

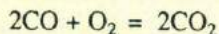
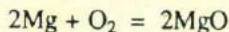
CHAPTER 7

OXIDATION-REDUCTION REACTIONS

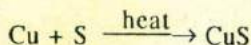
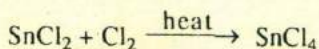
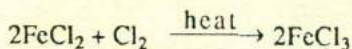
There are many different kinds of chemical reactions, some of which have been discussed in the previous chapter. One very important class of chemical reaction deserves special study and these are oxidation-reduction reactions. Oxidation-reduction reactions are defined according to various concepts.

1. The Classical Concept : According to the classical concept, "oxidation" simply means the addition of oxygen to elements or compounds. This was the original idea about oxidation and likewise the word "reduction" was used to indicate the removal of oxygen from a compound. The definitions were further extended to include other electronegative and electropositive atoms or groups as well as the removal and addition of hydrogen to make the terms more generalized.

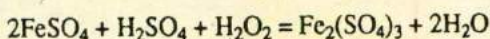
(a) *Addition of oxygen :*



(b) *Addition of electronegative element or group :*

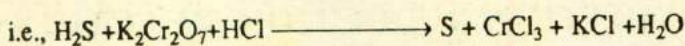
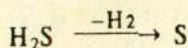


Hydrogen peroxide oxidizes an acidified solution of ferrous sulphate to ferric sulphate increasing the proportion of SO_4^{-2} radical :

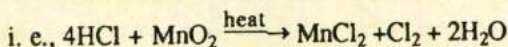
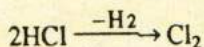


(c) *Removal of hydrogen :*

When H_2S is passed into an acidified solution of potassium dichromate, it is oxidized to sulphur :

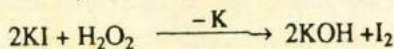


Chlorine is evolved when HCl is heated with MnO_2 . Here HCl is oxidized to chlorine :

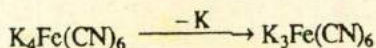


(d) *Removal of electropositive element or group :*

Potassium iodide is oxidized to iodine by the action of hydrogen peroxide. Here K^+ is removed from KI :



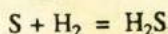
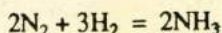
Potassium ferrocyanide is oxidized to potassium ferricyanide by removal of K^+ :



It can now be easily seen that the definition of the term "reduction" will be just the reverse of that of "oxidation" from the classical point of view.

The term "reduction" may be illustrated by the following reaction.

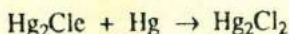
(a) *Addition of hydrogen :*



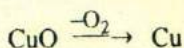
In the above reactions N and S are reduced to NH_3 and H_2S respectively by addition of H_2 .

(b) *Addition of electropositive element or group :*

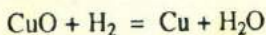
Mercuric chloride is reduced to mercurous chloride on heating with mercury. Here the electropositive Hg is added to HgCl_2 :



(c) *Removal of oxygen :*



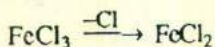
i. e., when hydrogen is passed over heated CuO, it is reduced to Cu by removal of oxygen. Thus,



Similarly, $\text{Fe}_2\text{O}_3 + 3\text{C} = 2\text{Fe} + 3\text{CO}$

Fe_2O_3 is reduced to iron by removal of oxygen on heating with carbon.

(d) *Removal of electronegative element or group :*



FeCl_3 is reduced to FeCl_2 by removal of Cl. This can happen in presence of zinc in acid solution or by means of SnCl_2 . Thus,



Similarly, $\text{CuSO}_4 + \text{Fe} = \text{Cu} + \text{FeSO}_4$

CuSO_4 is reduced to copper by removal of SO_4^{-2} by Fe.

2. Valence state Concept : It will be observed that the oxidation-reduction reactions take place with changes in the valence state of certain atom in the compounds undergoing the reaction. Thus when ferrous chloride is oxidized to ferric chloride, the valence state of iron is increased from divalent to trivalent. Similarly, when H_2S is oxidized to elementary sulphur, the valence state of sulphur is increased from -2 to zero and when CuO is reduced to Cu, the valence state of copper is decreased from $+2$ to zero. On the basis of valence state, therefore, the following simplified definitions for oxidation and reduction may be put forward:—

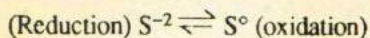
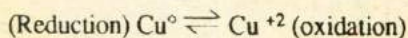
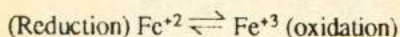
Oxidation is a chemical reaction which involves change of valence state in the positive direction.

Reduction is a chemical reaction which involves change of valence state in the negative direction.

3. The Electronegativity Concept : Electronegativity is defined as the tendency for an atom in a molecule to attract electrons. During oxidation-reduction reaction it can be observed that certain atoms in the compounds undergo decrease or increase of electronegativity value. During oxidation there is always a decrease in the electronegativity of an atom, whereas reduction involves increase of electronegativity value. Substances having high electronegativity act as oxidizing agent such as fluorine, halogen, oxygen etc. Substances having low values of electronegativity act as reducing agent, such as hydrogen, sodium, potassium etc.

4. The Charge Concept : Since the terms electropositive and electronegative elements have been used in the classical concept of oxidation-reduction reactions. The following procedure may be adopted to illustrate the phenomena :—

When ferrous salt is oxidized to ferric salt, it can be seen that Fe^{+2} is converted to Fe^{+3} . Similarly, when copper is converted to copper sulphate, CuSO_4 , the charge on copper increases from zero to +2. When H_2S is oxidized to elementary sulphur, the charge on sulphur is changed from -2 to zero.



Naturally, when the reaction takes place in the reverse manner i. e., to the left, this indicates reduction. Hence the following definition :

Oxidation is a process which involves increase of positive charges on an element or removal of negative charges.

Reduction is a process which involves increase of negative charges or decrease of positive charges on an element.

If we examine this definition of oxidation-reduction reaction it is not quite clear as to how this increase of positive charges or removal of negative charges occurs. Obviously, there is no mechanism to consider direct addition of positive

charges to an atom by chemical reaction. Oxidation-reduction reaction is best explained on the basis of electron transfer process as given by the electronic concept.

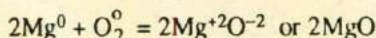
5. The Electronic Concept : When ferrous chloride is oxidized to ferric chloride by chlorine in aqueous solution, Fe^{+2} is converted to Fe^{+3} and Cl^0 is changed to Cl^- . Similarly, the oxidation of magnesium to MgO involves the change of Mg to Mg^{+2} and of O^0 to O^{-2} . The only way to account for this change is by means of electron transfer process. The electrons in the outermost energy level, i. e., valence electrons in an atom undergo changes during the chemical reaction. The electrons in the outermost energy level may be lost or electrons may be gained depending upon the electronic arrangements of the atom. Thus when Mg^0 is oxidized to Mg^{+2} , the two electrons in the outermost energy level, $2s^2$, are lost. Similarly, oxidation of Fe^0 to Fe^{+2} is due to the loss of two electrons from $4s$ energy level. Subsequent oxidation of Fe^{+2} to Fe^{+3} is due to the loss of one electron from $3d$ level which originally contains 6 electrons, i. e., $3d^6$ which has tendency to lose one electron to become $3d^5$ which, now, half-filled represents a stable electronic arrangement.

Now we can give a generalized definition of oxidation :

Oxidation is a process which involves loss of electrons by an atom or an ion.

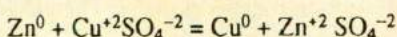
Similarly, reduction can be attributed due to the gain of electrons by an atom. Thus when oxygen is reduced to O^{-2} , or Fe^{+3} is reduced to Fe^{+2} and subsequently to Fe , the entire process can be easily explained on the basis of gain of electrons by an atom or an ion.

An oxidizing agent is one that accepts electrons and is thereby reduced. A reducing agent is one that gives electrons and is thereby oxidized. Therefore, in oxidation-reduction reactions, electrons are transferred from the reducing agent to the oxidizing agent. The oxidation-reduction reactions (also known as *redox* reactions) are complementary and take place simultaneously. Consequently, oxidation (the loss of electrons) and reduction (the gain of electrons) must always accompany each other in a reaction. In other words, if a given reaction involves an oxidation it must also involve a reduction. Thus the reaction between Mg and oxygen :



Hence, Mg^0 is oxidized to Mg^{+2} by loss of two electrons and oxygen O^0 is reduced to oxide O^{-2} ion. Mg is the reducing agent and O_2 is acting as an oxidizing agent.

In the reaction between Zn and CuSO_4 solution, metallic copper is deposited and some of the zinc rapidly dissolves :

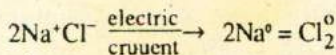


Notice that the SO_4^{-2} ion does not undergo any change in this oxidation-reduction reaction. The zinc metal is oxidized from Zn^0 to Zn^{+2} ion obviously by loss of two electrons. The copper ion, Cu^{+2} , is reduced to Cu^0 by the gain of these two electrons. Here Zn^0 is oxidized and acts as the reducing agent and Cu^{+2} is reduced and acts as oxidizing agent.

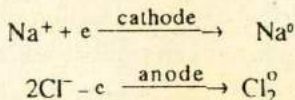
It may be mentioned here that this is the simplest and at the same time most comprehensive theory of oxidation-reduction reactions that has ever been put forward.

The simple explanation of electron transfer may be readily demonstrated with test tube experiment.

Oxidation-reduction reactions according to the electronic concept is essentially an electrical phenomenon. This means that it should be possible to accomplish oxidation-reduction simply by means of electric energy. The chemical reactions, therefore, can be made to occur by passing electricity through solutions of ions :

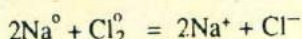


Thus, where Na^+ is reduced to Na^0 and Cl^- is oxidized to Cl^0 and, therefore, represented as,



Thus electrolysis is a simple electron transfer reaction. These oxidation-reduction reactions do not occur spontaneously but take place only if electrical energy is supplied.

Not only oxidation-reduction can be accomplished by electric current but also, *vice versa*, electricity can be generated by proper arrangements of an oxidation-reduction reaction. Thus the reverse reaction,

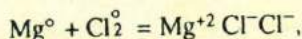


where Na^0 is oxidized to Na^+ and Cl^0 is reduced to Cl^- , takes place spontaneously and spontaneous oxidation-reduction reactions of this sort, which involve the loss and gain of electrons, can actually be used as a means of generating electric current. The arrangements require that electrons lost by Na^0 and gained by Cl_2 pass through a conducting wire during the oxidation-reduction reaction between the two, thereby we can produce a source of electric current. Similarly, the reactions between Zn and H_2SO_4 or CuSO_4 solutions produce electric current by the same mechanism of electron transfer from Zn to H^+ ions or Cu^{+2} ion respectively.

Important application of the oxidation-reduction reactions have been made in connection with the manufacture of dry cells, storage batteries and other type of appliances for producing electricity.

Oxidation State and Oxidation Number

When the electrons in the outermost energy level (or valence electrons) are removed from an atom during a chemical reaction, the atom is said to be in a positive oxidation state. Similarly, when an atom takes up electron during a chemical reaction, the atom is said to be in a negative oxidation state. The number of electrical charges on an atom is known as the *Oxidation Number*. Thus in the reaction,



the oxidation number of Mg undergoes a change from zero in the free state to +2 and the oxidation number of chlorine changes from zero in the free state to -1. It may be noted that during oxidation generally the oxidation number of an element is increased and during reduction the oxidation number is decreased. A substance

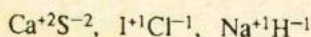
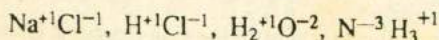
that causes an increase in the oxidation number of another substance is called an oxidizing agent. A substance that causes a decrease in the oxidation number of another substance is called a reducing agent.

Assignment of Oxidation Number

In connection with oxidation-reduction reaction it is convenient to adopt a generalization in order to assign the correct value for the oxidation number of an element in a compound. Oxidation-reduction reactions are important in chemistry, and writing of balanced equations of these reactions often involves cumbersome process by trial and error method. But the writing of equations has been, for the most part, simplified by adopting the use of oxidation numbers and their changes which occur during oxidation-reduction reactions. The following rules for assigning oxidation number are generally followed :—

(1) Neutral atoms and molecules have zero oxidation number.

(2) When atoms of different elements are present in a molecule, the more electronegative atoms will have a negative oxidation number and the less electronegative atoms have positive oxidation number. Thus,



Generally metallic atoms in a compound have positive oxidation number and non-metallic atoms in a compound have negative oxidation number.

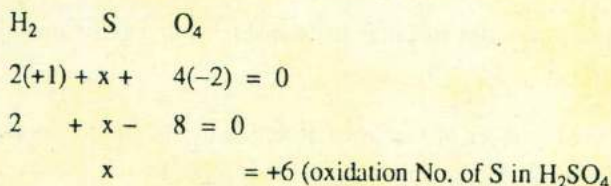
(3) Hydrogen is +1 when combined with non-metal and -1 when combined with metals.

(4) Oxygen is -2 except in peroxides when it is -1.

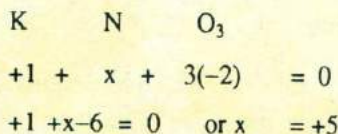
(5) The oxidation number of a compound is always zero. It is determined by the sum of oxidation numbers of the individual atoms, each multiplied by the number of atoms of the element present in the molecule.

In a given compound the sum of the positive oxidation numbers is equal to the sum of the negative oxidation numbers and since the molecule as a whole is neutral, the algebraic sum of the positive and negative oxidation numbers is zero.

Thus knowing the oxidation numbers of some of the well-known elements in a compound, the oxidation number of the unknown can be calculated. For instance, in H_2SO_4 , The oxidation number of H is +1 and that of oxygen is -2; the oxidation number of sulphur is easily found out :

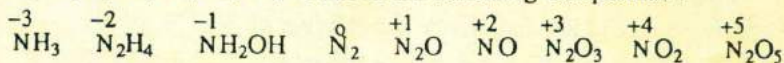


Similarly, in the case of KNO_3 the oxidation number of N can be calculated as follows :

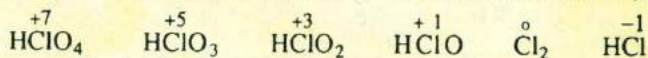


Some element may exist in several oxidation states and can have several oxidation numbers. Thus nitrogen can have oxidation states :

-3, -2, -1, 0, +1, +2, +3, +4, +5, as in the following compounds :



Similarly, chlorine has oxidation numbers +7, +5, +3, +1, 0 and -1, as in,



Rules for Writing of Equations Involving Oxidation-Reduction Reactions

There are various methods for writing the oxidation-reduction equations and one of the most convenient procedures for balancing such equations is based upon the transfer of electrons. This involves consideration of the change in the oxidation numbers of the elements undergoing oxidation-reduction reactions. The following simple rules provide a convenient means to write the oxidation-reduction equations in the balanced and completed forms.

Rule 1. Indicate the oxidation numbers of each element in the oxidizing and reducing agents in both the states respectively.

Rule 2. Note the elements which undergo a change in the oxidation numbers during the reaction and indicate the electrons gained and lost by them.

Rule 3. Use H^+ ions to form undissociated molecules of water where necessary.

Rule 4. Use H_2O molecules in order to form higher oxygen containing product during oxidation.

Rule 5. Make total number of electrons accepted by the oxidizing agent equal to the total number of electrons given by the reducing agent.

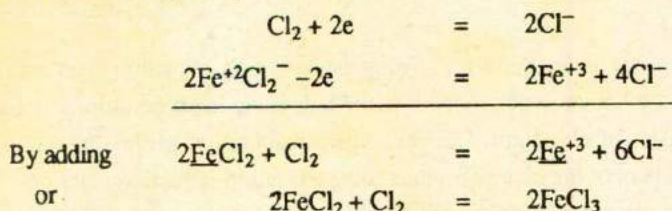
Rule 6. Complete the equation by providing appropriate missing ionic species to form molecules after adding both the sides of the equation and cancelling out equal terms.

Various types of oxidation-reduction reactions have been selected to illustrate the application of the above rules. It may be noted that all the rules may not always be required to write oxidation-reduction equations. Which of the rules will be applicable could be easily determined.

Example 1. Ferrous chloride is oxidized by chlorine to ferric chloride. Writing the change in ferrous chloride and chlorine we get,



Since the loss and gain of electrons during the process must be equal, the second part has to be multiplied by 2 :

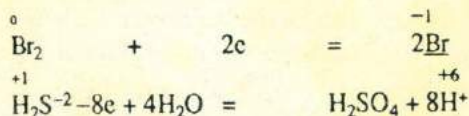


The equation is obtained in the completed and balanced form.

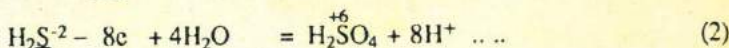
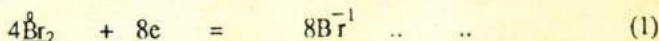
Example 2. H_2S is oxidized to H_2SO_4 when passed into a concentrated aqueous solution of bromine.

Here bromine acts as an oxidising agent; hence it accepts one electron per atom and is reduced to bromide. When H_2S is oxidized to H_2SO_4 the oxidation number of S is changed from -2 to $+6$ by loss of 8 electrons.

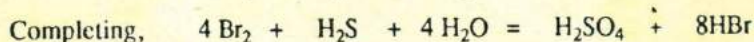
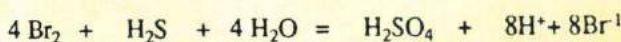
Now, we find that a higher oxygen containing substance H_2SO_4 is formed by oxidation of H_2S which has no oxygen atom. Hence 4 oxygen atoms in H_2SO_4 will require the use of 4 molecules of H_2O . Thus we write two half-reaction underlining the symbols of those elements which undergo change in the reactions :



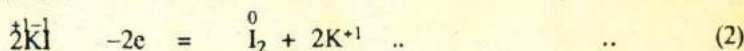
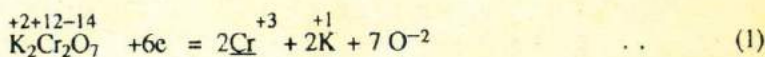
The loss and gain of electrons must be equal. Hence the upper half-reaction is to be multiplied by 4 :



On adding (1) and (2) we have,

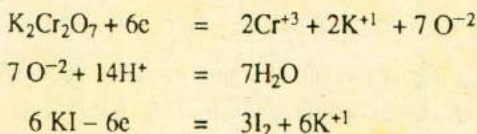


Example 3. Potassium dichromate oxidizes potassium iodide in acid solution liberating iodine :

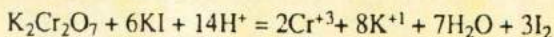


Now, 7O^{-2} require 14H^+ ions to form $7\text{H}_2\text{O}$ and, therefore, 14H^+ is to be introduced in the half-reaction in (1); and in order to make the number of

electron lost and gained equal, the half-reaction (2) is to be multiplied by 3. Thus we get,

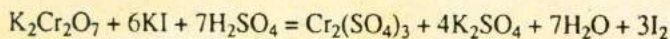


On adding and cancelling equal terms,

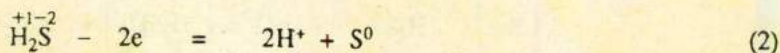
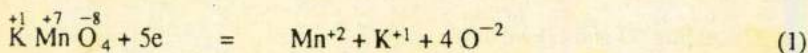


The above equation is almost complete, except the requirement arising out of the use of H^+ ions. The H^+ ions can come from an acid. Generally the acid used is HCl or H_2SO_4 and hence the anionic portion for the various cations will depend upon the acid used. HCl will give chlorides and H_2SO_4 will form sulphates. Thus the complete equation is automatically derived :

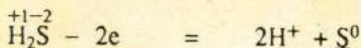
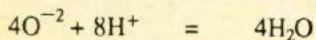
$\text{K}_2\text{Cr}_2\text{O}_7 + 6\text{KI} + 14\text{HCl} = 2\text{CrCl}_3 + 8\text{KCl} + 7\text{H}_2\text{O} + 3\text{I}_2$ or, in the case of H_2SO_4 ,



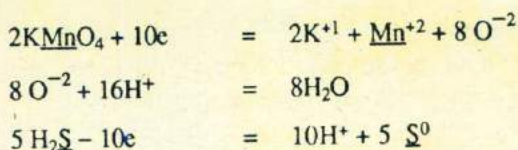
Example 4. Potassium permanganate oxidizes H_2S in aqueous solution and sulphur is liberated :



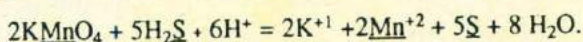
Now 4O^{-2} require 8H^+ to form $4\text{H}_2\text{O}$ and, therefore 8H^+ is to be introduced in (1) and we get,



Multiplying (1) by 2 and (2) by 5 in order to make the loss and gain of electrons equal, we have,

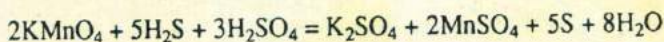


On adding, cancelling equal terms and adjusting the species involved we have,

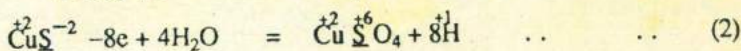
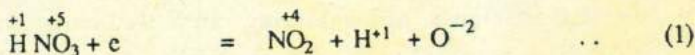


In order to complete the equation, again it is required to supply the anionic species which will obviously depend upon the acid used. Generally, the acid used is H_2SO_4 because HCl is oxidized by KMnO_4 and HNO_3 itself is an oxidizing agent besides an acid.

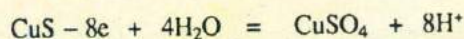
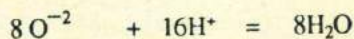
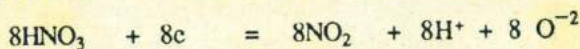
Hence the complete equation is :



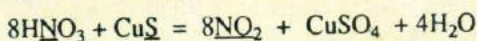
Example 5. Hot and concentrated nitric acid oxidizes CuS to CuSO_4 and NO_2 is evolved :



One O^{-2} requires 2H^{+} for conversion to H_2O and again (1) has to be multiplied by 8 in order to make the loss and gain of electrons equal. Thus,



On adding and cancelling equal terms,



The equation is complete without further adjustment.

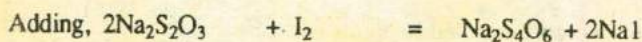
Example 6. The oxidation of sodium thiosulphate by iodine :

$\text{Na}_2\text{S}_2\text{O}_3$ is converted to $\text{Na}_2\text{S}_4\text{O}_6$ (sodium tetrathionate) I_2^0 is converted to iodide I^{-} .

Taking +1 as the oxidation number of Na and -2 as the oxidation number of oxygen, the average oxidation number of each S in Na_2SO_3 is +2 and that the average oxidation number of each S atom in $\text{Na}_2\text{S}_4\text{O}_6$ is $2\frac{1}{2}$. Hence,



Thus each S atom of thiosulphate loses $\frac{1}{2}$ electron for oxidation to tetrathionate. 4 S atoms in tetrathionate must come from 2 molecules of thiosulphate. Hence the total change in oxidation number of S is from 2 (+4) = +8 to $4 \times 2\frac{1}{2} = +10$



Equivalent Weights of Oxidizing and Reducing Substances in Reactions

The fundamental definition of equivalent weight is as follows :—

The equivalent weight of a substance is that weight which combines with or displaces 1.008 parts by weight of hydrogen or 8.000 parts by weight of oxygen. This fundamental definition may be extended and modified to the following definition which seems to be applicable to all ordinary cases.

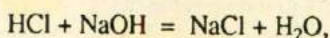
The gramme-equivalent weight of a substance taking part in chemical reaction is the number of grams of the substance associated with the transfer of N electron or proton or with the neutralization of N negative or positive charge (N is the Avogadro's Number). N may be conveniently replaced by 1 or unity which gives the same result. In acid-base reaction where neutralization reactions occur, protons (H^+) are transferred from the acid to the base and the number of protons transferred determines the equivalent weight of the acid or the base.

The changes in the oxidation numbers of some of the important oxidizing and reducing substances are given in Table 6-1.

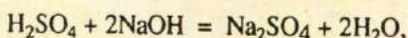
Table 6.1. Change in the oxidation numbers of some oxidizing and reducing reagents.

<i>Reagents</i>	<i>Effective elements</i>	<i>Oxidation number of effective element</i>	<i>No. of electrons involved</i>	<i>Change due to redox reaction</i>	<i>New oxidation number of effective element</i>	<i>Change in oxidation number</i>
KMnO ₄ (acid)	Mn	+7	+5e	Mn ⁺²	+2	5
KMnO ₄ (alk)	Mn	+7	+1e	K ₂ MnO ₄	+6	1
KMnO ₄ (neutral)	Mn	+7	+3e	MnO ₂	+4	3
K ₂ Cr ₂ O ₇	Cr	+6	+3e	Cr ⁺³	+3	3 per Cr atom
KClO ₃	Cl	+5	+6e	Cl ⁻¹	-1	6
Ce(SO ₄) ₂	Ce	+4	+1e	Ce ⁺³	+3	1
NaClO	Cl	+1	+2e	Cl ⁻¹	-1	2
H ₂ O ₂ (redn.)	O	-1	-2e	O ₂	0	1 per O atom
H ₂ O ₂ (oxn)	O	-1	+2e	O ⁻²	-2	1 per O atom
FeCl ₃	Fe	+3	+1e	Fe ⁺²	+2	1
H ₂ S	S	-2	-2e	S	0	2
H ₂ S	S	-2	-8e	H ₂ SO ₄	+6	8
SnCl ₂	Sn	+2	-2e	Sn ⁺⁴	+4	2
H ₂ C ₂ O ₄	C	+3	-1e	CO ₂	+4	1 per C atom
SO ₂	S	+4	-2e	SO ₄ ⁻²	+6	2
KI	I	-1	-1e	I ₂	0	1 per I atom
H ₂	H	0	-1e	H ⁺¹	+1	1 per H atom
Cu	Cu	0	-2e	Cu ⁺²	+2	2
Zn	Zn	0	-2e	Zn ⁺²	+2	2
I ₂	I	0	-1e	I ⁻¹	-1	1 per I atom

Thus in the reaction,

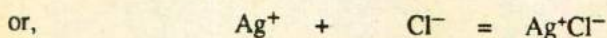
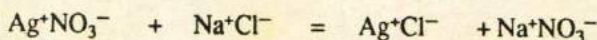


N protons (6.023×10^{23}) are transferred from HCl to NaOH. The g. equivalent weights of HCl or NaOH are, therefore, equal to one mole (36.5g.) of HCl and one mole (40.0g) of NaOH. When one mole of H_2SO_4 reacts with 2 moles of NaOH in the reaction :



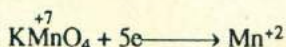
we have $2N$ protons transferred from H_2SO_4 to NaOH. hence one gramme-equivalent of H_2SO_4 is equal to g. mole divided by 2, i.e., $98.0/2 = 49.0$.

When silver nitrate reacts with sodium chloride, silver chloride is precipitated out according to the reaction,



The gramme-equivalent weights of AgNO_3 and NaCl are calculated from the number of charges neutralized electrically in the reaction. Here 1 positive charge of Ag^+ and 1 negative charge of Cl^- are neutralized. Hence the gramme-equivalent weight of AgNO_3 and that of NaCl are equal to one mole of AgNO_3 and NaCl (169.89g. and 58.46 g.) respectively. In the case of precipitation of BaSO_4 (i.e., $\text{Ba}^{+2} + \text{SO}_4^{-2} = \text{Ba}^{+2}\text{SO}_4^{-2}$) one mole of Ba^{+2} ion reacts with one mole of SO_4^{-2} ; 2 positive charges and 2 negative charges are neutralized. Hence the gramme-equivalent weight of BaCl_2 will be one-half the gramme-formula weight and that of Na_2SO_4 is also one-half the molecular weight.

In the case of oxidation-reduction reactions which always involve transfer of electrons from the substance oxidized to the substance reduced, the equivalent weights are easily calculated. The gramme-equivalent weight of an oxidizing or reducing substance is the weight which loses or gains 1 electron during the process. It may also be put as the weight of the substance which undergoes a change of one unit in the oxidation number of the effective element in the substance. In other words, the gramme-equivalent weight may be obtained by dividing the molecular weight by the total number of electrons transferred or from the total change in oxidation number . Thus,

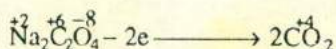


The change in oxidation number of Mn is 5 or the number of electrons accepted by Mn in KMnO_4 is also 5. Hence the gramme-equivalent weight of KMnO_4 for this reaction is equal to the molecular weight divided by 5, i.e., $158.02/5 = 31.63\text{g}$. Similarly,



Thus the effective element Cr accepts 6 electrons to change from +6 to +3 state. (The total charge on Cr in $\text{K}_2\text{Cr}_2\text{O}_7$ is $2 \times +6 = +12$ and 2Cr^{+3} has the total charge = $2 \times +3 = +6$. Hence a change of +12 to +6 involves the gain of 6 electrons.) The change in oxidation number is of 6 units. The gramme-equivalent weight of $\text{K}_2\text{Cr}_2\text{O}_7$ for the reduction to Cr^{+3} state is, therefore, equal to the molecular weight divided by 6. That is, $294.22/6 = 49.037\text{ g}$.

Similarly, the equivalent-weight of $\text{Na}_2\text{C}_2\text{O}_4$ may be calculated from the reaction



The total change in the oxidation number of carbon is from $(2 \times +3) = +6$ to $(2 \times +4) = +8$. This can be accomplished by the loss of 2 electrons. The total change in electron number is also 2. Hence the gramme-equivalent weight of $\text{Na}_2\text{C}_2\text{O}_4$ for this reaction is the molecular weight divided by 2.

The normality of an oxidizing or reducing agent is defined as :

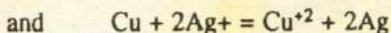
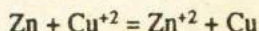
$$\text{Normality} = \frac{\text{No. of electrons gained or lost by 1 g. mole}}{1 \text{ litre of solution}}$$

Oxidation-Reduction Potential (Electrode Potential)

Oxidation potential or redox potential is the direct consequence of electron transfer phenomenon of oxidation-reduction reaction. It has been mentioned that electric current can be generated by carrying out oxidation-reduction reactions. When two electrodes are immersed in a solution containing oxidation-reduction system and then connected by a wire, a current flows through the wire from the anode to the cathode. The use of the reactions as a source of electrical energy is possible only if the reactions taking part in the redox reaction are not permitted to come into direct contact. If the reactants come into direct contact, the energy

is liberated as heat energy rather than as electrical energy. The conditions for the generations of electricity are that the cell assembly must have both the electron path between the electrodes via the metallic wire and also the ion path through the solutions. The ion path is generally created via a porous membrane or by suitable connections by a bridge containing ionic solution. The oxidation process always takes place at the anode and reduction at the cathode. It is obvious, therefore, that a chemical reaction involving oxidation-reduction generates electric potential commonly known as redox potential. The values of the redox potentials for the oxidation-reduction system have been determined in most cases and are of great theoretical and practical value. The details of these descriptions may be found in advanced text books on electrochemistry but an elementary qualitative treatment with respect to the applications of oxidation potential to understand the chemical reactions is given here briefly.

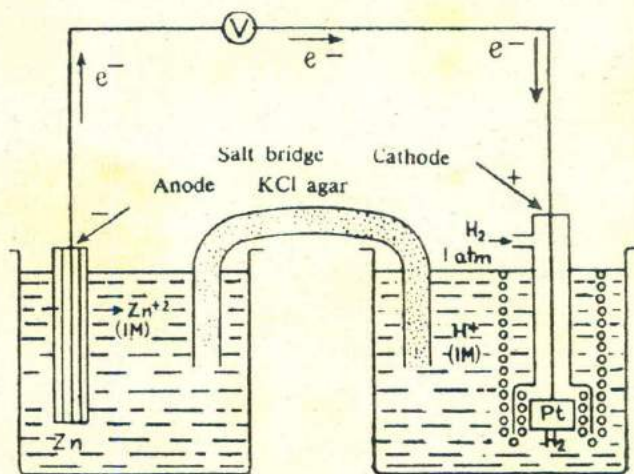
Considering the equations :



we know that the above reactions do take place and we say that Zn is more electropositive than Cu, and Cu is more electropositive than Ag and hence the electropositive metals in solutions are replaced by more electropositive metals. *The term "electropositive" of a metal means the "driving force" with which the metal tends to give up the valence electrons to form a positive ion.* Thus the electropositivity of Zn means the driving force, also known as "Solution Pressure", with which the reaction $\text{Zn} = \text{Zn}^{+2} + 2e$ takes place. Now, when the driving force is exerted during a reaction, energy must be spent. This means that energy is spent when Zn changes to Zn^{+2} in the reaction $\text{Zn} = \text{Zn}^{+2} + 2e$. Thus the effective energy content of Zn^{+2} must be less than that of Zn atoms. This effective energy content of a system is known as the "free energy" of the system. The free energy originates from the resultant (or product) of the heat content and tendency for the heat energy to be spent. A system of lower heat content but a higher tendency to spend it will have a higher free energy than one which has a larger heat content but less tendency to spend it. The difference between free energy of Zn and Zn^{+2} is called the change in the free energy that occurs when reaction $\text{Zn} = \text{Zn}^{+2} + 2e$ takes place. The change in free energy provides the

driving force of the reaction and makes it go. The driving force of a reaction is referred to as "Potential". The reactions involving oxidation, therefore, involves "Oxidation Potential". The oxidation potential, therefore, represents the change in the free energy of reaction. The values of oxidation potential is expressed in volts. More generally the driving force is known as "electrode potential" (E^0). The potential of a standard hydrogen electrode is arbitrarily considered to be zero. The standard hydrogen electrode is made by bubbling H_2 gas at a pressure of 1 atmosphere over platinized platinum immersed in a solution of H^+ ions of 1 M concentration.

To determine the electrode potential of any element, an electro-chemical cell is set up consisting of a strip of the element (say Zn) in contact with a 1 M solution (of Zn^{+2} ions). This is known as the *half-cell* and a standard hydrogen electrode is the other half-cell. The two half-cells connected by a salt bridge (KCl solution in a gel of agar) is shown in Fig. 7—1.



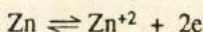
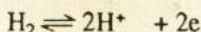
Zinc electrode
 $Zn \rightarrow Zn^{+2} + 2e^-$

Hydrogen electrode
 $2H^+ + 2e^- \rightarrow H_2$

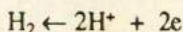
Fig. 7—1. Electrode Potential

This bridge allows the ions to migrate through it but does not allow the solutions to come in contact. On connecting the two half-cells with a voltmeter,

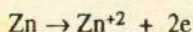
we can measure the potential difference of the cell as a whole. Each half-cell has the equilibrium reaction :



Because Zn has a greater tendency to go into solution as Zn^{+2} , the zinc acquires a higher electron density than the Pt of hydrogen electrode. Hence the greater electron pressure or electrode potential of Zn causes the electrons to flow to the hydrogen electrode through the wire connection. The flow of electrons from Zn to H increases the electron density at the hydrogen electrode and the equilibrium is shifted to the left causing H^+ ions to be reduced to H_2 :

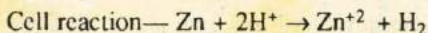
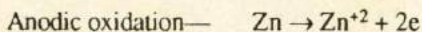


At the same time the electron density at the Zn-electrode is decreased, and the equilibrium is shifted to the right and more Zn is oxidized to Zn^{+2} ions :

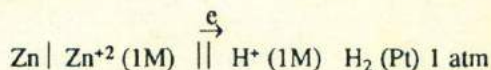


This difference in potential is measured by a voltmeter and is 0.76 volts. The force causing the electrons to move from the Zn-electrode to the H-electrode is called the electromotive force (E.M.F.) and is 0.76 volts. The Zn-electrode is the negative electrode (cathode) because its electron density is higher than that of H-electrode which is the positive electrode (anode). Since the potential of H-electrode is zero, we can say that the potential of Zn-electrode is above 0.76 volt than that of H-electrode. In other words, the sign of Zn-electrode is positive, i.e., + 0.76 volts.

The over-all reaction in the Zn—H cell is one of oxidation and reduction :

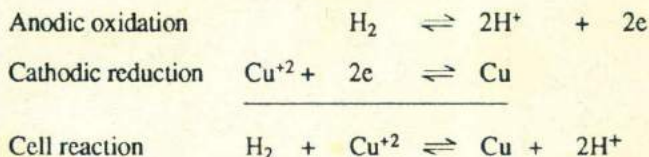


The cell is represented as :

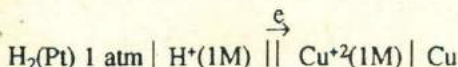


The Electromotive Series of the Elements

By measuring the electrode potentials of different metals, where ion concentrations are 1 Molar as in the case of Zn, the metals (or elements) can be arranged in accordance with the decreasing potentials. This series is known as the Electromotive Series or E. M. F. series of elements. The potential of $\text{H}_2 \rightleftharpoons 2\text{H}^+ + 2\text{e}$ has been arbitrarily assumed to be zero and there are negative values of the potentials for some metals also as shown in Table 7.2. For instance, when Cu metal in contact with Cu^{+2} is made the other electrode of a cell containing standard H-electrode, it is found that H has a greater tendency to form H^+ ions than does Cu. Consequently, electrons flow from the H-electrode to the Cu-electrode. The electrode processes are :



The E.M.F. of the cell,



has been measured by a voltmeter to be = 0.34 Volts (cell reversed)

The zero potential of H-electrode is above this figure of 0.34. Hence the electrode potential of Cu-electrode is -0.34 volt with respect to the H-electrode.

The electrode reactions given in Table 7.2 represent reversible reactions. This indicates that under one set of conditions a metal, say, Cu atoms, will give up electrons to form Cu^{+2} ions, while under another set of conditions Cu^{+2} ions will pick up electrons to give Cu atoms. This is the case with all the

Table 7.2. E.M.F. Series on Oxn-Redn. Potentials.

<i>Elements</i>	<i>Reduced form</i>	<i>Electrode reaction</i>	<i>Oxidized form</i>	<i>Electrode potential (volts)</i>
Potassium	K	\rightleftharpoons	$K^+ + e$	+ 2.92
Calcium	Ca	\rightleftharpoons	$Ca^{+2} + 2e$	+ 2.76
Sodium	Na	\rightleftharpoons	$Na^+ + e$	+ 2.71
Magnesium	Mg	\rightleftharpoons	$Mg^{+2} + 2e$	+ 2.34
Aluminium	Al	\rightleftharpoons	$Al^{+3} + 3e$	+ 1.67
Manganese	Mn	\rightleftharpoons	$Mn^{+2} + 2e$	+ 1.05
Zinc	Zn	\rightleftharpoons	$Zn^{+2} + 2e$	+ 0.76
Chromium	Cr	\rightleftharpoons	$Cr^{+3} + 3e$	+ 0.51
Iron	Fe	\rightleftharpoons	$Fe^{+2} + 2e$	+ 0.44
Cadmium	Cd	\rightleftharpoons	$Cd^{+2} + 2e$	+ 0.40
Cobalt	Co	\rightleftharpoons	$Co^{+2} + 2e$	+ 0.28
Nickel	Ni	\rightleftharpoons	$Ni^{+2} + 2e$	+ 0.25
Tin	Sn	\rightleftharpoons	$Sn^{+2} + 2e$	+ 0.14
Lead	Pb	\rightleftharpoons	$Pb^{+2} + 2e$	+ 0.13
Hydrogen	H_2	\rightleftharpoons	$2H^+ + 2e$	- 0.00
Copper	Cu	\rightleftharpoons	$Cu^{+2} + 2e$	- 0.34
Iodine	$2I^-$	\rightleftharpoons	$I_2 + 2e$	- 0.53
Silver	Ag	\rightleftharpoons	$Ag^+ + e$	- 0.80
Mercury	Hg	\rightleftharpoons	$Hg^{+2} + 2e$	- 0.85
Bromine	$2Br^-$	\rightleftharpoons	$Br_2 + 2e$	- 1.06
Platinum	Pt	\rightleftharpoons	$Pt^{+2} + 2e$	- 1.20
Oxygen	$2H_2O$	\rightleftharpoons	$O_2 + 4H^+ + 4e$	- 1.23
Chlorine	$2Cl^-$	\rightleftharpoons	$Cl_2 + 2e$	- 1.36
Gold	Au	\rightleftharpoons	$Au^+ + e$	- 1.68
Fluorine	$2F^-$	\rightleftharpoons	$F_2 + 2e$	- 2.85

electrode processes. The equations given indicate that the substance on the left is being oxidized and is acting as a reducing agent. The substances on the right side of the equation are formed and the reactions are proceeding to the right. When the reactions proceed to the left, the substances on the right side are acting as oxidizing agents.

The substances on the top of the table 7.2 are strongest reducing agents and the substances at the bottom are the weakest reducing agents. Thus the lower the oxidation potential, the weaker the reducing ability of the element. The elements at the bottom of table in the right side of the equilibrium equations are the strongest oxidizing agents. Thus the lower the oxidation potential, the stronger the oxidizing ability of the oxidizing agent.

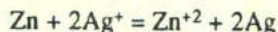
Uses of the E.M.F. Series

The oxidation potential values in the E.M.F. series of elements can be used to determine whether or not a reaction will take place. The most important uses may be mentioned as follows :—

(1) The metal with high electrode potential at the top of the series are good reducing agents. They are the metals most easily oxidized by removal of electrons. They have low electron affinities, low ionization potentials and low electronegativities.

(2) The elements with negative electrode potentials are good oxidizing agents when in the oxidized form, i.e., when the metals are in the form of ions and non-metals are in the form of neutral atoms or molecules.

(3) A reducing agent with a higher potential will reduce any oxidizing agent with a lower potential. The wider the potential difference, the more vigorous will be the reaction. This gives rise to the displacement reaction. To illustrate the application of the rules, the example of the reaction



may be mentioned. The electrodes involved have the following potentials :—



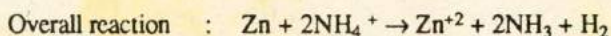
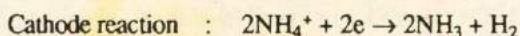
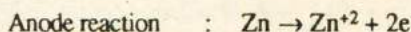
Therefore, Zn will be oxidized to Zn^{+2} by Ag^+ , and Ag^+ will be reduced to Ag by Zn. It means that Ag will be displaced from a solution of, say, $AgNO_3$, by adding Zn metal to the solution (dipping a strip of Zn to the solution of $AgNO_3$). Similarly, H_2 may be prepared by displacement reactions from an acid containing H^+ ions by means of metals which occur above H in the E.M.F. series. Metals with a high positive potential liberate hydrogen from acids with explosive violence and metals with low positive potential liberate hydrogen at a reasonable speed. The displacement reactions are generally applicable and any element will displace other which follows it in the E.M.F. series.

There are two types of cells which make use of oxidation-reduction reactions for generating electricity. They are :—

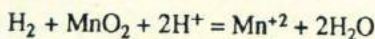
1. The Primary Cells : These are irreversible cells. The electrodes and electrolytes cannot be restored to their original states once they have been consumed for the production of current by the application of an external electrical potential. The "dry cell" is a primary cell and reactions are irreversible.

2. The Secondary Cells : In these cells the chemicals used and the electrodes may be regenerated after they have been consumed in producing electricity. This is done by passing a direct current of electricity to flow in the reverse direction of the discharge. This is called recharging the cell. The "lead storage battery or accumulators" is an example of secondary cells.

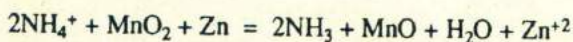
The Dry Cell : The container of the chemicals in this cell is made of Zn which serves as one of the electrodes and is separated from the chemicals by lining with porous paper. A carbon rod in the centre of the cells is the other electrode. The space around the carbon rod contains a mixture of NH_4Cl , MnO_2 , $ZnCl_2$ and some saw-dust, all moistened with H_2O in the form of a thick paste. The cells is sealed from top by shellac or pitch. When the dry cell generates electric current, Zn goes into solution as Zn^{+2} ions and electrons accumulate on Zn making it a negative electrode. NH_4^+ ions is reduced at the carbon electrode.



MnO_2 oxidizes H_2 , otherwise it will collect and stop the reaction :



The entire reaction :



NH_3 formed is taken up by ZnCl_2 forming the complex $\text{Zn}(\text{NH}_3)_4\text{Cl}_2$.

The voltage of the dry cell is generally 1.5 volts.

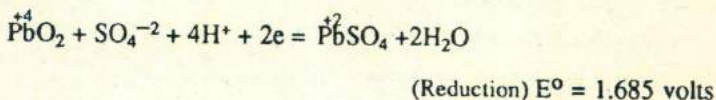
The Lead Accumulator (Storage cell) : The electrodes of lead storage battery consist of two lead plates. The negative plate consists of a spongy lead supported on grid made of Pb-Sb alloy. The positive pole is PbO_2 supported in a similar grid. The electrolyte is H_2SO_4 .

When the battery produces current, the following reaction takes place.

At the lead plate :

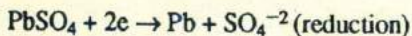


At the PbO_2 plate :

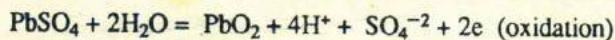


Electrons flow from the lead electrode through the external circuit and enter the lead dioxide electrode. The positively charged lead dioxide is the cathode and the lead electrode is the anode.

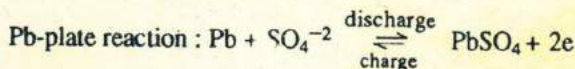
Recharging of lead accumulator is done by passing electrons through the cell in the reverse direction by applying an external potential. The lead electrode is now made the cathode. The reaction is :



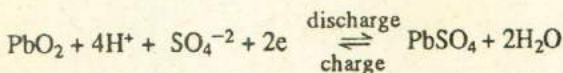
PbO_2 electrode is made positive and the oxidation reaction is :



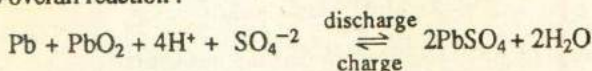
Thus the two processes may be written as :



PbO_2 -plate reaction :



The overall reaction :



H_2SO_4 consumed is replenished from time to time.

QUESTIONS AND PROBLEMS

- Explain oxidation and reduction.
- Explain what happens when :—
 - SO_2 is passed into a solution of Iodine.
 - A solution of $\text{Na}_2\text{S}_2\text{O}_3$ is added to acidified $\text{K}_2\text{Cr}_2\text{O}_7$ solution to which KI had been added.
 - Iodine reacts with a solution of $\text{Na}_2\text{S}_2\text{O}_3$.
- Explain the meaning of the term "oxidation state".
- Define oxidation and reduction in terms of change of oxidation number. What are oxidising and reducing agents ?
- What are oxidation numbers of nitrogen in each of the following compounds? N_2O , NO , N_2O_3 , N_2O_4 , HNO_2 , NH_3 , NH_4Cl , N_2H_4 , NH_2OH and AlN .
- Calculate the equivalent weight of the oxidising and reducing agents in the following reactions in term of the molecular weights of the respective compounds taken as M :—
 - $\text{H}_2\text{O}_2 + \text{KMnO}_4 + \text{H}^+ \rightarrow \text{Mn}^{+2} + \text{H}_2\text{O} + \text{O}_2$,
 - $\text{Zn} + \text{H}^+ + \text{NO}_3^- \rightarrow \text{Zn}^{+2} + \text{N}_2\text{O} + \text{H}_2\text{O}$,
 - $\text{K}_2\text{Cr}_2\text{O}_7 + \text{Fe}^{+2} + \text{H}^+ \rightarrow 2\text{Cr}^{+3} + 2\text{K}^+ + \text{Fe}^{+3} + \text{H}_2\text{O}$.
- What is meant by oxidation-reduction potentials ? How this can be applied for determining the feasibility of chemical reactions ?
- Write the equations of the following reactions :—
 - Chlorine is passed into a solution of ferrous chloride.

- (b) H_2S is passed into a neutral solution of KMnO_4 .
 - (c) Nitric acid is passed over heated copper.
 - (d) CuS is heated with strong HNO_3
 - (e) KBrO_3 reacts with KI in acid solution.
 - (f) KMnO_4 reacts with $\text{Na}_2\text{C}_2\text{O}_4$ in acid solution.
 - (g) H_2O_2 reacts with KI in neutral solution.
 - (h) $\text{Cr}(\text{OH})_3$ reacts with H_2O_2 in presence of NaOH
 - (i) HCl is dropped over KMnO_4 .
9. What is meant by the electromotive series of elements? What are the applications if this series ?
10. How do you use electromotive series in the preparation of some elements?
11. Complete and balance the following chemical equations :-
- (a) $\text{H}_2\text{S} + \text{KMnO}_4 + \text{H}_2\text{SO}_4 \rightarrow$
 - (b) $\text{As}_2\text{S}_3 + \text{HNO}_3 + \text{H}_2\text{O} \rightarrow$
 - (c) $\text{SnCl}_2 + \text{H}_2\text{SO}_3 + \text{HCl} \rightarrow$
 - (d) $\text{CrI}_3 + \text{KOH} + \text{Cl}_2 \rightarrow$
12. Write notes on :-
- (a) Oxidation and reduction
 - (b) Oxidation states and oxidation number of elements
13. Give the modern concept of oxidation and reduction , How can you prove experimentally that oxidation and reduction generate electricity ?
14. Discuss with examples (and equation) the disproportionation reactions and oxidation-reduction reactions. Mention their significance in chemistry.
15. Write explanatory note on Electronic Concept of oxidation and reduction.
16. Write note on variable oxidation states.
17. Discuss : Transfer of electrons occur during oxidation-reduction reaction.
18. Discuss the oxidation states of iron and chromium.

CHAPTER 8

OXIDES AND HYDROXIDES

The chemical facts concerning this important class of compounds have now been correlated with electronic arrangements, the ionic sizes, the oxidation states, electronegativity and bonding systems involved in the oxides and hydroxides of the elements.

Compounds containing oxygen as a constituent are most abundant and widely distributed. Among these, oxides of elements (other than halogen and noble metals) are by far the most important from the points of view of chemistry.

OXIDES

Oxides are binary compounds of oxygen and other elements. Oxides of all elements are known:-

The large number of oxides which are formed by various elements are subdivided into various classes. The classification is based upon two different considerations :-

A. Classification based upon reactions.

B. Classification based upon their structures and bonding systems.

A. Classification of Oxides based on reactions:

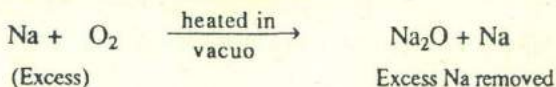
(a) Basic oxides, (b) Acidic oxides (c) Amphoteric oxides, (d) Neutral oxides, (e) Sub-oxides (f) Saline oxides (g) Nonstoichiometric oxides (h) Peroxides.

(a) **Basic oxides** : This class includes the normal oxides of most metals. They are derived from the metallic elements and their properties depend upon the degree of electropositive character of the metal. Basic oxides form salt and water

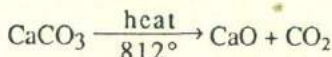
with acids, Basic oxides when soluble in water produce aqueous solutions of bases. For instance, Na_2O , CaO , MgO , Fe_2O_3 etc. are basic oxides. The ionic oxides are generally basic. The smaller the positive charge and larger the size of the element forming the oxide, the greater is the basic character, Thus K^+ forms a strong basic oxides than Mg^{+2} ion, Oxides of elements having low electronegativity values are more basic than those having high electronegativity values. Thus CaO is more basic than Al_2O_3

Method of Formation of Basic Oxides

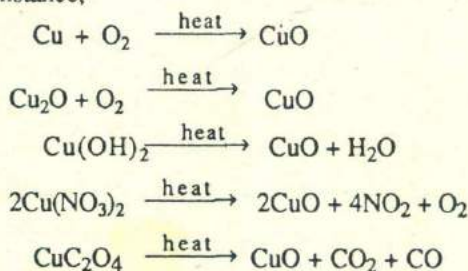
(i) The alkali metals take up oxygen from the air and are converted into oxides. The alkali metal oxides, however, are generally prepared by heating excess of the alkali metal with oxygen in vacuo having :



(ii) The alkaline earth metal oxides are generally prepared by strongly heating their hydroxides, carbonates and nitrates, e.g.

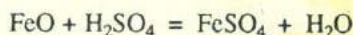


(iii) Heavy metal oxides are generally prepared by heating the metal or lower oxides in air. They are also formed by heating the hydroxides, carbonates, nitrates etc. For instance,

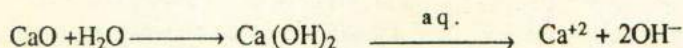
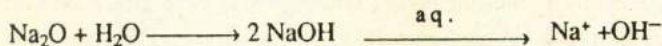


Reactions :

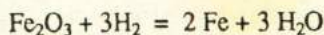
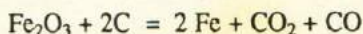
(i) Basic oxides react with acids to form salts and water :



(ii) Some of the basic oxides produce hydroxides with water and when soluble they are extensively dissociated to give strong alkaline reactions :

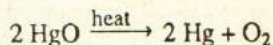
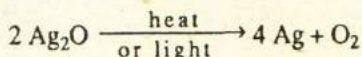


(iii) Oxides of the heavy metals are decomposed to metal when heated with carbon or hydrogen :



But the alkali and alkaline earth metal oxides do not undergo above reactions.

(iv) Some of the oxides of less electropositive elements are easily decomposed by heat into metal and oxygen :



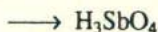
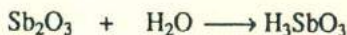
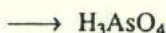
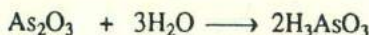
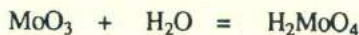
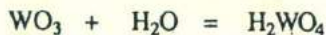
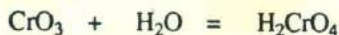
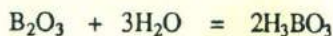
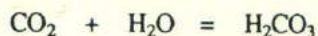
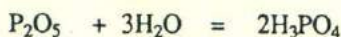
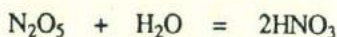
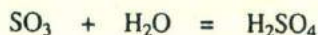
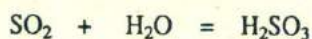
(b) **Acidic oxides** : The acidic oxides are generally derived from non-metals. They react with bases to form salt and water, and sometimes only salt. They are anhydrides of the respective acids and their hydroxides are oxyacids. For instance, SO_2 , SO_3 , N_2O_5 , P_2O_5 , B_2O_3 etc. are some of the acidic oxides. Elements with high electronegativity values form acidic oxides.

Acidic oxides are also formed by metals which can exert a high oxidation state by losing a number of electrons and thus combine with several oxygen atoms. Thus CrO_3 , SnO_2 , WO_3 , MoO_3 , etc. are examples of metallic acidic oxides. Elements having both metallic and nonmetallic properties, i e., metalloidal elements, also produce oxides which are acidic, such as, As_2O_3 , Sb_2O_3 , SiO_2 , etc.

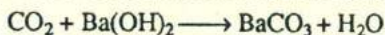
Both the non-metallic and metallic acidic oxides when soluble in water are extensively hydrolysed and produce acidic reactions.

Reactions :

(i) The acidic oxides react with water to give the respective acids :



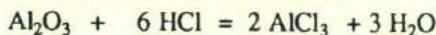
(ii) Acidic oxides combine with bases to form salts and water. Thus,



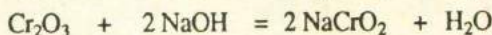
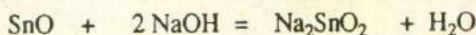
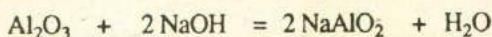
(c) **Amphoteric oxides :** The amphoteric oxides react with both acids and alkalis and, therefore, exhibit both acidic and basic properties. Thus, Al_2O_3 , ZnO , SnO , Cr_2O_3 etc. are examples of amphoteric oxides. These oxides are generally insoluble in water and dissolve readily in an acid or a base.

Reactions :

(i) With acids these form salt and water. Thus,



(ii) The same oxides react with alkalis to give salt and water. Thus,

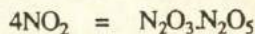
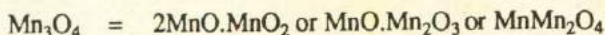
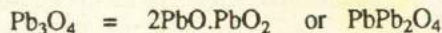
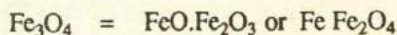


(d) **Neutral oxides** : The neutral oxides combine neither with acids nor with bases to form salts. They do not give acidic or basic reactions. Thus, H_2O , CO , N_2O , NO etc. are examples of neutral oxides.

(e) **Sub-oxides** : The sub-oxides or protoxides generally contain less number of oxygen atoms than what is actually required for the formation of normal oxides. Thus, Pb_2O , Ag_4O , Cu_4O , Pd_2O etc. are examples of sub-oxides.

(f) **Saline oxides** : The saline oxides are so called because they behave like salts. These are also known as *compound oxides* and *mixed oxides* since these may be assumed to be a combination of more than one oxide. Thus, Au_2O_2 , Fe_3O_4 , Pb_3O_4 , Mn_3O_4 , NO_2 etc. are examples of saline oxides. They are generally formed by combination of a basic oxide with an acidic oxide. Ferroso-ferric oxide, Fe_3O_4 , may be considered as a combination of FeO and Fe_2O_3 , and with acids it gives salts of both ferrous and ferric ions. Mixed-metal oxides are known as spinels having special types of crystal structures.

Similarly, red lead, Pb_3O_4 , is composed of PbO and PbO_2 and Mn_3O_4 , is composed of MnO and MnO_2 . NO_2 is a mixed anhydride of N_2O_3 and N_2O_5 . These combinations may be represented as follows :



(g) **Nonstoichiometric oxides** : There are also many oxides which are known as nonstoichiometric oxides. These are generally formed by metals having variable oxidation states. Thus ferrous oxide probably never has the

composition FeO , but usually something in the range $\text{FeO}_{0.9}$ to $\text{FeO}_{0.95}$ depending on the manner of preparation.

(h) **Peroxides** : These are oxides which contain more oxygen combined to an element than what is necessary for its highest oxides according to the periodic law. In terms of the oxidation states of oxygen, peroxides contain oxygen in $-\frac{1}{2}$ and -1 oxidation states. The most common oxidation state of oxygen in normal oxides is -2 . Exceptions are O_2F_2 and OF_2 .

Classification of Peroxides Based on Reactions

Peroxides have been classified into the following groups on the basis of their reactions :—

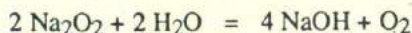
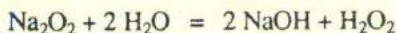
- (I) Basic Peroxides.
- (II) Acidic Peroxides.
- (III) Neutral Peroxides.

(I) **Basic Peroxides** : The basic peroxides when soluble in water produce bases. Na_2O_2 , KO_2 , CaO_2 , BaO_2 are examples of water-soluble basic peroxides.

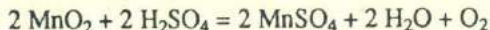
PbO_2 , Bi_2O_5 , MnO_2 etc. are, however, not true basic peroxides, because the oxygen content does not exceed that of the normal typical oxides. But these are classified as basic peroxides, because these react with acids to produce salts of the basic oxides of PbO , Bi_2O_3 and MnO respectively.

Reactions :

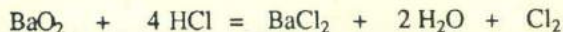
(i) Basic peroxides react with water to form hydrogen peroxides or oxygen in addition to bases :



(ii) With sulphuric acid these peroxides always give oxygen :

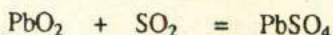
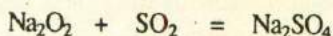


(iii) With hydrochloric acid, chlorine is always evolved :



Chlorine evolved is equivalent to the excess amount of oxygen present in the basic oxides. This amount of oxygen is generally known as the "available oxygen" of the peroxides.

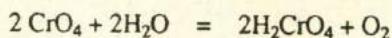
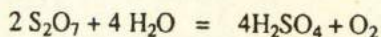
(iv) The basic peroxides form salts by direct union with acidic oxides :



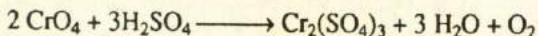
(II) *Acidic Peroxides* : The acidic peroxides generally produce typical acids in presence of water by loss of oxygen. CrO_4 , S_2O_7 , Cl_2O_7 , SnO_3 , Cl_2O_2 , ClO_2 , UO_4 etc. are examples of acidic peroxides.

Reactions :

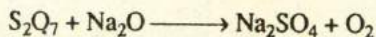
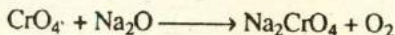
(i) With water the acidic peroxides react to form normal acids with the evolution of oxygen :



(ii) With sulphuric acid oxygen is evolved :



(iii) Acidic peroxides form salts with alkali oxides with the evolution of oxygen :



(III) *Neutral Peroxides* : As the name implies, it is neutral and has neither basic nor acidic characteristics. A well-known example is H_2O_2 .

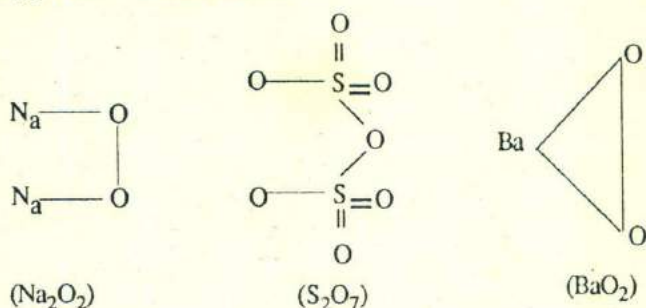
Classification of Peroxides Based Upon Structures

The classification of peroxides on a structural ground depends upon the oxidation state of the elements combining with oxygen. It has been assumed that the oxygen atom or atoms over and above those required to form the normal oxide may either be doubly linked to the metal atom or singly linked to both the metal and oxygen atom.

(i) The peroxides having the excess oxygen atom or atoms doubly linked to metal atom are known as "*polyoxides*".

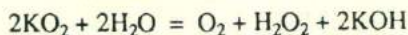


(ii) The peroxides having the excess oxygen atom or atoms singly linked to the metal and oxygen, forming a chain or ring are "*normal peroxides*". These contain oxygen in -1 oxidation state.



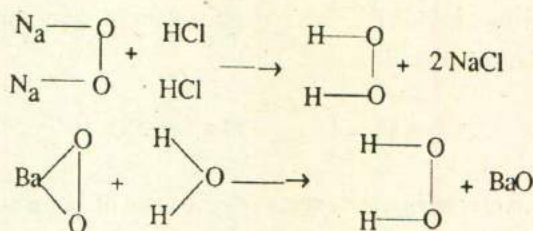
The direct oxygen-oxygen bonds in normal peroxides usually break down at high temperatures. Mostly electropositive metals form peroxides having O_2^{-2} ion which contains no unpaired electrons.

(iii) Oxides of alkali metals, such as K, Rb and Cs, contain oxygen with oxidation number $-\frac{1}{2}$ and are called *superoxides*. These have the general formula MO_2 (KO_2 , RbO_2 , CsO_2). These are ionic solids having M^+ cation and O_2^- , anion. These are coloured solids having magnetic properties and contain unpaired electrons. It is to be noted that superoxide ion, O_2^- , exists only in the solid state but gives O_2 and H_2O_2 in water :

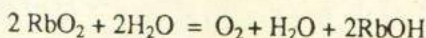


Polyoxides, peroxides and superoxides can be distinguished from one another by the actions of water or dilute acids upon them.

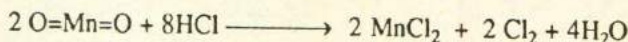
(i) Peroxides have group —O—O— and hence yield H_2O_2 as a characteristic product with water or dilute acid :



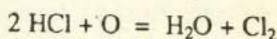
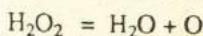
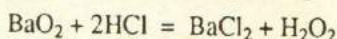
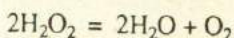
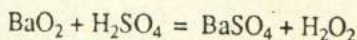
Superoxides produce H_2O_2 and also O_2 gas with water :



(iii) Polyoxides are not attacked by dilute acids and not at all by water, but with strong HCl or H_2SO_4 produce chlorine and oxygen respectively :



(iv) Both peroxides and superoxides also produce chlorine or oxygen when acted upon by strong HCl or H_2SO_4 but by a different mechanism :



The distinguishing reactions of polyoxides, peroxides and superoxides are given in Table 8-1.

Table 8-1. Distinction between Peroxides, Polyoxides and Superoxides.

Reagents	Peroxides	Superoxides	Polyoxides	Normal oxide
	O_2^{-2}	O_2^{-1}	O_2^{-2}	O^{-2}
1. Water	H_2O_2	$\text{H}_2\text{O}_2 + \text{O}_2$	No reaction	OH^-
2. Dil. Acids	H_2O_2	$\text{H}_2\text{O}_2 + \text{O}_2$	No reaction	
3. Conc. HCl	Cl_2	$\text{Cl}_2 + \text{O}_2$	Cl_2	
4. Conc. H_2SO_4	O_2	O_2	O_2	

B. Classification of Oxides on the Basis of Bonding Systems

There are three classes of oxides on the basis of the nature of chemical bonds.

(i) Ionic Oxides	(ii) Covalent Oxides	(iii) Intermediate Oxides
<i>e.g.</i> Li_2O	<i>e.g.</i> SO_2	<i>e.g.</i> Fe_2O_3
BaO	CO_2	ZnO
MgO	CO	BeO
CaO	Cl_2O_7	

The ionic oxides are generally formed by the alkali and alkaline earth metals.

The covalent oxides are mostly formed by the non-metals.

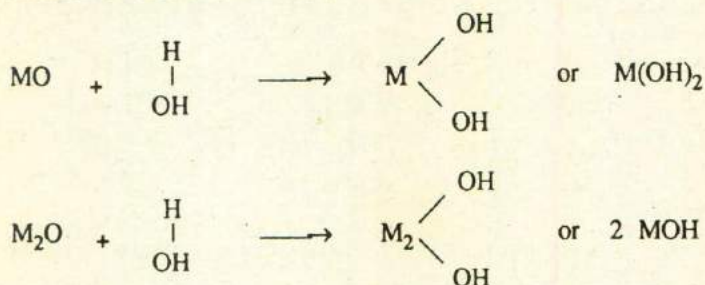
The transition metals and many other heavy metals form oxides containing bonds which are conveniently regarded as being intermediate between ionic and covalent bonds.

The ionic oxides when soluble in water give bases due to dissociation into ions. Whereas the covalent oxides of the non-metals are usually acidic, dissolving in water to produce solutions of acids. These oxides are, therefore, known as acid anhydrides. The ionic oxides function as basic anhydrides. Many of the intermediate oxides do not react appreciably with water and some of them show characteristic of both acids and bases generally known as amphoteric.

Elements having large positive oxidation number tend to form covalent oxides. Thus, CO_2 , SO_3 , Sb_2O_5 , Cl_2O_7 are some of the covalent oxides. If an element forms more than one oxides the covalent oxide will be that having the element in the highest oxidation state. Thus, As_2O_5 having +5 arsenic is more covalent (more acidic) than As_2O_3 containing +3 arsenic. SO_3 having S in +6 state is more acidic than SO_2 having S in +4 state. Similarly, CrO_3 is acidic, Cr_2O_3 amphoteric and CrO distinctly basic. Covalency is also favoured by the small size of the positive ion. Hence, BeO is almost covalent oxide as compared to the strongly basic BaO containing large barium ion.

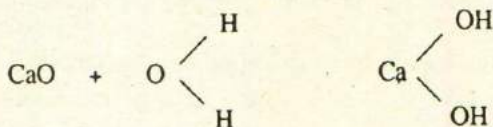
HYDROXIDES

Hydroxides are compounds of oxides with water. Thus, the following examples illustrate the formation of hydroxides of an element by the combination of its oxides with water :



The stability and definiteness of the hydroxides depend upon the reversibility of the above reactions. Definite and stable hydroxides are formed by those elements which are most electropositive and most electronegative. These can be isolated in the free state and have great stability when heated.

The hydroxides or hydroxy compounds are important class of compounds containing hydrogen, oxygen and at least one other element. They can often be made by the reaction of water with an oxide. Thus, when calcium oxide, CaO, is treated with a limited amount of water, the product is solid calcium hydroxide, Ca(OH)₂ :



Solutions of sodium hydroxide, NaOH, and calcium hydroxide are alkaline, but not all hydroxy compounds are alkaline and also not all of them are soluble in water. Some of the hydroxides, such as water, HOH, ethyl alcohol, C₂H₅OH, are neutral and again a large number of them such as sulphuric acid, SO₂(OH)₂, phosphoric acid, PO(OH)₃ and boric acid, B(OH)₃, are acidic. It has become customary to use the term hydroxide to hydroxy compounds which give basic

solutions or contain the hydroxyl group as OH^- ion. The ionic oxides which react with water generally produce bases whereas the covalent oxides give acids.

In general, if the hydroxyl group exists in a compound as the OH^- ion, the compound is called a hydroxide. The hydroxides may be classified into various groups. The main groups of hydroxides are :—

- I. Basic Hydroxides.
- II. Amphoteric Hydroxides.
- III. Acidic Hydroxides.
- IV. Neutral Hydroxides.

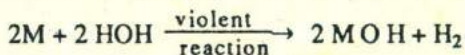
I. Basic Hydroxides

Basic hydroxides are generally formed by metallic elements and the degree of electropositive character of the metal determines the basic properties and also the solubility of the basic hydroxides. Thus the alkali metal hydroxides are strongly basic and highly soluble in water and give high concentration of OH^- ions in solution. The alkaline earth metal hydroxides are less basic and less soluble in water as compared to the alkali metal hydroxides. The heavy metal hydroxides which are mostly insoluble in water are regarded as basic because they have the ability to react with acids to form salts and water. The relationship of the properties with the charge and size of the metal ions will be discussed later. Thus, according to the properties, the basic hydroxides may be subdivided into three groups :—

- (a) alkali metal hydroxides.
- (b) Alkaline earth metal hydroxides.
- (c) Heavy metal hydroxides.

The mode of formation of these three groups of basic hydroxides also illustrates the difference in their properties.

(a) *Alkali metal hydroxides* : (i) When an alkali metal comes in contact with water, there is a violent reaction, in course of which the alkali metal hydroxide is formed with evolution of hydrogen from water. The hydrogen burns in air with a flame indicating as if the alkali metal is burning in water.

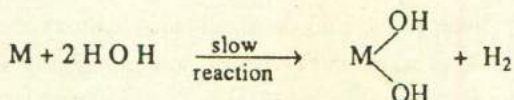


(ii) When an alkali metal salt solution in water is electrolysed, the alkali metal is liberated at the cathode and reacts with water forming the hydroxides.

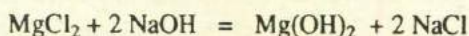
(iii) The alkali metal oxides are freely soluble in water to form alkali metal hydroxides in solution.

(iv) The alkali metal hydroxides are not converted to their oxides on strong heating.

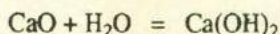
(b) *The alkaline earth metal hydroxides* : (i) The reaction between water and the alkaline earth metal is not as violent as in the case of the alkali metals. As expected, the reactivity with water increases in the group with increasing atomic number. Lithium, an alkali metal, in this respect resembles magnesium as already explained in connection with the diagonal relationship in the Periodic Table.



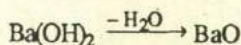
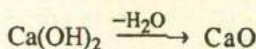
(ii) The alkaline earth metal hydroxides are also formed by precipitation from their salt solutions by adding alkali hydroxides. Thus,



(iii) The alkaline earth metal hydroxides are also formed by direct reaction of their oxides with water. thus,

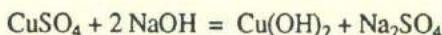
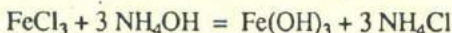


(iv) Unlike alkali metal hydroxides, the alkaline earth metal hydroxides are converted to their oxides on strong heating by loss of water. Thus,

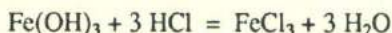


(c) *The heavy metal hydroxides* : (i) The hydroxides of copper, nickel, iron cobalt etc. are included in this sub-group. The formations of these hydroxides do not take place with the direct reaction of the heavy metal, or their oxides with water. These hydroxides are best prepared by the addition of a soluble

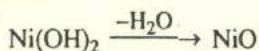
alkali hydroxide to the heavy metal salt solutions in water. The heavy metal hydroxides are precipitated in the form of insoluble product :



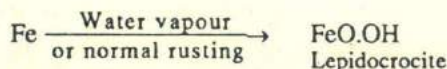
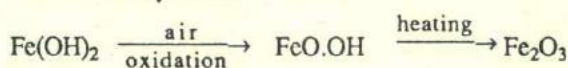
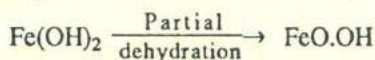
(ii) Since the heavy metal hydroxides are generally insoluble in water, their basic character is revealed by their dissolution in acids indicating neutralization reaction forming salts and water. Thus,



(iii) The heavy metal hydroxides are easily converted to their oxides by heating when water is lost. Thus,



It may be mentioned here that the results of the dehydration of a heavy metal hydroxide may produce intermediate products which may be described as oxyhydroxides. Some of these oxyhydroxides are formed during the direct reaction and no heating is required. However, on strong heating these oxyhydroxides also give the metallic oxides. Thus,



Similarly, MnO.OH , AlO.OH etc. are formed by partial dehydration of the normal hydroxides.

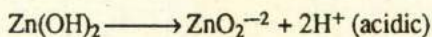
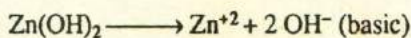
II. Amphoteric Hydroxides

In conformity with the definition of amphoteric oxides, the amphoteric hydroxides may be defined in a similar fashion since the latter are derived from the former. It is not possible to classify all hydroxides sharply as either basic or acidic. The hydroxides of those elements situated in the centre of the Periodic Table are amphoteric.

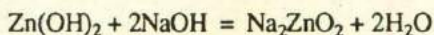
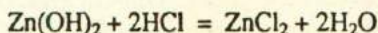
Amphoteric hydroxides are those which are able to neutralize both acids and bases and hence possess both acidic and basic characters.

For instance, $\text{Be}(\text{OH})_2$, $\text{Al}(\text{OH})_3$, $\text{Zn}(\text{OH})_2$, $\text{Pb}(\text{OH})_2$ etc. are amphoteric hydroxides and act both as acids or bases and hence are soluble in either strongly basic or strongly acidic solutions.

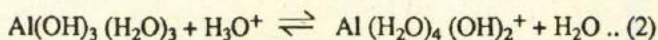
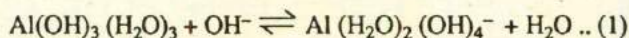
The acidic hydroxides generally give H^+ ions in solution and basic hydroxides produce OH^- ions as the case may be. Thus in the case of $\text{Zn}(\text{OH})_2$, we have,



Hence, such hydroxides are soluble in acids, as in HCl and also in alkali, e.g. NaOH :



A more precise equation showing the amphoteric behaviour of $\text{Al}(\text{OH})_3$ may be given as follows:—



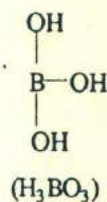
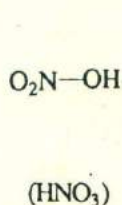
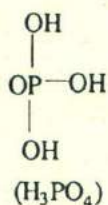
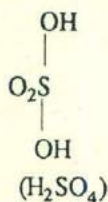
In equation (1), a proton is transferred from $\text{Al}(\text{OH})_3 (\text{H}_2\text{O})_3$ to OH^- . In equation (2), a proton is transferred from H_3O^+ to $\text{Al} (\text{OH})_3 (\text{H}_2\text{O})_3$.

Similarly, for other amphoteric hydroxides the replacement of the surrounding groups of the metal as shown in the case of Al may be used to show the amphoteric character.

III. Acidic Hydroxides (Hydroxy Acids)

Both the metals and non-metals can form acidic hydroxides and definition follows the same pattern as that of the acidic oxides. But the acidic hydroxides of the non-metals are more important since they behave as strong acids.

The acidic hydroxides are those which react with base to neutralize it producing salt and water :



From the above examples, we can derive a definition for the basicity of an acid.

Basicity of an acid is the number of OH groups combined with an element and capable of producing H^+ ions. The basicity of the acids have been given in Table 8-2.

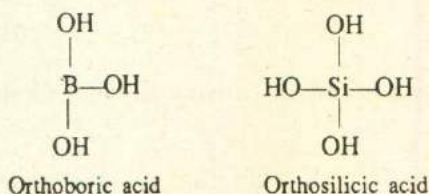
Table 8.2. Basicity of some acids.

Acid	Hydroxide form	Basicity
H_2SO_4	$\text{SO}_2(\text{OH})_2$	2
H_3PO_4	$\text{PO}(\text{OH})_3$	3
HNO_3	$\text{NO}_2(\text{OH})$	1
H_3BO_3	$\text{B}(\text{OH})_3$	3
✓ H_2SO_3	$\text{SO}(\text{OH})_2$	2
HClO_3	$\text{ClO}_2(\text{OH})$	1
HMnO_4	$\text{MnO}_3(\text{OH})$	1
H_3AsO_4	$\text{AsO}(\text{OH})_3$	3
H_3AsO_3	$\text{As}(\text{OH})_3$	3
H_3PO_3	$\text{POH}(\text{OH})_2$	2
H_3PO_2	$\text{I}(\text{OH})_2(\text{OH})$	1
CH_3COOH	$\text{CH}_3\text{CO}(\text{OH})$	1

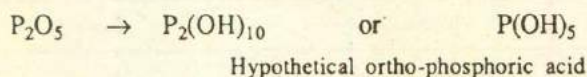
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Thus the acidic hydroxides contain one or more OH groups which are capable of producing H^+ ions by rupture of the O—H bond. The hydroxy acids are classified as ortho, meta- and pyro- acids on the basis of the OH groups and their elimination during condensation reaction.

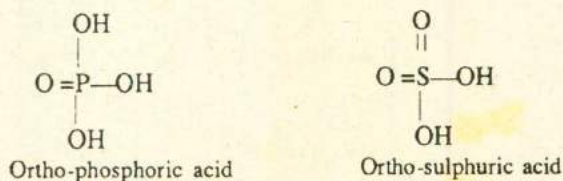
Ortho-acids : Theoretically the fully hydroxylated compounds from the valence considerations are generally known as ortho-acids. Thus,



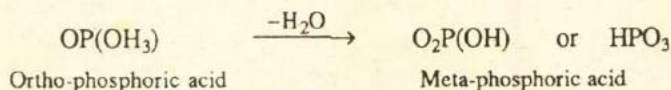
But in many cases the theoretical hydroxylated compounds are not formed or do not exist. The formula for the true orthocompounds may be written but these refer to only hypothetical compounds. Thus, ortho-phosphoric acid should be formed by the hydroxylation of P_2O_5 where all the 5 oxygen is replaced by OH :

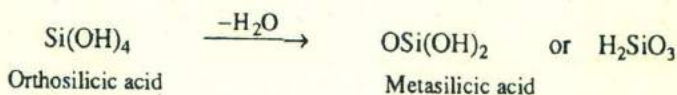
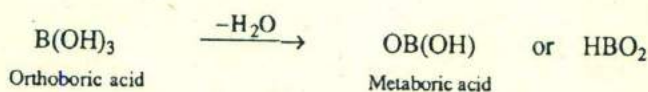


But $P(OH)_5$ does not exist. Hence the compounds which contain the maximum number of OH groups in actual practice are generally referred to as ortho-acids. For instance,

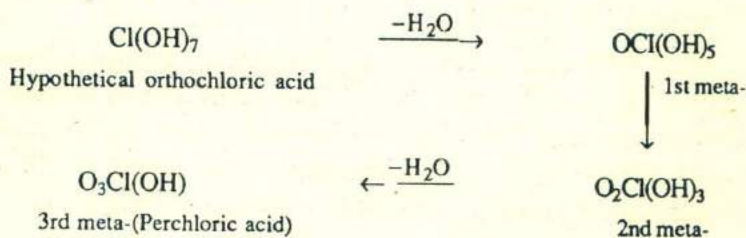


Meta-acids : The meta-acids result from the ortho-acids. When water molecule is eliminated from one molecule of the ortho-compound, the product obtained is called a meta-acid. Thus,

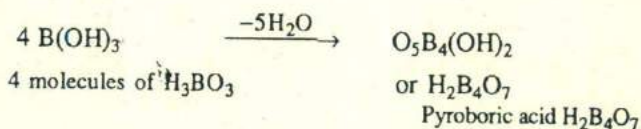
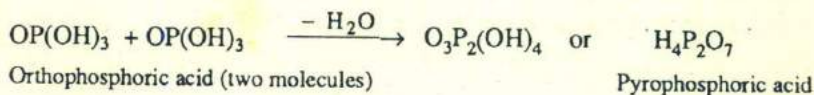




The meta-acids may also be derived from the hypothetical hydroxylated ortho-acids. Some of these compounds may give a series of meta-acids which may or may not exist. Thus fully hydroxylated ortho-acid of the compounds Cl_2O_7 may be formulated as given below. Thus, by elimination of one molecule of H_2O successively, gives rise to 1st-, 2nd- and 3rd meta-chloric acids.

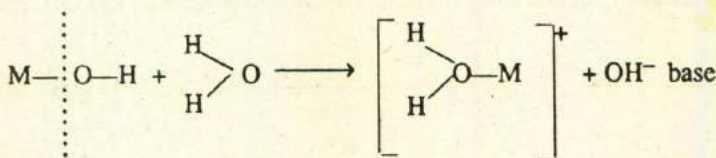
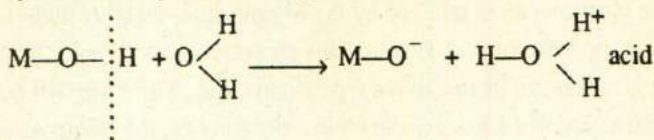


Pyro-acids : Pyro-acids are formed when two or more molecules of the true ortho- or any intermediate form or meta-acids combine together with the elimination of water molecule. The pyro-acids are formed by condensation reaction and the compounds formed are also known as condensed products. Thus, two molecules of orthophosphoric acid may combine by elimination of 1 molecule of H_2O to form pyrophosphoric acid.



or generally,

$M(OH)_n \rightleftharpoons M^{n+} + n(OH)^-$ and $M(OH)_n \rightleftharpoons MO_n^{-n} + nH^+$ The two ways in which hydroxides may react with H_2O are as follows :



If $M-O$ bond is almost covalent, then $O-H$ bond in the hydroxide is broken giving H^+ (H_3O^+) ion and hence acidic. If $M-O$ bond is ionic, water tends to attack M , displacing the OH^- ion and giving basic reaction with the formation of hydrated ion $[M-H_2O]^+$. It may also be mentioned that those cations that become attached to the oxygen of H_2O , break the $O-H$ bond releasing H^+ ion and are thus acidic. The anions that attack the H of H_2O , dislodge the OH^- ion and are basic. Thus Hg^{+2} , Cu^{+2} are acidic; C_2^{-2} , NH_2^- and S^{-2} are basic. These reactions are known as "hydrolysis" to which reference has already been made earlier.

The hydroxyl compounds of metals, which have various oxidation states, become less basic and more acidic as the oxidation state is increased. For instance, the hydroxides of manganese exhibit marked difference in acid-base behaviour as shown in Table 8.3.

Table 8.3. Acid-base character of hydroxides and oxidation states of Mn.

Compound	Hydroxide formulation	Oxidation state	Character
$Mn(OH)_2$	$Mn(OH)_2$	$Mn(+2)$	moderately basic
$Mn(OH)_3$	$Mn(OH)_3$	$Mn(+3)$	Weakly basic
H_2MnO_3	$MnO(OH)_2$	$Mn(+4)$	Weakly acidic
H_2MnO_4	$MnO_2(OH)_2$	$Mn(+6)$	Definitely acidic
$HMnO_4$	$MnO_3(OH)$	$Mn(+7)$	Strongly acidic

Manganese in its +2 state behaves as a typical metal giving the basic hydroxide $\text{Mn}(\text{OH})_2$. But in permanganic acid Mn has oxidation state +7 and shows a non-metallic character analogous to chlorine in HClO_4 . This may be viewed from the positions of both Mn and Cl in the Periodic Table since both occupy group VII, although Mn is a transition element. The high charge of Mn (+7) strongly attracts electrons. The O—H bonds in H_2O become very weak and protons are split off to leave the oxygen associated with Mn. Thus HMnO_4 behaves as a strong acid in water.

Questions and Problems

1. What are the different classes of oxides? Discuss their properties and reactions.
2. Why is $\text{Mg}(\text{OH})_2$ formed when magnesium reacts with water whereas MgO is produced when it burns in steam?
3. Arrange the following oxides in the order of increasing acidity:—
 As_2O_3 , B_2O_3 , BaO , BeO , FeO , N_2O_5 , P_2O_4 , P_2O_3 , Cl_2O_7 .
4. Write an equation showing that H_2O_2 is an acid.
5. Distinguish between dioxides and peroxides in terms of electronic structures.
6. How will you classify peroxides on the basis of their reactions and on the basis of their structures? Illustrate your answer with examples.
7. What are peroxides, superoxides and polyoxides? How will you distinguish them from one another?
8. What is meant by the basicity of an acid? Give examples.
9. Define with examples ortho-, meta- and pyro-acids. Discuss the modes of formation of meta-acid and pyro-acid from ortho-acids.
10. Discuss the amphoteric character of hydroxides.
11. What is the relationship between the oxidation states and the acidic and basic character of metal hydroxides?
12. How will you classify the oxides in terms of bonding systems? Give examples.
13. Predict the product in the following reactions:—
 - (a) A few drops of hot water are added to solid sodium peroxide.
 - (b) Sodium peroxide is dissolved in excess cold water.
 - (c) Potassium superoxide and manganese dioxide are added to dilute H_2SO_4 .
 - (d) SO_3 is added to H_2O_2 .
 - (e) SO_3 gas is passed over CaO .

14. Explain peroxides with examples.
15. Describe the preparation, properties and uses of sulphur trioxide, nitrogen tetroxide.
16. How is orthophosphoric acid converted to other phosphoric acids?
17. Write the acidic and basic characters of oxides.
18. Write a note on modern views of acids and bases.
19. Explain why H_2O is neutral, HOCl is acidic and NaOH is alkaline.
20. What are amphoteric oxides?
21. Classify the following as acidic, basic, amphoteric or neutral oxides :—
 SO_2 , Cr_2O_3 , P_4O_{10} , BeO , CO_2
22. Comment on the acidic and basic character of the following oxides :—
 MnO , MnO_2 , Mn_2O_3 , Mn_2O_7 , Mn_3O_4
23. Non-metal oxides create air pollution problems. Explain the reasons.
24. How would you distinguish between peroxides and super oxides ? Give examples of their reactions.

CHAPTER 9

ACIDS AND BASES

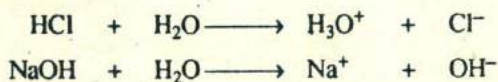
The acids and bases are among the most important classes of compounds and these two classes of substances are, in effect, opposite to each other and yet interrelated through neutralization reactions forming salts which, therefore, become closely related to acids and bases. It may be mentioned that the terms *acids* and *bases* have been defined in many ways according to various concepts. In this chapter a brief review of some of the elementary concepts regarding acids and bases are given.

1. The Arrhenius Concept

According to Arrhenius concept an acid is a hydrogen-containing substance which yields H^+ ion (i.e., H_3O^+ , hydronium ion) when dissolved in water.

Base is a substance which contains OH groups and produces OH^- ion when dissolved in water.

Arrhenius concept is based upon ionic dissociation of compound in water. Thus HCl is an acid because it produces H_3O^+ ion in water but CH_4 is not an acid. Similarly, NaOH is a base because it yields OH^- ion in water but C_2H_5OH is not a base. CH_4 does not yield H^+ ion in water, so also C_2H_5OH does not give OH^- ion in water :



The strengths of acids and bases according to the Arrhenius concept are defined in terms of the concentrations of H^+ ion and OH^- ion respectively that are present in aqueous solution.

The process of neutralization is, therefore, considered to be the combination of H^+ ions and OH^- ions to form neutral water :



The above definitions for acids, bases and acid-base reactions have been extended to apply to more general cases by several new concepts.

2. The Protonic or Brönsted Concept

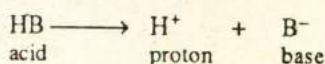
According to Brönsted concept, also known as Brönsted-Lowry concept, the following definitions for acids and bases have been adopted as a modification of the Arrhenius concept.

An acid is a substance that can give up protons to another species.

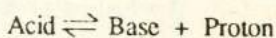
A base is a substance that can accept protons.

Stated more simply, an acid is a proton donor, while a base is a proton acceptor.

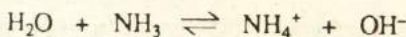
It can be seen that the Brönsted concept does not specify a solvent. Acids and bases are related by the general equation :



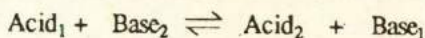
Generally, it may be written as



For instance, when ammonia is dissolved in water, the reaction

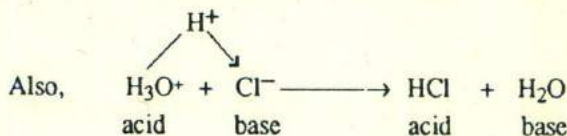
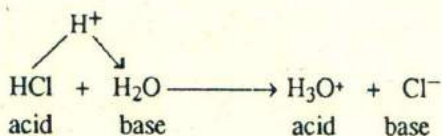


takes place. Here H_2O gives up the proton and is an acid and NH_3 accepts the proton and is, therefore, a base. Similarly, the reverse reaction indicates NH_4^+ as an acid and OH^- as a base. Thus in the above reaction, two acids and two bases are involved at equilibrium conditions. The acid-base pair associated with the loss or gain of proton is called a *Conjugate Pair*. Thus, NH_4^+ is the conjugate acid of the base NH_3 and H_2O is the conjugate acid of base OH^- and vice versa. The general equation for the equilibrium reaction may be written as

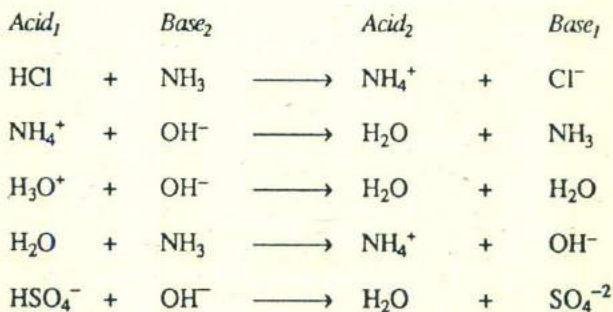


Thus, in order that an acid acts as a proton donor, a proton acceptor must be present to receive it. The ions which remain after protons have been donated from the acid molecule are the *Conjugate bases* of the respective acid. Similarly,

the species formed when a proton is added to a base is the *Conjugate acid* of that base.



Some of the acid-base systems according to the Brönsted concept are given below :



Thus, Cl⁻, SO₄⁻², OH⁻ are conjugate bases of HCl, HSO₄⁻ and H₂O respectively. H₂O, HSO₄⁻ and HCl are conjugate acids of the bases OH⁻, SO₄⁻² and Cl⁻ respectively.

Thus, the following species may be regarded as acids :—

Molecular species : HCl, H₂SO₄, CH₃COOH, HCN, H₂S, H₂O etc.

Anionic species : HSO₄⁻, HCO₃⁻, H₂PO₄⁻, HPO₄⁻², HS⁻ etc.

Cationic species : H₃O⁺, NH₄⁺, Al(H₂O)₆⁺³ etc.

The following species are regarded as bases :—

Molecular species : H_2O , NH_3 , CH_3NH_2 etc.

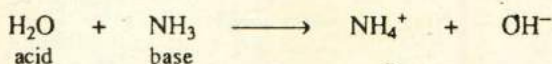
Anionic species : OH^- , HS^- , S^{2-} , HCO_3^- , HSO_4^- , Cl^- etc.

Cationic species : $\text{Fe}(\text{H}_2\text{O})_5\text{OH}^{+2}$, $\text{Cu}(\text{H}_2\text{O})_3\text{OH}^+$ etc.

From the above examples of acids and bases, it is seen that certain species are classed as both acids and bases depending upon the manner they behave in a given reaction.

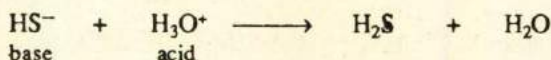
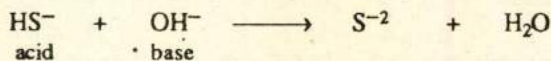
Amphiprotic species : A species that acts both as a proton donor and proton acceptor is said to be amphiprotic.

Thus, H_2O is amphiprotic. It loses proton to a base, such as NH_3 , or accepts a proton from an acid, such as HCl :

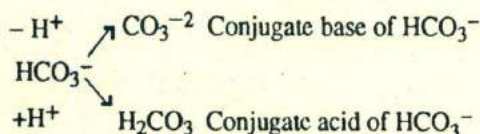
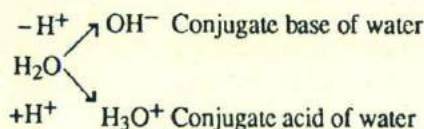


Hence neutralization reactions according to Brönsted concept are acid-base reactions between the conjugate acid and conjugate base of an amphiprotic solvent.

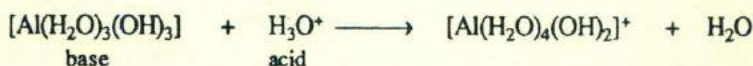
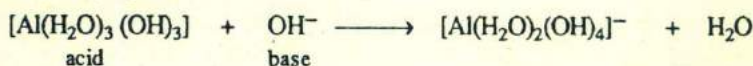
The proton-containing negative ions are amphiprotic;



The conjugate base and acid relationship may be shown as :



Amphoteric hydroxides react with both acids and bases because they are generally amphiprotic :



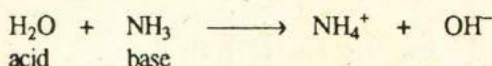
According to Brönsted concept a solution of NaCl in H_2O is neutral, since Na^+ and Cl^- do not exhibit any tendency to gain proton in H_2O which is the solvent and in which NaCl is not hydrolysed. But aqueous solutions of AlCl_3 , ZnCl_2 and FeCl_3 etc. show acidic reactions because the cations are hydrated and hydrolysed. Thus, Al^{+3} ion is hydrated $[\text{Al}(\text{H}_2\text{O})_6]^{+3}$ and hydrolysed as indicated above. $[\text{Al}(\text{H}_2\text{O})_6]^{+3}$ is an acid and donates a proton to H_2O , which acts as a base. The enhanced proton releasing tendency of Al^{+3} ion is due to the coordination of H_2O to Al^{+3} in which the electrons are shifted towards the posi-



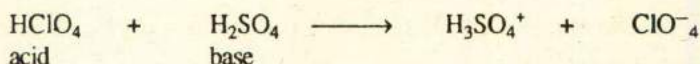
vely charged Al^{+3} , thereby weakening the O—H bond. H^+ ion is thus released easily. Generally, small ions with high positive charge become hydrated in aqueous solution and act as Brönsted Acids. Na^+ , K^+ etc. which are of large size and small charge do not show this character.

Polyprotic acid : Acids containing one proton which can be donated is *monoprotic acid*. Those acids containing more than one donatable proton are known as *polyprotic acids*. Thus HCl, HNO_3 , HCN etc. are monoprotic, whereas H_3PO_4 , H_2SO_4 , H_3AsO_4 are polyprotic.

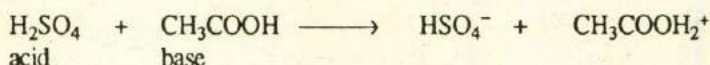
Non-aqueous system : Non-aqueous solutions also lose or gain proton and fit into the Brönsted concept of acids and bases. Thus when water is dissolved in liquid ammonia :



When perchloric acid is dissolved in concentrated H_2SO_4 , acid-base reaction occurs :



When concentrated H_2SO_4 is dissolved in glacial acetic acid, we have again acid-base reaction :



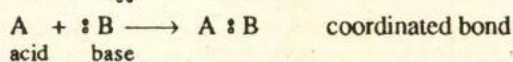
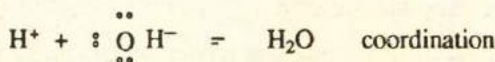
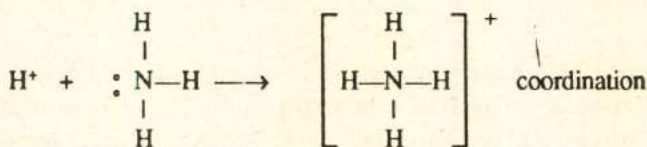
3. The Lewis Concept

G. N. Lewis has proposed a more generalized theory in which acids and bases have been defined on the basis of electronic structures.

An acid is a substance (molecules or ions) which can accept a pair of electrons.

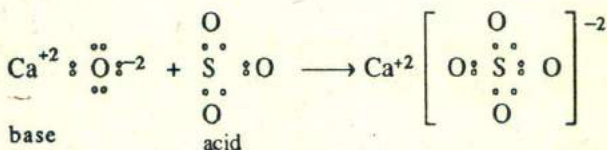
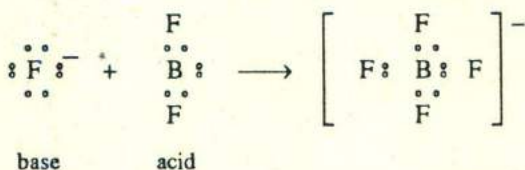
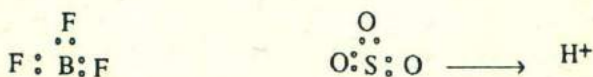
A base is a substance (molecules or ions) which can donate a pair of electrons.

An acid-base reaction, therefore, consists of the donation of a pair of electrons from a base to an acid with the formation of a coordinate bond between the two.

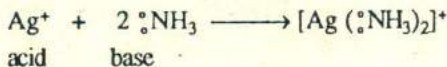


From the electronic configurations, different types of Lewis acids may be distinguished.

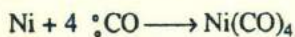
(i) Compounds having less than a full octet of electrons, e.g., BF_3 and SO_3 :



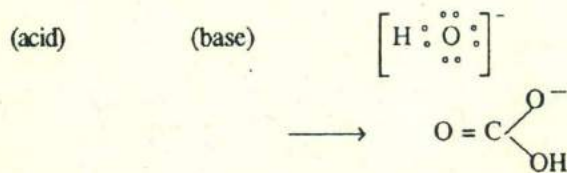
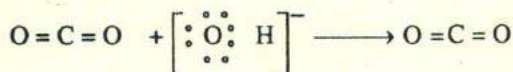
(ii) Positive ions are often considered as acids :



(iii) Metal atoms, such as Ni, function as an acid in the formation of nickel carbonyl :

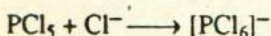
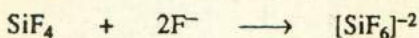
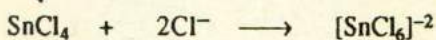


(iv) Compounds having double or multiple bonds (except C=C double bond). These have acidic sites :





(v) Compounds having the central atom capable of expanding its valence shell are Lewis acids :



Since Lewis acids draw electron towards it, they are known as "*electrophilic* (electron loving) reagents.

Lewis bases can also be grouped as follows :—

(i) Molecules containing an atom with two or less number of unshared electron-pairs. Thus the number of unshared electron-pairs in Ne, HF, H₂O, NH₃, PCl₃ etc. determines the properties and the reactions.

Atom or molecule	Electronic structure	No. of paired electrons (lone pairs)	Reaction	Example
Ne	$\begin{array}{c} \cdot\cdot \\ \cdot\cdot \\ \text{: Ne :} \\ \cdot\cdot \\ \cdot\cdot \end{array}$	4	Non-basic	×
HF	$\begin{array}{c} \cdot\cdot \\ \cdot\cdot \\ \text{H : F :} \\ \cdot\cdot \end{array}$	3	Very weakly basic	HF + $\cdot\cdot$ SO ₃ = HF $\cdot\cdot$ SO ₃
H ₂ O	$\begin{array}{c} \cdot\cdot \\ \cdot\cdot \\ \text{H} - \text{O} : \\ \\ \text{H} \end{array}$	2	basic	H ₂ O $\cdot\cdot$ H ⁺
NH ₃	$\begin{array}{c} \cdot\cdot \\ \cdot\cdot \\ \text{H} - \text{N} : \\ \\ \text{H} \end{array}$	1	Strongly basic	H ₃ N $\cdot\cdot$ BF ₃

Lewis bases supply electron pair to a nucleus and are "*nucleophilic* (nucleus loving) reagents".

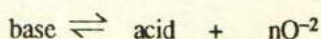
4. The Lux-Flood Concept

Protonic concept of Bronsted cannot be applied to systems having no proton particularly in the case of oxide systems. According to Lux-Flood concept, the definitions of acids and bases are as follows :—

Base : Any substance which gives up oxide ion (O^{-2}).

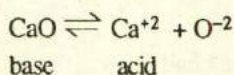
Acid : Any substance which gains or takes up oxide ions.

Hence,

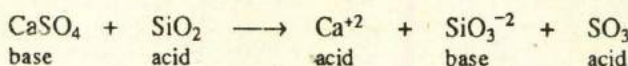
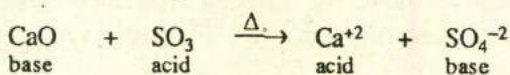
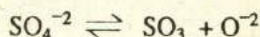


This view is particularly applicable to reaction at high temperature.

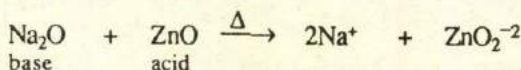
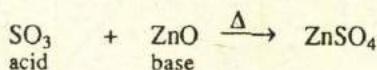
CaO is a base because it gives up O^{-2} ions :



SO_4^{-2} is a base because it gives up O^{-2} ions :



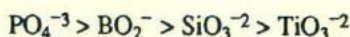
SO_3 and Ca^{+2} are acids because they take up oxide ions as shown by the above equation :



Strength of acids is determined by the magnitude of the equilibrium constant,

$$K = \frac{[\text{Acid}] \times [\text{O}^{-2}]}{[\text{base}]}$$

According to this concept, the strength of the following acids are given in the increasing order :



5. The Usanovich Concept

This concept gives a comprehensive definition of acids and bases comprising all aspects of their reactions.

An acid is defined as any substance which—

- (i) neutralizes a base,
- (ii) gives up cations,
- (iii) combines with anions or electrons.

Similarly, a base is defined as any substance which—

- (i) neutralizes an acid,
- (ii) gives up anions or electrons,
- (iii) combines with cations.

The following examples in a tabular form explain the various aspects of the Usanovich concept :—

<i>Acid</i>	<i>Base</i>	<i>Salt</i>	<i>Justification</i>
SO_3	Na_2O	Na_2SO_4	Na_2O gives O^{-2} SO_3 combines with O^{-2}
$\text{Fe}(\text{CN})_2$	KCN	$\text{K}_4\text{Fe}(\text{CN})_6$	KCN gives CN^{-} $\text{Fe}(\text{CN})_2$ combines with CN^{-}
Sb_2S_3	$(\text{NH}_4)_2\text{S}$	$(\text{NH}_4)_2\text{SbS}_4$	$(\text{NH}_4)_2\text{S}$ gives S^{-2} Sb_2S_3 gains S^{-2}
Cl_2	Na	NaCl	Na loses an electron Cl gains an electron
HCl	NH_3	NH_4Cl	HCl gives H^{+} NH_3 combines with H^{+}
NH_4^{+}	OH^{-}	$\text{NH}_3 + \text{H}_2\text{O}$	NH_4^{+} gives H^{+} OH^{-} combines with H^{+}

The Strengths of Acids

From the point of view of ionization theory, the strengths of acids (or bases) depend on the extent to which they dissociate into ions.

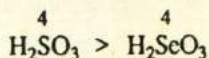
As mentioned in chapter 8, a molecule represented by MOH dissociate giving an OH^- or H^+ ions depending on the charge and size and electronegativity of M. A large ion with a small positive charge has less attraction for the electron of the OH^- ion than does a small ion with a positive charge.

Thus alkali metal hydroxides, MOH, form strong bases and their strength increases as the size of the alkali metal ion increases. The comparative strengths of the various bases are qualitatively given in Table 9.1.

Table 9.1. Strengths of bases on the basis of ion size and charge of the metals.

<i>Base</i>	<i>Size of the metal ion Å</i>	<i>Charge of metal ion</i>	<i>Qualitative strengths</i>
LiOH	0.60	+1	Weak base
NaOH	0.95	+1	Strong base
KOH	1.33	+1	Very strong base
CsOH	1.69	+1	Strongest base
$\text{Mg}(\text{OH})_2$	0.65	+2	Weaker base
$\text{Al}(\text{OH})_3$	0.50	+3	Weaker base (Amphoteric)

The strength of an acid is a measure of tendency of its conjugate base to part away with the proton to another base. A strong acid having a great tendency to donate proton is a conjugate to weak base with small tendency to accept proton. Hence stronger the acid the weaker is the conjugate base and stronger the base the weaker is the conjugate acid. Thus, strong HCl has a weak conjugate base Cl^- . The polyprotic acids, such as H_3PO_4 , undergo stepwise ionization reactions. The strength in this case can be measured by ionization constants K. Thus the smaller the value of ionization constant K, the less is the degree of ionization and hence less strong the acid. This applies to other polyprotic acids and provides an approximate measure of the relative strengths of acidity due to ionization. The neutral molecule more readily gives up the proton than does the negatively



because of the smaller size of S than Se although the oxidation number is the same in both cases.

Ionic Potential : The ratio between the charge and the radius of an ion is called ionic potential. If Z is the charge, r the radius of an ion, then the ionic potential ϕ is expressed as,

$$\phi = \frac{Z}{r}$$

It has been shown that values of ϕ also determine the acidic or basic character of a compound or an ion. Thus,

$$\sqrt{\phi} > 3.2 \text{ — acidic}$$

$$\sqrt{\phi} < 2.3 \text{ — basic}$$

$$2.3 < \sqrt{\phi} < 3.2 \text{ — amphoteric}$$

The strengths of acids may be correlated to the number of oxygen and hydrogen atoms in the molecule in two ways :—

(1) The greater the difference between the number of oxygen and number of hydrogen atoms, the stronger the acid.

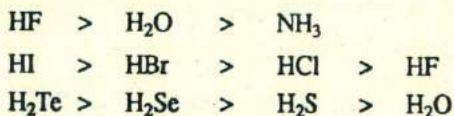
(2) The greater the number of non-hydrogenated oxygen atoms per molecule, the greater is the strength of acid.

These two points have been illustrated in the Table 9.2 regarding oxyacid of the general formula



where x and y are the numbers of hydrogen and oxygen atoms in the molecule respectively.

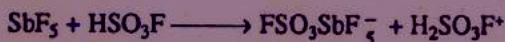
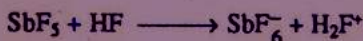
In the cases of acids which do not contain the oxygen atoms, the determination of strengths is based mainly on the ionic sizes or interatomic distance or electronegativity of H and the non-metallic element forming the acid molecule. Thus, the following two series have been arranged in decreasing acidity :



The decreasing electronegativity in the order $F > O > N$ gives rise to decreasing strengths of acids. But the decreasing atomic sizes of halogens and those in the chalcogens series produce acids of decreasing strengths. In the halogen acids, the bond distances $\text{H}-\text{X}$ increase from 1.0 \AA for HF to 1.7 \AA in HI and also the bond energy decreases. HI, therefore, is a stronger acid since it gives up proton relatively easily. The charge of the anion also influences base strengths. For instance, the base strength of the monoatomic anions increases in the series $\text{N}^{-3} > \text{O}^{-2} > \text{F}^{-}$, i.e., NH_3 is a stronger base than H_2O which is a stronger base than HF.

In the case of oxyacids the factors influencing the acid strengths are : (i) electronegativity, (ii) number of oxygen atoms and (iii) the oxidation state of the element forming the hydroxy compounds. These are shown in Table 9.2.

Superacids : When strong acids are dissolved in very acidic solvents, the solutions are highly effective protonating agents. Such solutions are known as *superacids*. Fluorosulphonic acid and hydrogen fluoride act as good systems for the formation of superacids :



Alkanes are easily protonated by superacids :

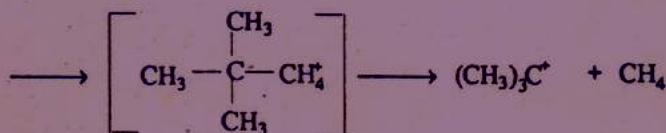
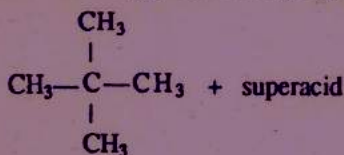


Table 9.2. Relative strengths of oxyacids of the general formula H_xMO_y .

Acid	Structural formula	No. of H atoms x	No. of O atoms y	$y-x$	No. of non-hydrogenated O atoms	First ionization constant (K)	Strengths of acid (Remarks)
$+1$ HClO	Cl(OH)	1	1	0	0	9.6×10^{-7}	very weak
$+3$ HClO ₂	ClO(OH)	1	2	1	1	1×10^{-2}	weak
$+5$ HClO ₃	ClO ₂ (OH)	1	3	2	2	$\sim 10^3$	strong
$+7$ HClO ₄	ClO ₃ (OH)	1	4	3	3	$\sim 10^8$	very strong
$+1$ HBrO	Br(OH)	1	1	0	0	2×10^{-2}	weak
$+1$ HIO	I(OH)	1	1	0	0	1×10^{-11}	very weak
$+3$ H ₃ BO ₃	B(OH) ₃	3	3	0	0	5×10^{-10}	very weak
$+3$ H ₃ AsO ₃	As(OH) ₃	3	3	0	0	6×10^{-10}	very weak
$+5$ H ₃ AsO ₄	AsO(OH) ₃	3	4	1	1	5×10^{-3}	weak
$+4$ H ₄ SiO ₄	Si(OH) ₄	4	4	0	0	1×10^{-10}	very weak
$+3$ HNO ₂	NO(OH)	1	2	1	1	4.5×10^{-4}	weak
$+5$ HNO ₃	NO ₂ (OH)	1	3	2	2	$\sim 10^3$	strong
$+4$ H ₂ SO ₃	SO(OH) ₂	2	3	1	1	1.7×10^{-3}	weak
$+6$ H ₂ SO ₄	SO ₂ (OH) ₂	2	4	2	2	$\sim 10^3$	strong
$+5$ H ₃ PO ₄	PO(OH) ₃	3	4	1	1	7.5×10^{-3}	weak
$+7$ HMnO ₄	MnO ₃ (OH)	1	4	3	3	$\sim 10^8$	very strong

Acids & base as catalysts :

1. $\text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH} \xrightarrow[\text{Catalyst}]{\text{H}_2\text{SO}_4} \text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O}$.
2. $\text{C}_6\text{H}_6 + \text{CH}_3\text{Cl} \xrightarrow[\text{Catalyst}]{\text{AlCl}_3} \text{C}_6\text{H}_5\text{CH}_3 + \text{HCl}$.
3. $\text{RX} + \text{H}_2\text{O} \xrightarrow[\text{Catalyst}]{\text{aq. KOH}} \text{ROH} + \text{HX}$.

Hard & Soft Acids and Bases (HSAB)

The classification is based on electronegativity values and size and is actually a form of Lewis acid-base concept.

Hard acids : These are metals having low electronegativity values usually 0.7 to 1.6. Exception is H^+ ion which is also a hard acid on the basis of very small size. Similarly ions such as B^{+3} , C^{+4} are hard acids because of very small size and high charge.

Hard Bases : Donor atoms of very high electronegativity values such as oxygen and fluorine. The oxoanions such as SO_4^{-2} , CO_3^{-2} , PO_4^{-3} etc. are included in this group.

Soft Acids : Metals having high electronegativities (1.9 — 2.5) and also having large size and low charge are soft acids. Ag^+ , Au^+ , Pt^{+2} , Hg^{+2} , Pb^{+2} etc. are soft acids.

Soft Bases : Group of ligands containing non-metal electronegative elements such as C, P, As, Br, I and H^- ion (having electronegativity values 2.1 - 2.96 are included in soft acids.

The equilibrium of the reaction between Hard and Soft acids and bases generally follow the equation :



Applications of HSAB principle :

1. Qualitative analysis scheme for metal cations.
2. Oxidation reduction reactions.
3. Geochemical classification of elements and their occurrence in nature as minerals.

4. Toxicology of the elements and medicinal chemistry.
5. Clinical application and chelation therapy.

QUESTIONS AND PROBLEMS

1. Write a brief note on Brönsted concept of acids and bases.
2. Write a note on modern views about acids and bases.
3. Write a short note on Lewis concept of acids and bases.
4. Write a note on Lewis and Brönsted concepts of acids and bases.
5. What is the relationship of charge and size of the acid-forming elements with the strength of the acid?
6. Arrange the following acids in terms of increasing strength :—
 H_3BO_3 , H_4SiO_4 , HNO_2 , HNO_3 , H_2SO_4 , HMnO_4 .
7. What is the basis of the strength of acids in halogen acids?
8. How will you determine the strength of acids in terms of the oxidation number of the acid-forming elements?
9. What are amphiprotic substances ? Illustrate with suitable examples.
10. Define the terms "acid" and "base" according to the Arrhenius concept and the protonic concept.
11. Write equations for the reaction of the following acids with water :—
 HCl , HNO_3 , HClO_4 and NH_4^+ . What is the role played by water in these acid-base reactions?
12. Classify the following substances as acids and bases giving reasons:—
 BF_3 , NH_3 , NH_4^+ , Ag^+ , SO_3 , CaO , KCN , OH^- , SO_4^{2-} , Na , Cl_2 , H^+ .
13. What are the conjugate acids and bases? What are the conjugate bases of the following acids?
 H_2CO_3 , H_2O , HClO_4 , HCN
14. Give a brief account of modern views regarding acids and bases.
15. Write a note on acids and bases.
16. Write a note on modern views on acids and bases.
17. What are hard and soft acids and bases? Mention about the applications of hard and soft acids and bases concept.