# 6. Redox Reactions

## 6.1 Introduction

**Can you tell?**

1. Why does cut apple turn brown when exposed to air ?
2. Why does old car bumper change colour?
3. Why do new batteries become useless after some days ?

Redox is an abbreviation used for the terms 'oxidation and reduction'. A large number of phenomena such as respiration, rusting, combustion of fuel involve redox reactions.

**Can you recall?**

1. What is combustion reaction?
2. Write an equation for combustion of methane.
3. What is the driving force behind reactions of elements?

### 6.1.1 Classical ideas of redox reactions

Classically oxidation refers to combination of an element or a substance with oxygen.

For example, Oxidation of carbon

$$C\,(s) + O_2\,(g) \longrightarrow CO_2\,(g) \quad \cdots\cdots (6.1)$$

Oxidation of magnesium

$$2\,Mg + O_2 \longrightarrow 2\,MgO(s) \quad \cdots\cdots (6.2)$$

In reaction (6.1) and (6.2) the carbon and magnesium are oxidized on reacting with oxygen. Now consider the reaction :

$$2\,Fe_2O_3 + 3\,C\,(s) \rightarrow 4\,Fe\,(s) + 3\,CO_2\,(g) \quad \cdots\cdots (6.3)$$

In this reaction there is removal of oxygen from $Fe_2O_3$. Hence it is a **reduction reaction**.

Further

$$2H_2S\,(g) + O_2\,(g) \longrightarrow 2\,S\,(s) + 2\,H_2O\,(l) \quad \cdots\cdots (6.4)$$

In this reaction there is removal of hydrogen and is also called **oxidation**. Here the sulfur in $H_2S$ loses hydrogen and undergoes oxidation while oxygen accepts hydrogen and undergoes reduction.

**Oxidants/ Oxidising agent :** A reagent/ substance which itself undergoes reduction and causes oxidation of another species is called **oxidant /oxidising agent**. Now consider some more examples.

$$Mg(s) + F_2\,(g) \longrightarrow Mg\,F_2(s) \quad \cdots\cdots (6.5)$$

$$Mg\,(s) + S(s) \longrightarrow MgS\,(s) \quad \cdots\cdots (6.6)$$

The above reactions are also examples of oxidation though no oxygen is involved and thus scope of oxidation can be expanded. Combination with electronegative element is oxidation. Oxidation can also be looked upon as the **removal of electropositive element**.

For example

$$Hg_2Cl_2\,(s) \longrightarrow HgCl_2\,(s) + Hg(s) \quad \cdots\cdots (6.7)$$

Now let us consider some examples of **reduction**.

a. Removal of oxygen from mercuric oxide

$$2\,HgO\,(s) \longrightarrow 2\,Hg\,(l) + O_2\,(g) \quad \cdots\cdots (6.8)$$

b. Removal of electronegative element from $FeCl_3$ as in

$$2\,FeCl_3 + H_2\,(g) \longrightarrow 2FeCl_2\,(aq) + 2\,HCl \quad \cdots\cdots (6.9)$$

c. Addition of hydrogen

$$CH_2 = CH_2\,(g) + H_2\,(g) \longrightarrow CH_3 - CH_3\,(g) \quad \cdots\cdots (6.10)$$

d. Addition of an elctropositive element

$$2\,HgCl_2(aq) + SnCl_2\,(aq) \rightarrow Hg_2Cl_2(s) + SnCl_4\,(aq) \quad \cdots\cdots (6.11)$$

In eq. (6.8) there is removal of oxygen from mercuric oxide Eq (6.9) shows removal of electronegative element from $FeCl_3$ Eq (6.10) involves addition of hydrogen. Equation (6.11) involves addition of an electropositive element Hg to $HgCl_2$. All these reactions represent **reduction**.

**Reductant / reducing agent** : A reagent / reducing agent is defined as a substance/ reagent which itself undergoes oxidation bringing about the reduction of another species. Now consider again equation (6.11). The equation (6.11) involves simultaneous oxidation and reduction. In this reaction $HgCl_2$ is reduced to $Hg_2Cl_2$ and $SnCl_2$ is oxidized to $SnCl_4$. Hence it is redox reaction.

**Key points**

**Oxidation it is defined as:**

a. addition of oxygen.

b. addition of electronegative element.

c. removal of hydrogen.

d. removal of electropositive element.

e. loss of electrons by any species.

**Reduction it is defined as:**

a. removal of oxygen.

b. removal of electronegative element.

c. addition of hydrogen.

d. addition of electropositive element.

e. gain of electrons by any species.

**6.1.2 Redox reaction in terms of electron transfer :** Redox reaction can be described as electron transfer as shown below.

$$Mg + \frac{1}{2} O_2 \longrightarrow Mg^{2\oplus} + O^{2\ominus} \quad \cdots\cdots (6.12)$$

$$Mg + F_2 \longrightarrow Mg^{2\oplus} + 2F^{\ominus} \quad \cdots\cdots (6.13)$$

Development of charges on the species produced suggest the reactions 6.12 and 6.13 can be written as :

Loss of $2e^{\ominus}$

$$Mg(s) + O_2(g) \longrightarrow Mg^{2\oplus} + O^{2\ominus}$$

Gain of $2e^{\ominus}$

Loss of $2e^{\ominus}$

$$Mg(s) + F_2(g) \longrightarrow Mg^{2\oplus} + 2F^{\ominus}$$

Gain of $2e^{\ominus}$

When Mg is oxidised to MgO, the neutral Mg atom loses electrons to form $Mg^{2\oplus}$ in MgO. The elemental oxygen gains electrons and forms $O^{2\ominus}$ in MgO.

Each of the above steps represents a half reaction which involves electron transfer (loss or gain). Sum of these two half reactions or the overall reaction is a redox reaction. Now consider the following half reactions.

$$Fe(s) \longrightarrow Fe^{2\oplus}(aq) + 2e^{\ominus} \quad \cdots\cdots (6.14)$$

$$Cu^{2\oplus}(aq) + 2e^{\ominus} \longrightarrow Cu(s) \quad \cdots\cdots (6.15)$$

$$Fe(s) + Cu^{2\oplus}(aq) \longrightarrow Fe^{2\oplus}(aq) + Cu(s) \quad \cdots\cdots (6.16)$$

In the half reaction (6.14) Fe acts as a reducing agent whereas $Cu^{2\oplus}$ acts as oxidising agent which accepts electrons from Fe. The half reaction involving loss of electrons is called oxidation reaction and that involving gain of electrons is called reduction. Thus eq. (6.14) is oxidation, eq. (6.15) is reduction and eq. (6.16) is a redox reaction.

**Key points : Oxidant / oxidizing agent :** A reagent / substance which itself undergoes reduction and causes oxidation of another species is called oxidant or oxidizing agent. This is an **electron acceptor**.

**Reductant / Reducing agent :** A reagent / reducing agent is defined as a substance / reagent which itself undergoes oxidation and brings about reduction of another species. A reductant is electron donor.

**Displacement reactions** can also be looked upon as redox reactions. In such reactions an ion (or atom) in a compound is replaced by an ion (or on atom) of another element.

$$X + YZ \longrightarrow XZ + Y$$

The reaction (6.16) is displacement reaction.

**Try this**

Complete the following table of displacement reactions. Identify oxidising and reducing agents involved.

| Reactants | Products |
|---|---|
| Zn (s) + ......... (aq) | ......... (aq) + Cu (s) |
| Cu (s) + 2 $Ag^{+}$ (aq) | ......... + ......... |
| ......... + ......... | $Co^{2+}$ (aq) + Ni (s) |

**6.2 Oxidation number :** Description of redox reaction in terms of electron transfer suggest involvement of only ionic species in it. But many reactions involving only covalent bonds also fulfil the classical definition of oxidation and reduction. For example:

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l) \quad \cdots\cdots (6.17)$$

$$H_2(g) + Cl_2(g) \longrightarrow 2HCl(g) \quad \cdots\cdots (6.18)$$

Eq (6.17) represents oxidation of $H_2$ as it is combination with oxygen. An electronegative element Cl is added to $H_2$, and therefore, eq (6.18) also represents oxidation of $H_2$. As products of both these oxidations are polar covalent molecules, there is an electron shift rather than complete electron transfer from one species to the other.

A practical method based on **oxidation number** is developed to describe all the redox reactions, which are either ionic involving complete electron transfer or covalent which refer to shift of electrons. In this method the electron pair in a covalent band is assumed to belong to more electronegative element, that is, it shifts completely to more electronegative element.

**Oxidation number** of an element in a compound **is defined** as the number of electrical charges it carries (assuming complete electron transfer in the case of covalent bond). The following rules have been formulated to determine the oxidation number of an element in a compound.

### 6.2.1 Rules to assign oxidation number

1. The **oxidation number** of each atom of an **element** in free state is zero. For example : each atom in $H_2$, $Cl_2$, $O_3$, $S_8$, $P_4$, $O_2$, Ca, etc. has oxidation number of zero.
2. The **oxidation number** of an atom in a **monoatomic** ion is equal to its charge. Thus alkali metals have oxidation number +1 in all their compounds (NaCl, KCl, etc.). Alkaline earth metals have oxidation number +2 in all their compouds ($CaCO_3$, $MgCl_2$, etc.). Al is considered to have +3 as its oxidation number in all its compounds.
3. The **oxidation number of O** is usually -2 in all of its compounds except in peroxide or peroxide ion where it has oxidation number of -1 and in superoxide each oxygen has oxidation number -1/2.

| Ca-O | H-O-O-H | (O-O) | $KO_2$ |
|---|---|---|---|
| ↑ ↑ | ↑ ↑ ↑ ↑ | ↑ ↑ | ↑ ↑ |
| +2 -2 | +1 -1 -1 +1 | -1 -1 | +1 -1/2 |

In $OF_2$ oxidation number of oxygen is +2.

4. The **oxidation number of H** atom is either +1 or -1. When the H atom is bonded to nonmetals, its oxidation number is +1. When it is bonded to metals, it possesses oxidation number of -1.

| $(O\text{-}H)^-$ | H-O-H | Li-H | H-Ca-H |
|---|---|---|---|
| ↑ ↑ | ↑ ↑ ↑ | ↑ ↑ | ↑ ↑ ↑ |
| -2 +1 | +1 -2 +1 | +1 -1 | -1 +2 -1 |

5. The oxidation number of F is -1 in all of its compounds. The other halogens Cl, Br and I usually exhibit oxidation number of -1 in their halide compounds. However in compounds in which halogens Cl, Br and I are bonded to oxygen, oxidation number of halogens is +1 For example,

| H-F | KBr | Cl-O-Cl | H-O-Cl |
|---|---|---|---|
| ↑ ↑ | ↑ ↑ | ↑ ↑ ↑ | ↑ ↑ ↑ |
| +1-1 | +1-1 | +1 -2 +1 | +1 -2 +1 |

6. The algebraic sum of oxidation numbers of all the atoms in a neutral molecule is zero.
7. The algebraic sum of oxidation numbers of all the atoms in a polyatomic ion is equal to net charge of the ion.
8. When two or more atoms of an element are present in molecule or ion, oxidation number of the atom of that element will be average oxidation number of all the atoms of that element in that molecules.

By applying rules 1 to 5 it is possible to determine oxidation number(s) of atoms of various elements in molecules or ions. For doing this the rules 6, 7 and 8 are useful.

**Problem 6.1:** Deduce the oxidation number of S in the following species:

i. $SO_2$ ii. $SO_4^{2\ominus}$

**Solution:**

i. $SO_2$ is a neutral molecule :

∴ Sum of oxidation number of all atom of $SO_2$ = 0 = (oxidation number of S) + 2 x (oxidation number of O)

∴ 0 = (oxidation number of S) + 2 x (-2)

∴ Oxidation number of S in $SO_2$ = 0 – (2x (-2)) = 0 – (-4) = + 4

ii. $SO_4^{2\ominus}$ is an ionic species.

∴ Sum of oxidation number of all atom of $SO_4^{2\ominus}$ = -2

= Oxidation number of S + 4 x (Oxidation number of O)

∴ Oxidation number of S in $SO_4^{2\ominus}$ = -2 -4 x (-2) = -2+8 = + 6

**Remember**

Oxidation number of an element can be positive or negative and a whole number or a fraction.

**6.2.2 Stock notation :** Oxidation number represents the oxidation state of an atom and is also denoted by Roman numeral in parentheses after the chemical symbol of the concerned element in the molecular formula. This representation is called **Stock notation** after the German Scientist Alfred Stock. For example :

1. $Au^{1\oplus}\ Cl^{1\ominus} \longrightarrow Au(I)Cl$
2. $Au^{3\oplus}Cl_3^{1\ominus} \longrightarrow Au(III)Cl_3$
3. $Sn^{4\oplus}Cl_4^{1\ominus} \longrightarrow Sn(IV)Cl_4$
4. $Sn^{2\oplus}Cl_2^{1\ominus} \longrightarrow Sn(II)Cl_2$
5. $Mn^{4\oplus}O_2^{2\ominus} \longrightarrow Mn(IV)O_2$

The Stock notation is used to specify the oxidation number of the metal. The idea of oxidation number is very convenient to define oxidation, reduction and the substances like oxidizing agent (oxidant) and reducing agent (reductant) of the redox reaction.

**6.2.3 Redox reaction in terms of oxidation number :**

**Oxidation :** An increase in the oxidation number of an element in a given substance.

**Reduction :** A decrease in the oxidation number of an element in a given substance.

**Oxidizing agent :** A substance which increases the oxidation number of an element in a given substance, and itself undergoes decrease in oxidation number of a constituent element.

**Reducing agent :** A substance that lowers the oxidation number of an element in a given substance, and itself undergoes an increase in the oxidation number of a constituent element in it.

**Problem 6.2 :** Assign oxidation number to each element in the following compounds or ions.

a. $KMnO_4$ b. $K_2Cr_2O_7$ c. $Ca_3(PO_4)_2$

**Solution :**

**a. $KMnO_4$**

1. Oxidation number of K = +1
2. Oxidation number of O = -2
3. Sum of the oxidation numbers of all atoms = 0

$\therefore$ Oxidation no. of K + oxidation of Mn + 4 x oxidation number of O = 0

(+1) + oxidation number of Mn + 4 x (-2) = 0

oxidation number of Mn + 1 - 8 = 0

oxidation number of Mn - 7 = 0

oxidation number of Mn = +7

**b. $K_2Cr_2O_7$**

1. oxidation number of K =+1
2. oxidation number of O = -2
3. sum of oxidation number of all atoms = 0

$\therefore$ 2 x oxidation no. of K + 2x oxidation number of Cr +7x oxidation number of O = 0

$\therefore$ 2 x (+1) + 2 x oxidation number of Cr + 7 x (–2) = 0

$\therefore$ +2 +2 x oxidation number of Cr - 14 = 0

$\therefore$ 2x oxidation number of Cr + 2 - 14 = 0

$\therefore$ 2x oxidation number of Cr - 12 = 0

$\therefore$ 2x oxidation number of Cr = +12

$\therefore$ oxidation number of Cr = +12 /2

$\therefore$ oxidation number of Cr = +6

**c. $Ca_3(PO_4)_2$**

1. oxidation number of Ca = +2 (alkaline earth metal ion)
2. oxidation number of O = -2
3. sum of oxidation number of all atoms = 0

$\therefore$ 3 x O.N. of Ca + 2 x oxidation number of P + 8 x oxidation number of O = 0

$\therefore$ 3 x(+2) + 2 x oxidation number of P + 8 x (-2) = 0

$\therefore$ (+6) + 2 x oxidation number of P -16 = 0

$\therefore$ 2 x oxidation number of P -16 + 6 = 0

$\therefore$ 2 x oxidation number of P -10 = 0

$\therefore$ 2 x oxidation number of P = +10

$\therefore$ oxidation number of P = +10/2

$\therefore$ oxidation number of P = + 5

**Problem 6.3 :** Assign oxidation number to the atoms other than O and H in the following species.

i. $SO_3^{2\ominus}$ ii. $BrO_3^{\ominus}$ iii. $ClO_4^{\ominus}$ iv. $NH_4^{\oplus}$ v. $NO_3^{\ominus}$ vi. $NO_2^{\ominus}$ vii. $SO_3$ viii. $N_2O_5$

**Solution :** The oxidation number of O atom bonded to a more electropositive atom is -2 and that of H atom bonded to electronegative atom is +1. Using these values the oxidation numbers of atoms of the other elements in a given polyatomic species are calculated.

i. $SO_3^{2\ominus}$

$-2 =$ oxidation number of S + 3 x (oxidation number of O)

$\therefore$ Oxidation number of S = - 2 - 3 (-2)

= - 2 + 6 = 4

ii. $BrO_3^{\ominus}$

$-1 =$ oxidation number of Br + 3 x (oxidation number of O)

$\therefore$ Oxidation number of Br = - 1 - 3 (-2)

= - 1 + 6 = 5

Similarly the oxidation number in the remaining species are found to be

iii. Cl in $ClO_4^{\ominus}$ : +7 iv. N in $NH_4^{\oplus}$ : -3

v. N in $NO_3^{\ominus}$ : +5 vi. N in $NO_2^{\ominus}$: +3

vii. S in $SO_3$ : +6 viii. N in $N_2O_5$ : +5

**Problem 6.4 :** Identify whether the following reactions are redox or not. State oxidants and reductants therein.

a. $3H_3AsO_3(aq) + BrO_3^{\ominus}(aq) \longrightarrow Br^{\ominus}(aq) + 3H_3AsO_4(aq)$

1. Write oxidation number of all the atoms of reactants and products by doing required calculations. (a) stands for known O.N. and (b) for calculated O.N.

$$3H_3AsO_3 + BrO_3^{\ominus} \longrightarrow Br^{\ominus} + 3H_3AsO_4$$

(a) 3 x(+1) | 3 x(-2) | 3 x (-2) -1 3 x (+1) | 4x(-2)

(b) +3 +5 +5

2. Identify the species that undergoes change in oxidation number

$$3H_3AsO_3(aq) + BrO_3^-(aq) \longrightarrow Br^-(aq) + 3H_3AsO_4(aq)$$

Loss of $2e^{\ominus}$

Gain of $6e^{\ominus}$

The oxidation number of As increases from +3 to +5 and that of Br decreases from +5 to -1. Because oxidation number of one species increases and that of other decreases, the reaction is therefore redox reaction.

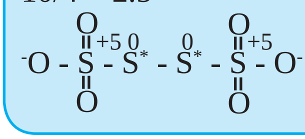
The oxidation number of As increases by loss of electron. Thus As is a reducing agent and is itself oxidized. On the other hand, the oxidation number of Br decreases. Hence, it is reduced by the gain of electron and act as an oxidizing agent.

**Result :**

1. The reaction is redox reaction.
2. Oxidant/oxidizing agent - $BrO_3^-$
3. Reductant/Reducing agent - $H_3AsO_3$

**Do you know ?**

Some elements in a particular compound may possess fractional oxidation number. For example : $C_3O_2$, $Br_3O_8$, $Na_2S_4O_6$, $C_8H_{18}$, etc. In these compounds oxidation number of C, Br, S, C are 4/3, 16/3, 2.5, 9/4, respectively. These oxidation numbers are actually the average oxidation number of all the atoms of elements in that compound. Different atoms of the element in such species exhibit different oxidation states. For example : Tertra thionate ion has two S atoms with oxidation number +5 and two with zero (0). Therefore, the average oxidation number of S in these species is 10/4 = 2.5




structure of $S_4O_6^{2-}$ (tetrathionate ion)

**6.3 Balancing of redox reactions :** Two methods are used to balance chemical equation for redox processes : Oxidation number method and Half reaction method or Ion electron method.

**6.3.1 The Oxidation number method is illustrated in the following steps :**

**Step I :** Write the unbalanced equation for redox reaction. Balance the equation for all atoms in the reactions, except H and O. Identify the atoms which undergo change in oxidation number and by how much. Draw the bracket to connect atoms of the elements that changes the oxidation number.

**Step II :** Show an increase in oxidation number per atom of the oxidised species and hence the net increase in oxidation number. Similarly show a decrease in the oxidation number per atom of the reduced species and the net decrease in oxidation number. Determine the factors which will make the total increase and decrease equal. Insert the coefficients into the equation.

**Step III :** Balance oxygen atoms by adding $H_2O$ to the side containing less O atoms, One $H_2O$ is added for one O atom. Balance H atoms by adding $H^{\oplus}$ ions to the side having less H atoms.

**Step IV :** If the reaction occurs in basic medium, then add $OH^{\ominus}$ ions, equal to the number of $H^{\oplus}$ ions added in step III, on both the sides of equation. The $H^{\oplus}$ and $OH^{\ominus}$ on same sides of reactions are combined to give $H_2O$ molecules.

**Step V :** Check the equation with respect to both, the number of atoms of each element and the charges. It is balanced.

**Note :** For acidic medium step IV is omitted.

**Problem 6.5 :** Using the oxidation number method write the net ionic eqvation for the reaction of potassium permanganate, $KMnO_4$, with ferrous sulphate, $FeSO_4$.

$$MnO_4^{\ominus}(aq) + Fe^{2\oplus}(aq) \longrightarrow Mn^{2\oplus}(aq) + Fe^{3\oplus}(aq)$$

**Solution :**

**Step 1 :** The skeletal ionic equation is

$$MnO_4^{\ominus}(aq) + Fe^{2\oplus}(aq) \longrightarrow Mn^{2\oplus}(aq) + Fe^{3\oplus}(aq)$$

**Step 2 :** Assign oxidation number to Mn and Fe, and calculate the increase and decrease in the oxidation number and make them equal. (a) stands for known O.N. and (b) for calculated O.N.

$$\underset{\substack{(a)\ \ 4\times(-2)\\(b)\ +7}}{MnO_4^{\ominus}} + \underset{+2}{Fe^{2\oplus}} \longrightarrow \underset{+2}{Mn^{2\oplus}} + \underset{+3}{Fe^{3\oplus}}$$

increase in oxidation number :

$$Fe\ (+2) \longrightarrow Fe\ (+3)$$

increase per atom = 1

decrease in oxidation number :

$$Mn(+7) \longrightarrow Mn(+2)$$

decerase per atom = 5

to make the net incerase and decrease equal we must take 5 atoms of $Fe^{2\oplus}$

$$MnO_4^{\ominus}(aq) + 5Fe^{2\oplus}(aq) \longrightarrow Mn^{2\oplus}(aq) + 5Fe^{3\oplus}(aq)$$

**Step 3 :** Balance the 'O' atoms by adding $4H_2O$ to the right hand side.

$$MnO_4^{\ominus}(aq) + 5Fe^{2\oplus}(aq) \longrightarrow Mn^{2\oplus}(aq) + 5Fe^{3\oplus}(aq) + 4H_2O(l)$$

**Step 4:** The medium is acidic. To make the charges and hydrogen atoms on the two sides equal, add $8H^{\oplus}$ on the left hand side.

$$MnO_4^{\ominus}(aq) + 5\ Fe^{2\oplus}(aq) + 8H^{\oplus}(aq) \longrightarrow Mn^{2\oplus}(aq) + 5Fe^{3\oplus}(aq) + 4H_2O(l)$$

**Step 5:** Check the two sides for balance of charges and atoms. The net ionic equation obtained in step 4 is the balanced equation.

$$\mathbf{MnO_4^{\ominus}(aq) + 5\ Fe^{2\oplus}(aq) + 8H^{\oplus}(aq) \longrightarrow Mn^{2\oplus}(aq) + 5Fe^{3\oplus}(aq) + 4H_2O}$$

**Problem 6.6 :** Balance the following reaction by oxidation number mathod.

$$CuO + NH_3 \longrightarrow Cu + N_2 + H_2O$$

**Solution :**

**Step I :** Write skeletal equation and balance the elements other that O and H.

$$CuO + 2\ NH_3 \longrightarrow Cu + N_2 + H_2O$$

**Step II :** Assign oxidation number to Cu and N. Calculate the increase and decrease in the oxidation number and make them equal. (a) stands for known O.N. and (b) for calculated O.N.

$$\underset{\substack{(a)\ \ -2\\(b)\ +2}}{CuO} + \underset{\substack{3x(+1)\\-3}}{2NH_3} \longrightarrow \underset{0}{Cu} + \underset{0}{N_2} + H_2O$$

increase in oxidation number :

$$\underset{-3}{2NH_3} \longrightarrow \underset{0}{N_2}$$

increase per atom = 3

decrease in oxidation number

$$\underset{+2}{CuO} \longrightarrow \underset{0}{Cu}$$

decrease per atom = 2

to make the net increase and decrease equal we must take 3 atoms of Cu and 2 atoms of N

$$3CuO+2NH_3 \longrightarrow 3Cu+N_2+ H_2O$$

**Step III :** Balance 'O' atoms by addition $2H_2O$ to the right hand side.

$$3CuO+2NH_3 \longrightarrow 3Cu+N_2+ 3H_2O$$

**Step IV :** Charges are already balanced

**Step V :** Check two sides for balanced of atoms and charges. The equation obtain in step IV is balanced.

$$\mathbf{3CuO+2NH_3 \longrightarrow 3Cu+N_2+ 3H_2O}$$

### 6.3.2 Ion electron method (Half reaction method) :

In this method two half equations are balanced separately and then added together to give balanced equation. Following steps are involved

**Step I :** Write unbalanced equation for the redox reaction. Assign oxidation number to all the atoms in the reactants and products. Divide the equation into two half equations. One half equation involves increase in oxidation number and another involves decrease in oxidation number (Write two half equation separately)

**Step II :** Balance the atoms except O and H in each half equation. Balance oxygen atom by adding $H_2O$ to the side with less O atoms.

**Step III :** Balance the H atom by adding $H^+$ ions to the side with less H atoms.

**Step IV :** Balance the charges by adding appropriate number of electrons to the right side of oxidation half equation and to the left of reduction half equation.

**Step V :** Multiply half equation by suitable factors to equalize the number of electrons in two half equations. Add two half equations and cancel the number of electrons on both sides of equation.

**Step VI :** If the reaction occurs in basic medium then add $OH^-$ ions, equal to number of $H^\oplus$ ions on both sides of equation. The $H^\oplus$ and $OH^-$ ions on same side of equation combine to give $H_2O$ molecules.

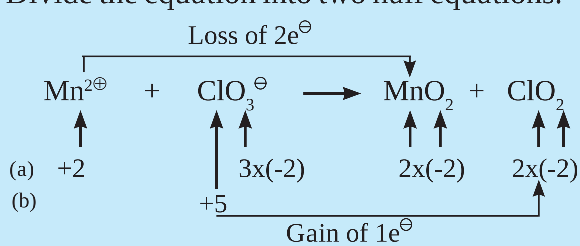
**Step VII :** Check that the equation is balanced in both, the atoms and the charges.

**Problem 6.7 :** Balance the following unbalanced equation (in acidic medium) by ion electron (half reaction method)

$Mn^{2\oplus}(aq) + ClO_3^\ominus(aq) \rightarrow MnO_2(s) + ClO_2(aq)$

**Solution :**

**Step I :** Write unbalanced equation for the redox reaction. Assign oxidation number to all the atoms in reactants and product then. Divide the equation into two half equations.




Oxidation half reaction

$Mn^{2\oplus}(aq) \longrightarrow MnO_2(s)$

Reduction half reaction

$ClO_3^\ominus(aq) \longrightarrow ClO_2(aq)$

**Step II :** Balance half equations for O atoms by adding $H_2O$ to the side with less O atoms. Add $2H_2O$ to left side of oxidation and one $H_2O$ to the right side of reduction.

Oxidation

$Mn^{2\oplus}(aq) + 2H_2O(l) \longrightarrow MnO_2(s)$

Reduction

$ClO_3^\ominus(aq) \longrightarrow ClO_2(aq) + H_2O(l)$

**Step III :** Balance $H^-$ atoms by adding $H^\oplus$ ions to the side with less H. Hence add $4H^\oplus$ ions to the right side of oxidation and $2H^\oplus$ ions to the left side of reduction.

Oxidation

$Mn^{2\oplus}(aq) + 2H_2O(l) \longrightarrow MnO_2 + 4H^\oplus(aq)$

Reduction

$ClO_3^\ominus(aq) + 2H^\oplus(aq) \longrightarrow ClO_2(aq) + H_2O(l)$

**Step IV :** Now add 2 electrons to the right side of oxidation and 1 electron to the left side of reduction to balance the charges.

Oxidation

$Mn^{2\oplus}(aq) + 2H_2O(l) \longrightarrow MnO_2(s) + 4H^\oplus(aq) + 2e^\ominus$

Reduction

$ClO_3^\ominus(aq) + 2H^\oplus(aq) + e^\ominus \longrightarrow ClO_2(aq) + H_2O(l)$

**Step V :** Multiply reduction half equation by 2 to equalize number of electrons in two half equations. Then add two half equation.

Oxidation

$Mn^{2\oplus}(aq) + 2H_2O(l) \longrightarrow MnO_2(s) + 4H^\oplus(aq) + 2e^\ominus$ Reduction ....... (1)

$2ClO_3^\ominus(aq) + 4H^\oplus(aq) + 2e^\ominus \longrightarrow 2ClO_2(aq) + 2H_2O(l)$ ....... (2)

eq. (1) + eq. (2) gives the net reaction

$Mn^{2\oplus}(aq) + 2ClO_3^\ominus(aq) \longrightarrow MnO_2(s) + 2ClO_2(aq)$

The equation is balanced in terms of number of atoms and the charges.

**Problem 6.8 :** Balance the following unbalanced equation by ion electron (half reaction method)

$H_2O_2(aq) + ClO_4^\ominus(aq) \longrightarrow ClO_2^\ominus(aq) + O_2(g)$

**Solution :**

**Step I :** Write unbalanced equation for the redox reaction and assign oxidation number to all the atoms in reactants and products. (a) stands for known O.N. and (b) for calculated O.N.

Divide the equation into two half equations.

Loss of $2e^{\ominus}$

$$\underset{\substack{(a)\ 2x(+1)\\(b)\ 2\times(-1)}}{H_2O_2} + \underset{\substack{4x(-2)\\+7}}{ClO_4^{\ominus}} \longrightarrow \underset{\substack{2x(-2)\\+3}}{ClO_2^{\ominus}} + \underset{0}{O_2}$$

Gain of $4e^{\ominus}$

Oxidation

$H_2O_2\,(aq) \longrightarrow O_2\,(g)$

Reduction

$ClO_4^{\ominus}(aq) \longrightarrow ClO_2^{\ominus}\,(aq)$

**Step II :** Balance the half equation for O atoms by adding $H_2O$ to the side with less O atoms. Hence add 2 $H_2O$ to the right side of reduction half equation and none to the oxidation half equation

Oxidation

$H_2O_2\,(aq) \longrightarrow O_2(g)$

Reduction

$ClO_4^{\ominus}(aq) \longrightarrow ClO_2^{\ominus}\,(aq) + 2\,H_2O(l)$

**Step III :** Balance H atoms by adding $H^+$ ions to the side with less H. Hence add $2H^{\oplus}$ ions to the right side of oxidation half equation and $4H^{\oplus}$ ions to the left side of reduction half equation.

Oxidation

$H_2O_2\,(aq) \longrightarrow O_2(g) + 2H^{\oplus}\,(aq)$

Reduction

$ClO_4^{\ominus}(aq) + 4H^{\oplus}\,(aq) \longrightarrow ClO_2^{\ominus}\,(aq) + 2H_2O\,(l)$

**Step IV :** Add 2 electrons to the right side of oxidation half equation and 4 electrons to the left side of reduction half equation to balance the charges.

Oxidation

$H_2O_2\,(aq) \longrightarrow O_2(g) + 2H^{\oplus}(aq) + 2e^{\ominus}$

Reduction

$ClO_4^{\ominus}\,(aq) + 4H^{\oplus}(aq) + 4e^{\ominus} \longrightarrow ClO_2^{\ominus} + 2H_2O$

**Step V :** Multiply oxidation half equation by 2 to equalize the number of electrons and then add two half equations.

Oxidation

$2\,H_2O_2\,(aq) \longrightarrow 2O_2(g) + 4H^{\oplus}(aq) + 4e^{\ominus}$

Reduction

$ClO_4^{\ominus}\,(aq) + 4H^{\oplus}(aq) + 4e^{\ominus} \longrightarrow ClO_2^{\ominus} + 2\,H_2O(l)$

$2\,H_2O_2\,(aq) + ClO_4^{\ominus}(aq) + 4H^{\oplus}(aq) + 4e^{\ominus} \longrightarrow 2\,O_2(g) + ClO_2^{\ominus}(aq) + 4\,H^{\oplus}(aq) + 4e^{\ominus} + 2\,H_2O(l)$

$2\,H_2O_2\,(aq) + ClO_4^{\ominus}(aq) \longrightarrow 2\,O_2(g) + ClO_2^{\ominus}(aq) + 2\,H_2O(l)$

This equation is balanced in terms of atoms and charges.

**Try this**

**Classify the following unbalanced half equations as oxidation and reduction**

| Example | Type |
|---|---|
| $Cl^{\ominus}(aq) \longrightarrow Cl_2\,(g)$ | oxidation |
| $OCl^{\ominus}(aq) \longrightarrow Cl^{\ominus}\,(g)$ | |
| $Fe(OH)_2 \longrightarrow Fe(OH)_3$ | |
| $VO^{2\oplus}\,(aq) \longrightarrow V^{3\oplus}\,(aq)$ | |

## 6.4 Redox reaction and electrode potential

We noted in the section 6.1.1 that displacement reaction can be looked upon as redox reaction. Consider the following displacement reaction.

Loss of $2e^{\ominus}$

$$Zn\,(s) + Cu^{2\oplus}(aq) \longrightarrow Zn^{2\oplus}(aq) + Cu\,(s) \qquad ........ (6.17)$$

Gain of $2e^{\ominus}$

This reaction can be brought about in two ways. The simpler method to observe this reaction is to take copper sulfate solution in a container and dip zinc rod in it. The redox reaction (6.17) takes place in that container. Zinc gets oxidized to $Zn^{2\oplus}$ ion and $Cu^{2\oplus}$ ions get reduced to metallic Cu. A direct transfer of electrons from zinc atom to cupric ions takes place in this case.

The electron transfer from Zn atom to $Cu^{2\oplus}$ ions can be demonstrated by carrying out two half reactions in two separate containers as shown in Fig. 6.1.

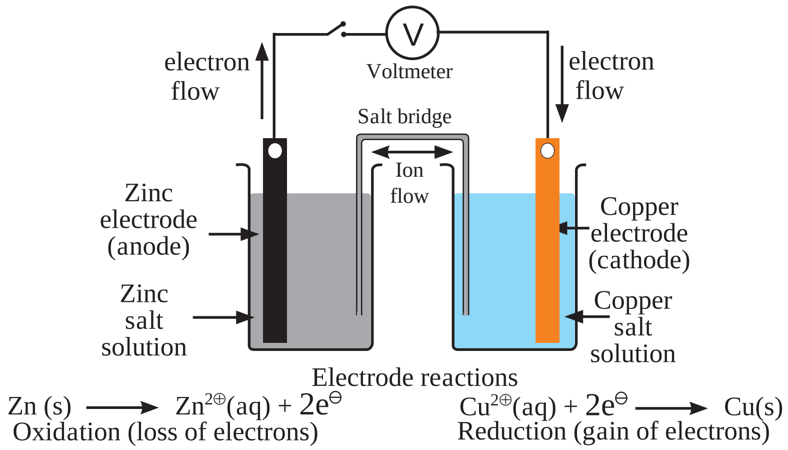



**Fig. 6.1 : Daniel Cell**

The set up in Fig. 6.1 is that of Daniel cell. The zinc and copper plates are connected by an electric wire through a switch and voltmeter. The solution in two containers are connected by salt bridge (U-shaped glass tube containing a gel of KCl or $NH_4NO_3$ in agar-agar). When switch is on, electrical circuit is complete as indicated by the deflection in the voltmeter. The circuit has two parts, one called external circuit, in the form of electrical wire which allows the flow of electrons and the other in the form of two solutions joined by salt bridge. In solution part of the circuit, the electric current is carried by movement of ions. When a circuit is complete, the zinc atoms on zinc plates spontaneously lose electrons which are picked up in the external circuit. The electrons flow from the zinc plate to copper plate through the wire. $Cu^{2\oplus}$ ions in the second container receive these electrons through the copper plate and are reduced to copper atoms which get deposited on the copper plate. Here, zinc plate acts as anode (negative electrode) and the copper plate acts as cathode (positive electrode). Thus, when two half reactions, namely, oxidation and reduction, are allowed to take place in separate containers and a provision is made for completing the electrical circuit, electron transfer takes place through the external circuit. This results in flow of electric current in the circuit as indicated by deflection in voltmeter. At the same time ions move within the solution resulting in completion of the electrical circuit. This is a simple electrochemical cell called Daniel cell, in which electricity is generated by redox reaction.

In an electrochemical cell electrons flow in the external circuit from anode to cathode while the conventional current flows from cathode to anode. An electrical potential is said to be established at the two electrodes of an electrochemical cell. It is called **electrode potential**. The magnitude and direction of the electrode potential depends upon the nature of the metal and ions, concentration of ions and temperature. The reaction associated with an electrode is called **electrode reaction**. The two chemical species linked by transfer of electrons form a **redox couple**.

**6.4.1 Standard electrode potential :** When concentration of each species taking part in the electrode reaction is unity and the temperature is 298 K, observed electrode potential is called standard electrode potential ($E^0$). By convention the standard electrode potential of hydrogen electrode is 0.00 Volt. Standard hydrogen electrode is used as reference electrode for determination of $E^0$ values of various redox couples.

**Significance of $E^0$ value :** The electrode reaction considered for the electrode potential is reduction reaction. Therefore, value and sign of standard electrode potential is a measure of the tendency of active species in the electrode reaction to remain in the oxidized / reduced form. A negative $E^0$ means redox couple is a stronger reducing agent than the $H^{\oplus}/H_2$ couple. Table 6.1 shows standard electrode potentials of reduction process of some redox couples.

Large negative value of $E^0$ means that redox couple is strong reducing agent. On the other hand, more positive value of $E^0$ means the redox couple is strong oxidizing agent. From the Table 6.1 it is seen that alkali metals have high negative value of $E^0$, which means that they are strong reducing agents. The alkali metals have great tendency to give away electron and form cations. On the other hand, fluorine has highly positive value of $E^0$ and thus great tendency to gain electron and is therefore, very strong oxidizing agents.

**Table 6.1 : Standand electrode protentianls of some redox couples**

| Oxidised form + $ne^{\ominus}$ $\longrightarrow$ reduced from | $E^0/V$ |
|---|---|
| $F_2(g)+2e^{\ominus} \longrightarrow 2F^{\ominus}$ | 2.87 |
| $H_2O_2+2H^{\oplus}+2e^{\ominus} \longrightarrow 2H_2O$ | 1.78 |
| $MnO_4^{\ominus}+8H^{\oplus}+5e^{\ominus} \longrightarrow Mn^{2\oplus}+4H_2O$ | 1.51 |
| $Cl_2(g)+2e^{\ominus} \longrightarrow 2Cl^{\ominus}$ | 1.36 |
| $Cr_2O_7^{2\ominus}+14H^{\oplus}+6e^{\ominus} \longrightarrow 2Cr^{3\oplus}+7H_2O$ | 1.33 |
| $O_2(g)+4H^{\oplus}+4e^{\ominus} \longrightarrow 2H_2O$ | 1.23 |
| $Br_2+2e^{\ominus} \longrightarrow 2Br^{\ominus}$ | 1.09 |
| $2Hg^{2\oplus}+2e^{\ominus} \longrightarrow Hg_2^{2\oplus}$ | 0.92 |
| $Fe^{3\oplus}+e^{\ominus} \longrightarrow Fe^{2\oplus}$ | 0.77 |
| $I_2(s)+2e^{\ominus} \longrightarrow 2I^{\ominus}$ | 0.54 |
| $2H^{\oplus}+2e^{\ominus} \longrightarrow H_2(g)$ | 0.00 |
| $Zn^{2\oplus}+2e^{\ominus} \longrightarrow Zn(s)$ | -0.76 |
| $Al^{3\oplus}+3e^{\ominus} \longrightarrow Al(s)$ | -1.66 |
| $Mg^{2\oplus}+2e^{\ominus} \longrightarrow Mg(s)$ | -2.36 |
| $Na^{\oplus}+e^{\ominus} \longrightarrow Na(s)$ | -2.71 |
| $Ca^{2\oplus}+2e^{\ominus} \longrightarrow Ca(s)$ | -2.87 |
| $K^{\oplus}+e^{\ominus} \longrightarrow K(s)$ | -2.93 |
| $Li^{\oplus}+e^{\ominus} \longrightarrow Li(s)$ | -3.05 |

We shall learn more about electrode potential and electrochemical cells in the 12th standard.

**Problem 6.9 :** By using standard electrode potential table justify that the reaction between the following is spontaneous. (a) $Fe^{3\oplus}$ (aq) and $I^{\ominus}$ (aq), (b) $Ag^{\oplus}$ (aq) and Cu(s)

**Solution :** Write oxidation half reaction for one species and reduction half reaction for the other species. Change the sign of $E^0$ of oxidation half reaction. Take the sum of two $E^0$ values. If the sum is positive the reaction between two species is spontaneous.

(a) $Fe^{3\oplus}$ (aq) and $I^{\ominus}$ (aq)

Reduction : $2\,Fe^{3\oplus}(aq) + 2e^{\ominus} \longrightarrow 2\,Fe^{2\oplus}$, $\quad E^0 = +0.77$ V

Oxidation : $2I^{\ominus}(aq) \longrightarrow I_2(s) + 2e^{\ominus}$, $\quad E^0 = -0.54$ V

$2\,Fe^{3\oplus}(aq) + 2I^{\ominus}(aq) \longrightarrow 2\,Fe^{2\oplus}(aq) + I_2(s)$ $\quad$ Sum = + 0.23 V

**The sum of $E^0$ values is positive, therefore the reaction is spontaneous.**

(b) $Ag^{\oplus}$ (aq) and Cu(s)

Reduction : $2\,Ag^{\oplus}(aq) + 2e^{\ominus} \longrightarrow 2Ag(s)$, $\quad E^0 = +0.80$ V

Oxidation : $Cu(s) \longrightarrow Cu^{2\oplus}(aq) + 2e^{\ominus}$, $\quad E^0 = -0.34$ V

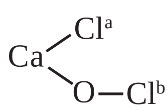
$2\,Ag^{\oplus}(aq) + Cu(s) \longrightarrow 2\,Ag(s) + Cu^{2\oplus}(aq)$ $\quad$ Sum = + 0.46 V

**The sum of $E^0$ values is positive, therefore reaction is spontaneous.**

## Exercises

### 1. Choose the most correct option

A. Oxidction numbers of Cl atoms marked as $Cl^a$ and $Cl^b$ in $CaOCl_2$ (bleaching powder) are



a. zero in each

b. -1 in $Cl^a$ and +1 in $Cl^b$

c. +1 in $Cl^a$ and -1 in $Cl^b$

d. 1 in each

B. Which of the following is not an example of redox reacton ?

a.$CuO+H_2 \longrightarrow Cu+H_2O$

b.$Fe_2O_3+3CO_2 \longrightarrow 2Fe+3CO_2$

c. $2K+F_2 \longrightarrow 2KF$

d. $BaCl_2+H_2SO_4 \longrightarrow BaSO_4+2HCl$

C. A compound contains atoms of three elements A, B and C. If the oxidation state of A is +2, B is +5 and that of C is -2, the compound is possibly represented by

a. $A_2 (BC_3)_2$

b. $A_3 (BC_4)_2$

c. $A_3 (B_4C)_2$

d. $ABC_2$

D. The coefficients p, q, r, s in the reaction

$$p\ Cr_2O_7^{2\ominus} + q\ Fe^{2\oplus} \longrightarrow r\ Cr^{3\oplus} + s\ Fe^{3\oplus} + H_2O$$

respectively are :

a. 1, 2, 6, 6

b. 6, 1, 2, 4

c. 1, 6, 2, 6

d. 1, 2, 4, 6

E. For the following redox reactions, find the correct statement.

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

a. $Sn^{2\oplus}$ is undergoing oxidation

b. $Fe^{3\oplus}$ is undergoing oxidation

c. It is not a redox reaction

d. Both $Sn^{2\oplus}$ and $Fe^{3\oplus}$ are oxidised

F. Oxidation number of carbon in $H_2CO_3$ is

a. +1 b. +2

c. +3 d. +4

G. Which is the correct stock notation for magenese dioxide ?

a. $Mn(I)O_2$ b. $Mn(II)O_2$

c. $Mn(III)O_2$ d. $Mn(IV)O_2$

I. Oxidation number of oxygen in superoxide is

a. -2 b. -1 c. $-\frac{1}{2}$ d. 0

J. Which of the following halogens does always show oxidation state -1 ?

a. F

b. Cl

c. Br

d. I

K. The process $SO_2 \longrightarrow S_2Cl_2$ is

a. Reduction

b. Oxidation

c. Neither oxidation nor reduction

d. Oxidation and reduction.

### 2. Write the formula for the following compounds :

A. Mercury(II) chloride

B. Thallium(I) sulphate

C. Tin(IV) oxide

D. Chromium(III) oxide

### 3. Answer the following questions

A. In which chemical reaction does carbon exhibit variation of oxidation state from -4 to +4 ? Write balanced chemical reaction.

B. In which reaction does nitrogen exhibit variation of oxidation state from -3 to +5 ?

C. Calculate the oxidation number of underlined atoms.

a. $H_2\underline{S}O_4$ b. $H\underline{N}O_3$ c. $H_3\underline{P}O_3$

d. $K_2\underline{C}_2O_4$ e. $H_2\underline{S}_4O_6$ f. $\underline{Cr}_2O_7^{2-}$

g. $NaH_2\underline{P}O_4$

D. Justify that the following reactions are redox reaction; identify the species oxidized/reduced, which acts as an oxidant and which act as a reductant.

a. $2Cu_2O\ (s) + Cu_2S\ (s) \longrightarrow 6Cu\ (s) + SO_2\ (g)$

b. $HF\ (aq) + OH^{\ominus}(aq) \longrightarrow H_2O(l) + F^{\ominus}(aq)$

c. $I_2\ (aq) + 2\ S_2O_3^{2\ominus}(aq) \longrightarrow S_4O_6^{2\ominus}(aq) + 2I^{\ominus}(aq)$

E. What is oxidation? Which one of the following pairs of species is in its oxidized state ?

a. $Mg\ /\ Mg^{2\oplus}$ b. $Cu\ /\ Cu^{2\oplus}$

c. $O_2\ /\ O^{2\ominus}$ d. $Cl_2\ /\ Cl^{\ominus}$

F. Justify the following reaction as redox reaction.

$2\ Na(s) + S(s) \longrightarrow Na_2\ S(s)$

Find out the oxidizing and reducing agents.

G. Provide the stock notation for the following compounds : $HAuCl_4$, $Tl_2O$, $FeO$, $Fe_2O_3$, $MnO$ and $CuO$.

H. Assign oxidation number to each atom in the following species.

a. $Cr(OH)_4^{\ominus}$ b. $Na_2S_2O_3$

c. $H_3BO_3$

I. Which of the following redox couple is stronger oxidizing agent ?

a. $Cl_2\ (E^0 = 1.36\ V)$ and $Br_2\ (E^0 = 1.09\ V)$

b. $MnO_4^{\ominus}\ (E^0 = 1.51\ V)$ and

$Cr_2O_7^{2\ominus}\ (E^0 = 1.33\ V)$

J. Which of the following redox couple is stronger reducing agent ?

a. $Li\ (E^0 = -\ 3.05\ V)$ and

$Mg\ (E^0 = -\ 2.36\ V)$

b. $Zn\ (E^0 = -\ 0.76\ V)$ and

$Fe\ (E^0 = -\ 0.44\ V)$

## 4. Balance the reactions/equations :

A. Balance the following reactions by oxidation number method

a. $Cr_2O_7^{2\ominus}(aq) + SO_3^{2\ominus}(aq) \longrightarrow Cr^{3\oplus}\ (aq) + SO_4^{2\ominus}(aq)$ (acidic)

b. $MnO_4^{\ominus}(aq) + Br^{\ominus}(aq) \longrightarrow MnO_2\ (s) + BrO_3^{\ominus}(aq)$ (basic)

c. $H_2SO_4\ (aq) + C\ (s) \longrightarrow CO_2\ (g) + SO_2\ (g) + H_2O\ (l)$ (acidic)

d. $Bi\ (OH)_3\ (g) + Sn(OH)_3^{\ominus}(aq) \longrightarrow Bi\ (s) + Sn\ (OH)_6^{2\ominus}(aq)$ (basic)

B. Balance the following redox equation by half reaction method

a. $H_2C_2O_4\ (aq) + MnO_4^{\ominus}\ (aq) \longrightarrow CO_2(g) + Mn^{2\oplus}(aq)$ (acidic)

b. $Bi\ (OH)_3\ (s) + SnO_2^{2\ominus}(aq) \longrightarrow SnO_3^{2\ominus}\ (aq) + Bi\ (s)$ (basic)

## 5. Complete the following table :

Assign oxidation number to the underlined species and write Stock notation of compound

| Compound | Oxidation number | Stock notation |
|---|---|---|
| $\underline{Au}Cl_3$ | | |
| $\underline{Sn}Cl_2$ | | |
| $\underline{V}_2O_7^{4\ominus}$ | | |
| $\underline{Pt}Cl_6^{2\ominus}$ | | |
| $H_3\underline{As}O_3$ | | |

**Activity :**

**Perform redox reaction experiment with the help of Daniel cell under teacher guidance.**