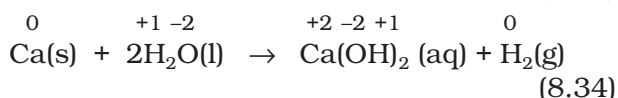
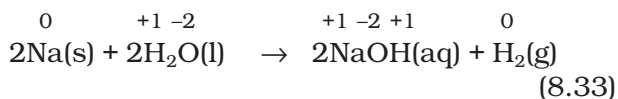
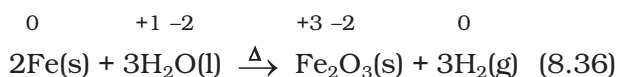
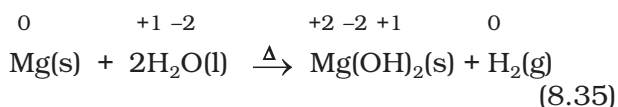


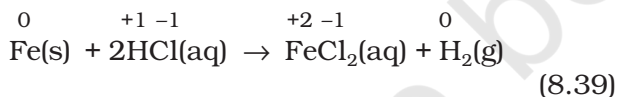
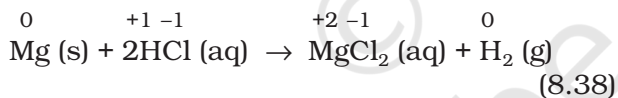
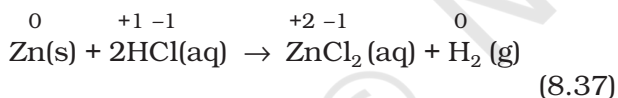
All alkali metals and some alkaline earth metals (Ca, Sr, and Ba) which are very good reductants, will displace hydrogen from cold water.



Less active metals such as magnesium and iron react with steam to produce dihydrogen gas:



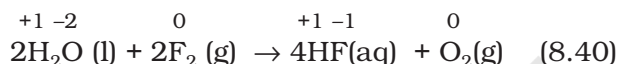
Many metals, including those which do not react with cold water, are capable of displacing hydrogen from acids. Dihydrogen from acids may even be produced by such metals which do not react with steam. Cadmium and tin are the examples of such metals. A few examples for the displacement of hydrogen from acids are:



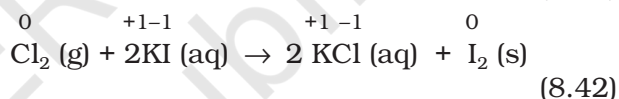
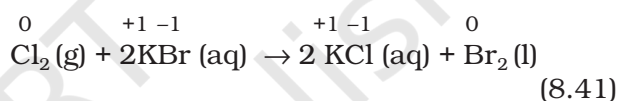
Reactions (8.37 to 8.39) are used to prepare dihydrogen gas in the laboratory. Here, the reactivity of metals is reflected in the rate of hydrogen gas evolution, which is the slowest for the least active metal Fe, and the fastest for the most reactive metal, Mg. Very less active metals, which may occur in the native state such as silver (Ag), and gold (Au) do not react even with hydrochloric acid.

In section (8.2.1) we have already discussed that the metals – zinc (Zn), copper (Cu) and silver (Ag) through tendency to lose electrons show their reducing activity in the

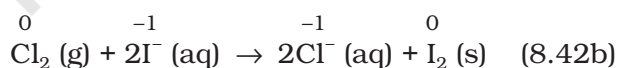
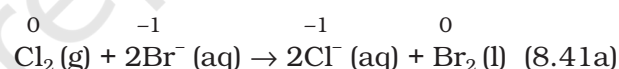
order Zn > Cu > Ag. Like metals, activity series also exists for the halogens. The power of these elements as oxidising agents decreases as we move down from fluorine to iodine in group 17 of the periodic table. This implies that fluorine is so reactive that it can replace chloride, bromide and iodide ions in solution. In fact, fluorine is so reactive that it attacks water and displaces the oxygen of water :



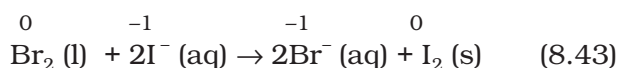
It is for this reason that the displacement reactions of chlorine, bromine and iodine using fluorine are not generally carried out in aqueous solution. On the other hand, chlorine can displace bromide and iodide ions in an aqueous solution as shown below:



As Br₂ and I₂ are coloured and dissolve in CCl₄, can easily be identified from the colour of the solution. The above reactions can be written in ionic form as:



Reactions (8.41) and (8.42) form the basis of identifying Br⁻ and I⁻ in the laboratory through the test popularly known as 'Layer Test'. It may not be out of place to mention here that bromine likewise can displace iodide ion in solution:



The halogen displacement reactions have a direct industrial application. The recovery of halogens from their halides requires an oxidation process, which is represented by:

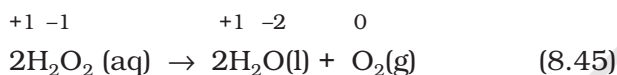


here X denotes a halogen element. Whereas chemical means are available to oxidise Cl⁻, Br⁻ and I⁻, as fluorine is the strongest oxidising

agent; there is no way to convert F^- ions to F_2 by chemical means. The only way to achieve F_2 from F^- is to oxidise electrolytically, the details of which you will study at a later stage.

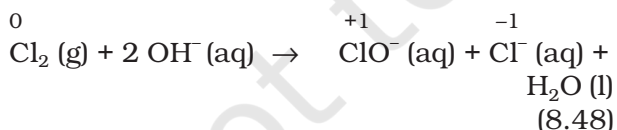
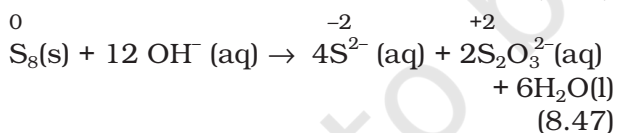
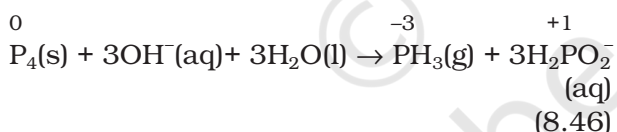
4. Disproportionation reactions

Disproportionation reactions are a special type of redox reactions. In a disproportionation reaction an element in one oxidation state is simultaneously oxidised and reduced. One of the reacting substances in a disproportionation reaction always contains an element that can exist in at least three oxidation states. The element in the form of reacting substance is in the intermediate oxidation state; and both higher and lower oxidation states of that element are formed in the reaction. The decomposition of hydrogen peroxide is a familiar example of the reaction, where oxygen experiences disproportionation.



Here the oxygen of peroxide, which is present in -1 state, is converted to zero oxidation state in O_2 and decreases to -2 oxidation state in H_2O .

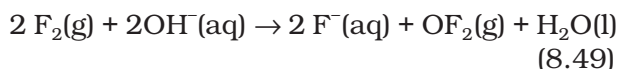
Phosphorous, sulphur and chlorine undergo disproportionation in the alkaline medium as shown below :



The reaction (8.48) describes the formation of household bleaching agents. The hypochlorite ion (ClO^-) formed in the reaction oxidises the colour-bearing stains of the substances to colourless compounds.

It is of interest to mention here that whereas bromine and iodine follow the same trend as exhibited by chlorine in reaction (8.48),

fluorine shows deviation from this behaviour when it reacts with alkali. The reaction that takes place in the case of fluorine is as follows:



(It is to be noted with care that fluorine in reaction (8.49) will undoubtedly attack water to produce some oxygen also). This departure shown by fluorine is not surprising for us as we know the limitation of fluorine that, being the most electronegative element, it cannot exhibit any positive oxidation state. This means that among halogens, fluorine does not show a disproportionation tendency.

Problem 8.5

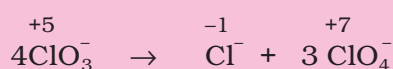
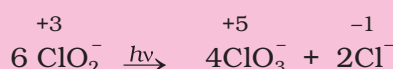
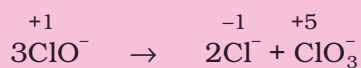
Which of the following species, do not show disproportionation reaction and why ?



Also write reaction for each of the species that disproportionates.

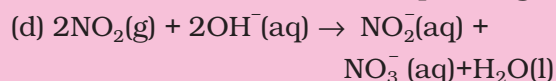
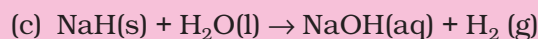
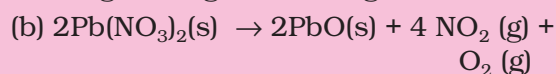
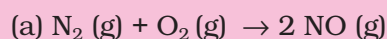
Solution

Among the oxoanions of chlorine listed above, ClO_4^- does not disproportionate because in this oxoanion chlorine is present in its highest oxidation state that is, $+7$. The disproportionation reactions for the other three oxoanions of chlorine are as follows:



Problem 8.6

Suggest a scheme of classification of the following redox reactions



Solution

In reaction (a), the compound nitric oxide is formed by the combination of the elemental substances, nitrogen and oxygen; therefore, this is an example of combination redox reactions. The reaction (b) involves the breaking down of lead nitrate into three components; therefore, this is categorised under decomposition redox reaction. In reaction

(c), hydrogen of water has been displaced by hydride ion into dihydrogen gas. Therefore, this may be called as displacement redox reaction. The reaction (d) involves disproportionation of NO_2 (+4 state) into NO_2^- (+3 state) and NO_3^- (+5 state). Therefore reaction (d) is an example of disproportionation redox reaction.

The Paradox of Fractional Oxidation Number

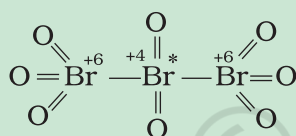
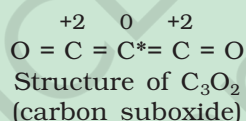
Sometimes, we come across with certain compounds in which the oxidation number of a particular element in the compound is in fraction. Examples are:

C_3O_2 [where oxidation number of carbon is (4/3)],

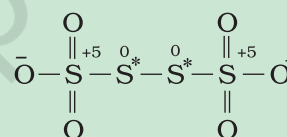
Br_3O_8 [where oxidation number of bromine is (16/3)]

and $\text{Na}_2\text{S}_4\text{O}_6$ (where oxidation number of sulphur is 2.5).

We know that the idea of fractional oxidation number is unconvincing to us, because electrons are never shared/transferred in fraction. Actually this fractional oxidation state is the average oxidation state of the element under examination and the structural parameters reveal that the element for whom fractional oxidation state is realised is present in different oxidation states. Structure of the species C_3O_2 , Br_3O_8 and $\text{S}_4\text{O}_6^{2-}$ reveal the following bonding situations:



Structure of Br_3O_8 (tribromooctaoxide)



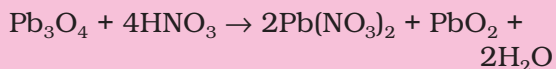
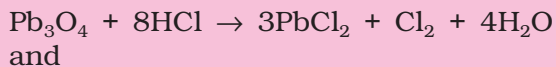
Structure of $\text{S}_4\text{O}_6^{2-}$ (tetrathionate ion)

The element marked with asterisk in each species is exhibiting the different oxidation state (oxidation number) from rest of the atoms of the same element in each of the species. This reveals that in C_3O_2 , two carbon atoms are present in +2 oxidation state each, whereas the third one is present in zero oxidation state and the average is 4/3. However, the realistic picture is +2 for two terminal carbons and zero for the middle carbon. Likewise in Br_3O_8 , each of the two terminal bromine atoms are present in +6 oxidation state and the middle bromine is present in +4 oxidation state. Once again the average, that is different from reality, is 16/3. In the same fashion, in the species $\text{S}_4\text{O}_6^{2-}$, each of the two extreme sulphurs exhibits oxidation state of +5 and the two middle sulphurs as zero. The average of four oxidation numbers of sulphurs of the $\text{S}_4\text{O}_6^{2-}$ is 2.5, whereas the reality being +5, 0, 0 and +5 oxidation number respectively for each sulphur.

We may thus, in general, conclude that the idea of fractional oxidation state should be taken with care and the reality is revealed by the structures only. Further, whenever we come across with fractional oxidation state of any particular element in any species, we must understand that this is the average oxidation number only. In reality (revealed by structures only), the element in that particular species is present in more than one whole number oxidation states. Fe_3O_4 , Mn_3O_4 , Pb_3O_4 are some of the other examples of the compounds, which are mixed oxides, where we come across with fractional oxidation states of the metal atom. However, the oxidation states may be in fraction as in O_2^+ and O_2^- where it is $+1/2$ and $-1/2$ respectively.

Problem 8.7

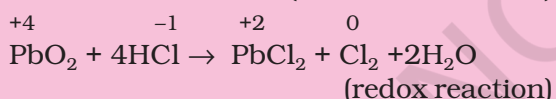
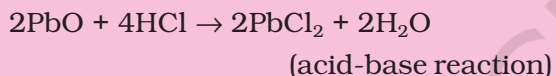
Why do the following reactions proceed differently ?

**Solution**

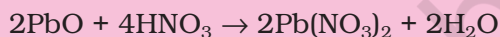
Pb_3O_4 is actually a stoichiometric mixture of 2 mol of PbO and 1 mol of PbO_2 . In PbO_2 , lead is present in +4 oxidation state, whereas the stable oxidation state of lead in PbO is +2. PbO_2 thus can act as an oxidant (oxidising agent) and, therefore, can oxidise Cl^- ion of HCl into chlorine. We may also keep in mind that PbO is a basic oxide. Therefore, the reaction



can be splitted into two reactions namely:



Since HNO_3 itself is an oxidising agent therefore, it is unlikely that the reaction may occur between PbO_2 and HNO_3 . However, the acid-base reaction occurs between PbO and HNO_3 as:



It is the passive nature of PbO_2 against HNO_3 that makes the reaction different from the one that follows with HCl .

(a) Oxidation Number Method: In writing equations for oxidation-reduction reactions, just as for other reactions, the compositions and formulas must be known for the substances that react and for the products that are formed. The oxidation number method is now best illustrated in the following steps:

Step 1: Write the correct formula for each reactant and product.

Step 2: Identify atoms which undergo change in oxidation number in the reaction by assigning the oxidation number to all elements in the reaction.

Step 3: Calculate the increase or decrease in the oxidation number per atom and for the entire molecule/ion in which it occurs. If these are not equal then multiply by suitable number so that these become equal. (If you realise that two substances are reduced and nothing is oxidised or vice-versa, something is wrong. Either the formulas of reactants or products are wrong or the oxidation numbers have not been assigned properly).

Step 4: Ascertain the involvement of ions if the reaction is taking place in water, add H^+ or OH^- ions to the expression on the appropriate side so that the total ionic charges of reactants and products are equal. If the reaction is carried out in acidic solution, use H^+ ions in the equation; if in basic solution, use OH^- ions.

Step 5: Make the numbers of hydrogen atoms in the expression on the two sides equal by adding water (H_2O) molecules to the reactants or products. Now, also check the number of oxygen atoms. If there are the same number of oxygen atoms in the reactants and products, the equation then represents the balanced redox reaction.

Let us now explain the steps involved in the method with the help of a few problems given below:

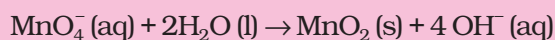
Problem 8.8

Write the net ionic equation for the reaction of potassium dichromate(VI), $\text{K}_2\text{Cr}_2\text{O}_7$ with sodium sulphite, Na_2SO_3 , in an acid solution to give chromium(III) ion and the sulphate ion.

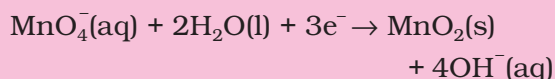
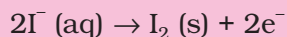
8.3.2 Balancing of Redox Reactions

Two methods are used to balance chemical equations for redox processes. One of these methods is based on the change in the oxidation number of reducing agent and the oxidising agent and the other method is based on splitting the redox reaction into two half reactions — one involving oxidation and the other involving reduction. Both these methods are in use and the choice of their use rests with the individual using them.

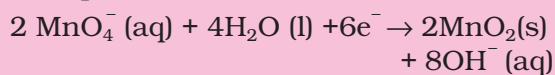
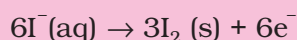
the resultant equation is:



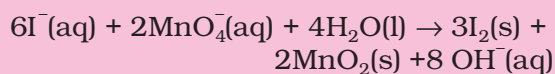
Step 5: In this step we balance the charges of the two half-reactions in the manner depicted as:



Now to equalise the number of electrons, we multiply the oxidation half-reaction by 3 and the reduction half-reaction by 2.



Step 6: Add two half-reactions to obtain the net reactions after cancelling electrons on both sides.



Step 7: A final verification shows that the equation is balanced in respect of the number of atoms and charges on both sides.

8.3.3 Redox Reactions as the Basis for Titrations

In acid-base systems we come across with a titration method for finding out the strength of one solution against the other using a pH sensitive indicator. Similarly, in redox systems, the titration method can be adopted to determine the strength of a reductant/oxidant using a redox sensitive indicator. The usage of indicators in redox titration is illustrated below:

- (i) In one situation, the reagent itself is intensely coloured, e.g., permanganate ion, MnO_4^- . Here MnO_4^- acts as the self indicator. The visible end point in this case is achieved after the last of the reductant (Fe^{2+} or $\text{C}_2\text{O}_4^{2-}$) is oxidised and the first lasting tinge of pink colour appears at MnO_4^- concentration as low as $10^{-6} \text{ mol dm}^{-3}$ ($10^{-6} \text{ mol L}^{-1}$). This ensures a minimal 'overshoot' in colour beyond the equivalence point, the point where the reductant and the oxidant are equal in terms of their mole stoichiometry.

- (ii) If there is no dramatic auto-colour change (as with MnO_4^- titration), there are indicators which are oxidised immediately after the last bit of the reactant is consumed, producing a dramatic colour change. The best example is afforded by $\text{Cr}_2\text{O}_7^{2-}$, which is not a self-indicator, but oxidises the indicator substance diphenylamine just after the equivalence point to produce an intense blue colour, thus signalling the end point.

- (iii) There is yet another method which is interesting and quite common. Its use is restricted to those reagents which are able to oxidise I^- ions, say, for example, Cu(II) :
 $2\text{Cu}^{2+} (\text{aq}) + 4\text{I}^- (\text{aq}) \rightarrow \text{Cu}_2\text{I}_2 (\text{s}) + \text{I}_2 (\text{aq})$ (8.59)

This method relies on the facts that iodine itself gives an intense blue colour with starch and has a very specific reaction with thiosulphate ions ($\text{S}_2\text{O}_3^{2-}$), which too is a redox reaction:



I_2 , though insoluble in water, remains in solution containing KI as KI_3 .

On addition of starch after the liberation of iodine from the reaction of Cu^{2+} ions on iodide ions, an intense blue colour appears. This colour disappears as soon as the iodine is consumed by the thiosulphate ions. Thus, the end-point can easily be tracked and the rest is the stoichiometric calculation only.

8.3.4 Limitations of Concept of Oxidation Number

As you have observed in the above discussion, the concept of redox processes has been evolving with time. This process of evolution is continuing. In fact, in recent past the oxidation process is visualised as a decrease in electron density and reduction process as an increase in electron density around the atom(s) involved in the reaction.

8.4 REDOX REACTIONS AND ELECTRODE PROCESSES

The experiment corresponding to reaction (8.15), can also be observed if zinc rod is dipped in copper sulphate solution. The redox reaction takes place and during the reaction,

zinc is oxidised to zinc ions and copper ions are reduced to metallic copper due to direct transfer of electrons from zinc to copper ion. During this reaction heat is also evolved. Now we modify the experiment in such a manner that for the same redox reaction transfer of electrons takes place indirectly. This necessitates the separation of zinc metal from copper sulphate solution. We take copper sulphate solution in a beaker and put a copper strip or rod in it. We also take zinc sulphate solution in another beaker and put a zinc rod or strip in it. Now reaction takes place in either of the beakers and at the interface of the metal and its salt solution in each beaker both the reduced and oxidized forms of the same species are present. These represent the species in the reduction and oxidation half reactions. A **redox couple** is defined as having together the oxidised and reduced forms of a substance taking part in an oxidation or reduction half reaction.

This is represented by separating the oxidised form from the reduced form by a vertical line or a slash representing an interface (e.g. solid/solution). For example in this experiment the two redox couples are

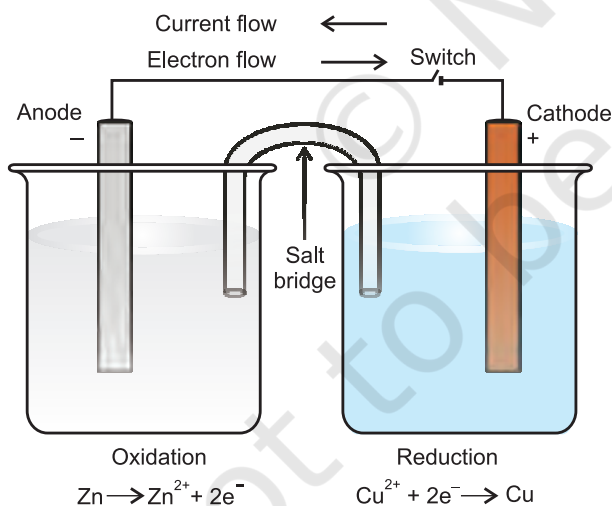


Fig.8.3 The set-up for Daniell cell. Electrons produced at the anode due to oxidation of Zn travel through the external circuit to the cathode where these reduce the copper ions. The circuit is completed inside the cell by the migration of ions through the salt bridge. It may be noted that the direction of current is opposite to the direction of electron flow.

represented as Zn^{2+}/Zn and Cu^{2+}/Cu . In both cases, oxidised form is put before the reduced form. Now we put the beaker containing copper sulphate solution and the beaker containing zinc sulphate solution side by side (Fig. 8.3). We connect solutions in two beakers by a salt bridge (a U-tube containing a solution of potassium chloride or ammonium nitrate usually solidified by boiling with agar agar and later cooling to a jelly like substance). This provides an electric contact between the two solutions without allowing them to mix with each other. The zinc and copper rods are connected by a metallic wire with a provision for an ammeter and a switch. The set-up as shown in Fig.8.3 is known as Daniell cell. When the switch is in the off position, no reaction takes place in either of the beakers and no current flows through the metallic wire. As soon as the switch is in the on position, we make the following observations:

1. The transfer of electrons now does not take place directly from Zn to Cu^{2+} but through the metallic wire connecting the two rods as is apparent from the arrow which indicates the flow of current.
2. The electricity from solution in one beaker to solution in the other beaker flows by the migration of ions through the salt bridge. We know that the flow of current is possible only if there is a potential difference between the copper and zinc rods known as **electrodes** here.

The potential associated with each electrode is known as **electrode potential**. If the concentration of each species taking part in the electrode reaction is unity (if any gas appears in the electrode reaction, it is confined to 1 atmospheric pressure) and further the reaction is carried out at 298K, then the potential of each electrode is said to be the **Standard Electrode Potential**. By convention, the standard electrode potential (E^\ominus) of hydrogen electrode is 0.00 volts. The electrode potential value for each electrode process is a measure of the relative tendency of the active species in the process to remain in the oxidised/reduced form. A negative E^\ominus means that the redox couple is a stronger