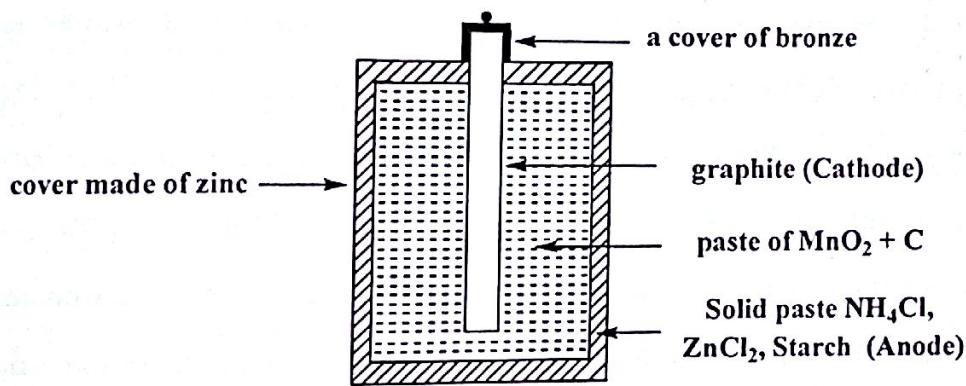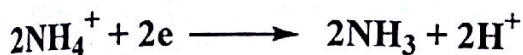When the cell is working, the following reactions take place:

On the anode:

The zinc/dissolved (oxidised) in the solution and left the electrons/on the surface of zinc:

$$Zn \longrightarrow Zn^{2+} + 2e$$
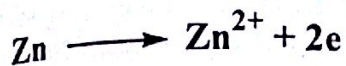
On the cathode:

The ammonium ions are discharged (reduced) from graphite which conducts the electrons:

$$2NH_4^+ + 2e \longrightarrow 2NH_3 + 2H^+$$

a cover of bronze

cover made of zinc

graphite (Cathode)

paste of MnO_2 + C

Solid paste NH_4Cl, $ZnCl_2$, Starch (Anode)

$Zn/Zn^{2+} // NH_4^+, NH_3, H^+$

Fig(10.5): Longitudinal section of dry cell.

The action of MnO_2 is to prevent the formation of hydrogen bubbles on cathode by oxidation hydrogen ions into water:

$$2MnO_2 + 2H^+ \longrightarrow Mn_2O_3 + H_2O$$

Ammonia is distributed through the electrolyte and combined with $ZnCl_2$ to form the following complex:

$$2NH_3 + ZnCl_2 \longrightarrow Zn(NH_3)_2Cl_2$$
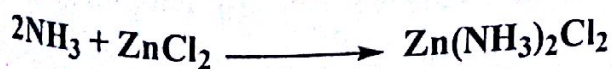
Although the emf of the single cell is 1.5V, but higher voltages are obtained by connecting a series of cells respectively which is called then a Battery.

This cell is characteristic with its suitability for working and it is easily carried, connected, transferred and used whatever is needed. This cell is irreversible and rejected after using it (discharging).

10.5.2 Electrolytic cells

The electrolytic cells are defined as the cells which could not be operated unless they are provided with an external source of electrical energy. The Daniel cell which contains positive zinc electrode and negative copper electrode can be operated as electrical cell when it is connected with a source pf electrical energy such as battery or external circuit of electrical energy. In this case, the process is reversed and the electrons are forced to flow in the opposite direction through the cell. Therefore, the copper electrode becomes the positive electrode and the zinc electrode becomes the negative electrode. The reactions on the electrodes are reversed and zinc would deposit and copper would dissolve.

$$Zn^{2+} + 2e \longrightarrow Zn_{(s)} \qquad \text{on negative electrode.}$$

$$Cu_{(s)} \longrightarrow Cu^{2+} + 2e \qquad \text{on positive electrode.}$$

The over all reaction becomes:

$$Zn^{2+} + Cu_{(s)} \longrightarrow Zn_{(s)} + Cu^{2+}$$
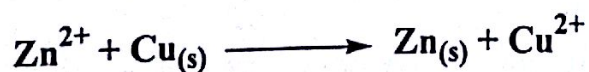
This process would consume energy from the battery or any type of external energy. If the above reactions are carried on, all copper will dissolve and all zinc will deposit.

10.5.2.1 Downs cell

It is another example of the electrical cell which requires external energy to be operated.

This cell represents the electrolysis of fused sodium chloride.

Solid sodium chloride is non-conductive although the ions can be found rotating about the constant centers because they have no free motion in the crystal lattice of the salt. But it was proved (practically) that fused NaCl (fused at 801°C) is an excellent conductive/because the ions are free by moving and transferring.

If we have two graphite electrodes, they constitute the electrodes of the cell connected to an external electrical current. Both electrodes are immersed in fused NaCl which has been heated at temperature above 801°C. When the electrical current flows through this cell, the following reactions occur on the electrodes:

1- Liberation of greenish-yellow gas of Cl_2 on the anode as a result of oxidation of $2Cl^-$ to Cl_2:

$$2Cl^- \longrightarrow Cl_{2 (g)} + 2e$$

2- The reduction of Na^+ on the cathode to form sodium metal which goes up the surface of fused NaCl (because of its lower density).
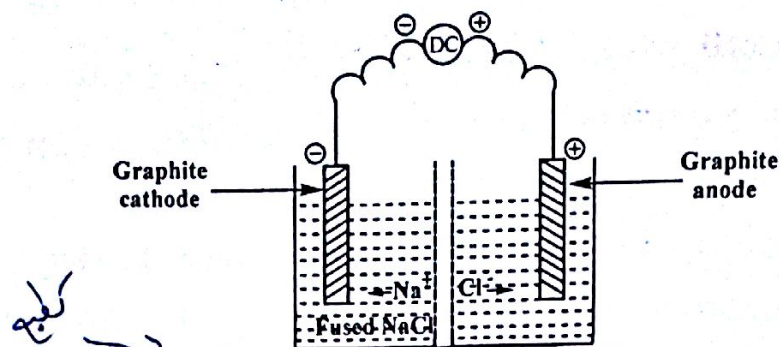
$$2Na^+ + 2e \longrightarrow 2Na_{(l)}$$

The overall reaction is:

$$2Cl^- + 2Na^+ \longrightarrow Cl_2 + 2Na_{(l)}$$

The electrons are generated on the anode and consumed on the cathode.

Fig(10-6) shows a schematic diagram of this Downs cell.
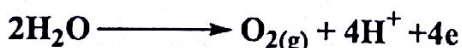
207

$$Na^+/Na \; || \; 2Cl^-/Cl_2$$

Fig(10-6): Electrolysis instrument of fused NaCl.

10.6 Anode and cathode

So far, we have considered a cell as being composed of two half cells, each of which associated with the process occurring at one of the electrodes. However, it is impossible to operate one half cell independently of the second. Also, the potential of an individual half-cell can not be measured without reference to another.

Anode:

It is the half cell where on it oxidation takes place as shown in the following reactions:

$$Cd_{(s)} \longrightarrow Cd^{2+} + 2e$$
$$2Cl^- \longrightarrow Cl_{2\,(g)} + 2e$$
$$Fe^{2+} \longrightarrow Fe^{3+} + e$$
$$2H_2O \longrightarrow O_{2(g)} + 4H^+ + 4e$$

Water is oxidised when the solution contains no easily oxidised species.

Cathode:

It is the half-cell where on it reduction takes place as shown in the following reactions:

$$Ag^+ + e \longrightarrow Ag_{(g)}$$
$$2H^+ + 2e \longrightarrow H_{2\,(g)}$$
$$Fe^{3+} + e \longrightarrow Fe^{2+}$$
$$NO_3^- + 10H^+ + 8e \longrightarrow NH_4^+ + 3H_2O$$