PHYSICS
TEST – 6

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12th Chemistry
1st lesson

## METALLURGY

### Occurrence of metals

In general, pure metals are shiny and malleable, however, most of them are found in nature as compounds with different properties. Metals having least chemical reactivity such as copper, silver, gold and platinum occur in significant amounts as native elements. Reactive metals such as alkali metals usually occurs in their combined state and are extracted using suitable metallurgical process.

### Mineral and ore

A naturally occurring substance obtained by mining which contains the metal in free state or in the form of compounds like oxides, sulphides etc... is called a mineral. In most of the minerals, the metal of interest is present only in small amounts and some of them contains a reasonable percentage of metal. For example iron is present in around 800 minerals. However, some of them such as hematite magnetite etc., containing high percentage of iron are commonly used for the extraction of iron. Such minerals that contains a high percentage of metal, from which it can be extracted conveniently and economically are called ores. Hence all ores are minerals but all minerals are not ores. Let us consider another example, bauxite and china clay ($Al_2O_3 .2SiO_2 .2H_2O$). Both are minerals of aluminium. However, aluminium can be commercially extracted from bauxite while extraction from china clay is not a profitable one. Hence the mineral, bauxite is an ore of aluminium while china clay is not.

The extraction of a metal of interest from its ore consists of the following metallurgical processes.

(i) concentration of the ore

(ii) extraction of crude metal

(iii) refining of crude metal

List of some metals and their common ores with their chemical formula

| Metal | Ore | Composition | Metal | Ore | Composition |
|---|---|---|---|---|---|
| Aluminum | Bauxite | $Al_2O_3.nH_2O$ | Zinc | Zinc blende or Sphalerite | $ZnS$ |
| | Diaspore | $Al_2O_3.H_2O$ | | Calamine | $ZnCO_3$ |
| | Kaolinite | $Al_2Si_2O_5(OH)_4$ | | Zincite | $ZnO$ |
| Iron | Haematite | $Fe_2O_3$ | Lead | Galena | $PbS$ |
| | Magnetite | $Fe_3O_4$ | | Anglesite | $PbSO_4$ |
| | Siderite | $FeCO_3$ | | Cerrusite | $PbCO_3$ |
| | Iron pyrite | $FeS_2$ | Tin | Cassiterite | $SnO_2$ |
| | Limonite | $Fe_2O_3.3H_2O$ | Silver | Silver glance (Argentite) | $Ag_2S$ |
| Copper | Copper Pyrite | $CuFeS_2$ | | Pyrargyrite (Ruby silver) | $Ag_3SbS_3$ |
| | Copper glance | $Cu_2S$ | | Chlorargyrite (Horn Silver) | $AgCl$ |
| | Cuprite | $Cu_2O$ | | Stefinite | $Ag_5SbS_4$ |
| | Malachite | $CuCO_3.Cu(OH)_2$ | | Proustite | $Ag_3AsS_3$ |
| | Azurite | $2CuCO_3.Cu(OH)_2$ | | | |

Concentration of ores

Generally, the ores are associated with nonmetallic impurities, rocky materials and siliceous matter which are collectively known as gangue. The preliminary step in metallurgical process is removal of these impurities. This removal process is known as concentration of ore. It increases the concentration of the metal of interest or its compound in the ore. Several methods are available for this process and the choice of method will depend on the nature of the ore, type of impurity and environmental factors. Some of the common methods of ore concentration are discussed below.

Gravity separation or Hydraulic wash

In this method, the ore having high specific gravity is separated from the gangue that has low specific gravity by simply washing with running water. Ore is crushed to a finely powdered form and treated with rapidly flowing current of water. During this process the lighter gangue particles are washed away by the running water. This method is generally applied to concentrate the native ore such as gold and oxide ores such as haematite ($Fe_2O_3$), tin stone ($SnO_2$) etc.

## Froth flotation

This method is commonly used to concentrate sulphide ores such as galena (PbS), zinc blende (ZnS) etc... In this method, the metallic ore particles which are preferentially wetted by oil can be separated from gangue.

In this method, the crushed ore is suspended in water and mixed with frothing agent such as pine oil, eucalyptus oil etc. A small quantity of sodium ethyl xanthate which acts as a collector is also added. A froth is generated by blowing air through this mixture. The collector molecules attach to the ore particle and make them water repellent. As a result, ore particles, wetted by the oil, rise to the surface along with the froth. The froth is skimmed off and dried to recover the concentrated ore. The gangue particles that are preferentially wetted by water settle at the bottom.

When a sulphide ore of a metal of interest contains other metal sulphides as impurities, depressing agents such as sodium cyanide, sodium carbonate etc are used to selectively prevent other metal sulphides from coming to the froth. For example, when impurities such as ZnS is present in galena (PbS), sodium cyanide (NaCN) is added to depresses the flotation property of ZnS by forming a layer of zinc complex $Na_2[Zn(CN)_4]$ on the surface of zinc sulphide.

## Leaching

This method is based on the solubility of the ore in a suitable solvent and the reactions in aqueous solution. In this method, the crushed ore is allowed to dissolve in a suitable solvent, the metal present in the ore is converted to its soluble salt or complex while the gangue remains insoluble. The following examples illustrate the leaching processes.

## Cyanide leaching

Let us consider the concentration of gold ore as an example. The crushed ore of gold is leached with aerated dilute solution of sodium cyanide. Gold is converted into a soluble cyanide complex. The gangue, aluminosilicate remains insoluble.

$$4Au(s) + 8CN^-(aq) + O_2(g) + 2H_2O(l) \rightarrow 4[Au(CN)_2]^-(aq) + 4OH^-(aq)$$

Recovery of metal of interest from the complex by reduction:

Gold can be recovered by reacting the deoxygenated leached solution with zinc. In this process the gold is reduced to its elemental state (zero oxidation sate) and the process is called cementation.

$$Zn(s) + 2[Au(CN)_2]^- (aq) \text{ ® } [Zn(CN)_4]^{-2} (aq) + 2Au(s)$$

### Ammonia leaching

When a crushed ore containing nickel, copper and cobalt is treated with aqueous ammonia under suitable pressure, ammonia selectively leaches these metals by forming their soluble complexes viz. $[Ni(NH_3)_6]^{2+}$, $[Cu(NH_3)_4]^{2+}$,and $[Co(NH_3)_5H_2O]^{3+}$ respectively from the ore leaving behind the gangue, iron(III)oxides/hydroxides and aluminosilicate.

### Alkali leaching

In this method, the ore is treated with aqueous alkali to form a soluble complex. For example, bauxite, an important ore of aluminum is heated with a solution of sodium hydroxide or sodium carbonate in the temperature range 470 - 520 K at 35 atm to form soluble sodium meta-aluminate leaving behind the impurities, iron oxide and titanium oxide.

$$Al_2O_3 (s) + 2NaOH (aq) + 3H_2O (l) \rightarrow 2Na[Al(OH)_4] (aq)$$

The hot solution is decanted, cooled, and diluted. This solution is neutralised by passing $CO_2$ gas, to form hydrated $Al_2O_3$ precipitate.

$$2Na[Al(OH)_4] (aq) + 2CO_2 (g) \rightarrow Al_2O_3.3H_2O (s) + 2NaHCO_3 (aq)$$

The precipitate is filtered off and heated around 1670 K to get pure alumina $Al_2O_3$.

### Acid leaching

Leaching of sulphide ores such as ZnS, PbS etc., can be done by treating them with hot aqueous sulphuric acid.

$$2ZnS (s) + 2H_2SO_4 (aq) + O_2 (g) \rightarrow 2ZnSO_4 (aq) + 2S (s) + 2 H_2O$$

In this process the insoluble sulphide is converted into soluble sulphate and elemental sulphur.

### Magnetic separation

This method is applicable to ferromagnetic ores and it is based on the difference in the magnetic properties of the ore and the impurities. For example tin stone can be separated from the wolframite impurities which is magnetic. Similarly, ores such as chromite, pyrolusite having magnetic property can be removed from the non

magnetic siliceous impurities. The crushed ore is poured on to an electromagnetic separator consisting of a belt moving over two rollers of which one is magnetic. The magnetic part of the ore is attracted towards the magnet and falls as a heap close to the magnetic region while the nonmagnetic part falls away from it

Extraction of crude metal

The extraction of crude metals from the concentrated ores is carried out in two steps namely,

(i) conversion of the ore into oxides of the metal of interest and
(ii) reduction of the metal oxides to elemental metals. In the concentrated ore, the metal exists in positive oxidation state and hence it is to be reduced to its elemental state. We can infer from the principles of thermodynamics, that the reduction of oxide is easier when compared to reduction of other compounds of metal and hence, before reduction, the ore is first converted into the oxide of metal of interest.

Let us discuss some of the common methods used to convert the concentrated ore into the oxides of the metal of interest.

Conversion of ores into oxides

Roasting

Roasting is the method, usually applied for the conversion of sulphide ores into their oxides. In this method, the concentrated ore is oxidised by heating it with excess of oxygen in a suitable furnace below the melting point of the metal.

$$2PbS + 3O_2 \xrightarrow{\Delta} 2PbO + 2SO_2 \uparrow$$

$$2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2O + 2SO_2 \uparrow$$

$$2ZnS + 3O_2 \xrightarrow{\Delta} 2ZnO + 2SO_2 \uparrow$$

Roasting also removes impurities such as arsenic, sulphur, phosphorous by converting them into their volatile oxides.

For example

$$4As + 3O_2 \longrightarrow 2As_2O_3 \uparrow$$

$$S_8 + 8O_2 \longrightarrow 8SO_2 \uparrow$$

$$P_4 + 5O_2 \longrightarrow P_4O_{10} \uparrow$$

Calcination

Calcination is the process in which the concentrated ore is strongly heated in the absence of air. During this process, the water of crystallisation present in the hydrated oxide escapes as moisture. Any organic matter (if present) also get expelled leaving behind a porous ore. This method can also be carried out with a limited supply of air.

For examples,
During calcination of carbonate ore, carbon dioxide is expelled

$$PbCO_2 \xrightarrow{\Delta} PbO + CO_2 \uparrow$$

$$CaCO_3 \longrightarrow CaO + CO_2 \uparrow$$

$$ZnCO_3 \xrightarrow{\Delta} ZnO + CO_2 \uparrow$$

$$MgCO_3.CaCO_3 \xrightarrow{\Delta} MgO + CaO + 2CO_2 \uparrow$$

During calcination of hydrated ore, the water of hydration is expelled as vapour

$$Fe_2O_3.3H_2O \xrightarrow{\Delta} Fe_2O_3(s) + 3H_2O(g) \uparrow$$

$$Al_2O_3.2H_2O \xrightarrow{\Delta} Al_2O_3(s) + 2H_2O(g) \uparrow$$

Reduction of metal oxides

Metal oxide can be reduced to crude metal by using a suitable reducing agent like carbon, carbon monoxide, hydrogen, aluminium and other reactive metals such as sodium etc...The choice of reducing agent depends on the nature of the metal. For example, carbon cannot be used as a reducing agent for the reactive metals such as sodium, potassium, aluminium etc...Similarly CO cannot be used to reduce oxides such as ZnO, $Al_2O_3$ . Later in this,we study selection of suitable reducing agents by applying Ellingham diagram.

Smelting

In this method, a flux (a chemical substance that forms an easily fusible slag with gangue) and a reducing agent such as carbon, carbon monoxide (or) aluminium is added to the concentrated ore and the mixture is melted by heating at an elevated temperature (above the melting point of the metal) in a smelting furnace. For example the oxide of iron can be reduced by carbon monoxide as follows.

$$Fe_2O_3(s) + 3CO\ (g) \longrightarrow 2Fe(s) + 3CO_2(g) \uparrow$$

In this extraction, a basic flux, quick lime (CaO) is used. Since the silica gangue present in the ore is acidic in nature, the quick lime combines with it to form calcium silicate (slag).

$$CaO(s) + SiO_2\ (s) \longrightarrow CaSio_3(s)$$

*Flux* *Gangue* *Slag*

In the extraction of copper from copper pyrites, the concentrated ore is heated in a reverberatory furnace after mixing with silica, an acidic flux. The ferrous oxide formed due to melting is basic in nature and it combines with silica to form ferrous silicate (slag). The remaining metal sulphides $Cu_2$ S and FeS are mutually soluble and form a copper matte.

$$2CuFeS_2(s) + O_2\ (g) \longrightarrow 2FeS(1) + Cu_2S(1) + SO_2(g)$$

$$2FeS(l) + 3O_2\ (g) \longrightarrow 2FeO(l) + 2SO_2(g)$$

$$FeO(s) + SiO_2\ (s) \longrightarrow FeSiO_3(s)$$

*Gangue* *Flux* *Slag*

The matte is separated from the slag and fed to the converting furnace. During conversion, the FeS present in the matte is first oxidised to FeO. This is removed by slag formation with silica. The remaining copper sulphide is further oxidised to its oxide which is subsequently converted to metallic copper as shown below.

$2Cu_2S\ (l,s) + 3O_2\ (g) \rightarrow 2Cu_2O\ (l,s) + 2SO_2\ (g)$
$2Cu_2O\ (l) + Cu_2S\ (l) \rightarrow 6Cu\ (l) + SO_2\ (g)$

The metallic copper is solidified and it has blistered appearance due to evolution of $SO_2$ gas formed in this process. This copper is called blistered copper.

Reduction by carbon:

In this method the oxide ore of the metal is mixed with coal (coke) and heated strongly in a furnace (usually in a blast furnace). This process can be applied to the metals which do not form carbides with carbon at the reduction temperature.
Examples:
$ZnO\ (s) + C(s) \rightarrow Zn(s) + CO(g) \uparrow$
$Mn_3O_4(s) + 4C(s) \rightarrow 3Mn(s) + 4CO(g) \uparrow$
$Cr_2O_3\ (s) + 3C(s) \rightarrow 2Cr\ (s) + 3CO\ (g) \uparrow$

Reduction by hydrogen:

This method can be applied to the oxides of the metals (Fe, Pb, Cu) having less electropositive character than hydrogen.
$Ag_2O(s) + H_2(g) \rightarrow 2Ag(s) = H_2O\ (l)$
$Fe_3O_4(s) + 4H_2(g) \rightarrow 3Fe(s) + 4H_2O(l)$

Nickel oxide can be reduced to nickel by using a mixture of hydrogen and carbon monoxide (water gas)
$2NiO(s) + CO(g) + H_2(g) \rightarrow 2Ni(s) + CO_2(g) + H_2O(l)$

Reduction by metal:

Metallic oxides such as $Cr_2O_3$ can be reduced by an aluminothermic process. In this process, the metal oxide is mixed with aluminium powder and placed in a fire clay crucible. To initiate the reduction process, an ignition mixture (usually magnesium and barium peroxide) is used.
$BaO_2 + Mg \rightarrow BaO + MgO$

During the above reaction a large amount of heat is evolved (temperature up to 2400°C, is generated and the reaction enthalpy is : 852 kJ mol$^{-1}$) which facilitates the reduction of $Cr_2O_3$ by aluminium power.
$Cr_2O_3 + 2Al \xrightarrow{\Delta} 2Cr + Al_2O_3$
Active metals such as sodium, potassium and calcium can also be used to reduce the metal oxide
$B_2O_3 + 6Na \xrightarrow{} 2B + 3Na_2O$

$Rb_2O_3 + 3Mg \longrightarrow 2Rb + 3MgO$

$TiO_2 + 2Mg \longrightarrow Ti + 2MgO$

$ThO_2 + 2Ca \xrightarrow{1250K} Th + 2CaO$

Auto-reduction:

Simple roasting of some of the ores give the crude metal. In such cases, the use of reducing agents is not necessary. For example, mercury is obtained by roasting of its ore cinnabar (HgS)

$HgS(s) + O_2(g) \longrightarrow Hg(l) + SO_2\uparrow$

Thermodynamic principle of metallurgy

As we discussed, the extraction of metals from their oxides can be carried out by using different reducing agents. For example, consider the reduction of a metal oxide Mx Oy .

$\frac{2}{y} M_xO_y(s) \rightarrow \frac{2x}{y} M(s) + O_2\,(g)$ ….. (1)

The above reduction may be carried out with carbon. In this case, the reducing agent carbon may be oxidised to either CO or $CO_2$ .

$C + O_2 \longrightarrow CO_2\,(g)$ ……. (2)

$2C + O_2 \longrightarrow 2CO(g)$ …… (3)

If carbon monoxide is used as a reducing agent, it is oxidised to $CO_2$ as follows,

$2CO + O_2 \rightarrow 2CO_2\,(g)$

A suitable reducing agent is selected based on the thermodynamic considerations. We know that for a spontaneous reaction, the change in free energy (ΔG) should be negative. Therefore, thermodynamically, the reduction of metal oxide [equation (1)] with a given

reducing agent [Equation (2), (3) or (4)] can occur if the free energy change for the coupled reaction. [Equations (1) & (2), (1) & (3) or (1) & (4)] is negative. Hence, the reducing agent is selected in such a way that it provides a large negative ΔG value for the coupled reaction.

Ellingham diagram

The change in Gibbs free energy (ΔG) for a reaction is given by the expression.

$$\Delta G = \Delta H - T\Delta S \text{ ------ } (1)$$

where, ΔH is the enthalpy change , T the temperature in kelvin and ΔS the entropy change. For an equilibrium process, $\Delta G^0$ can be calculated using the equilibrium constant by the following expression

$$\Delta G^0 = -RT \ln K_p$$

Harold Ellingham used the above relationship to calculate the $\Delta G^0$ values at various temperatures for the reduction of metal oxides by treating the reduction as an equilibrium process.

He has drawn a plot by considering the temperature in the x-axis and the standard free energy change for the formation of metal oxide in y-axis. The resultant plot is a straight line with $\Delta S$ as slope and $\Delta H$ as y-intercept. The graphical representation of variation of the standard Gibbs free energy of reaction for the formation of various metal oxides with temperature is called Ellingham diagram

Observations from the Ellingham diagram.

1. For most of the metal oxide formation, the slope is positive. It can be explained as follows. Oxygen gas is consumed during the formation of metal oxides which results in the decrease in randomness. Hence, $\Delta S$ becomes negative and it makes the term, $T\Delta S$ positive in the straight line equation.

2. The graph for the formation of carbon monoxide is a straight line with negative slope. In this case $\Delta S$ is positive as 2 moles of CO gas is formed by the consumption of one mole of oxygen gas. It indicates that CO is more stable at higher temperature.

3. As the temperature increases, generally $\Delta G$ value for the formation of the metal oxide become less negative and becomes zero at a particular temperature. Below this temperature, $\Delta G$ is negative and the oxide is stable and above this temperature $\Delta G$ is positive. This general trend suggests that metal oxides become less stable at higher temperature and their decomposition becomes easier.

4. There is a sudden change in the slope at a particular temperature for some metal oxides like MgO, HgO. This is due to the phase transition (melting or evaporation).

Applications of the Ellingham diagram:

Ellingham diagram helps us to select a suitable reducing agent and appropriate temperature range for reduction. The reduction of a metal oxide to its metal can be considered as a competition between the element used for reduction and the metal to combine with oxygen. If the metal oxide is more stable, then oxygen remains with the metal and if the oxide of element used for reduction is more stable, then the oxygen from the metal oxide combines with elements used for the reduction. From the Ellingham diagram, we can infer the relative stability of different metal oxides at a given temperature.

1. Ellingham diagram for the formation of $Ag_2O$ and HgO is at upper part of the diagram and their decomposition temperatures are 600 and 700 K respectively. It

indicates that these oxides are unstable at moderate temperatures and will decompose on heating even in the absence of a reducing agent.

2. Ellingham diagram is used to predict thermodynamic feasibility of reduction of oxides of one metal by another metal. Any metal can reduce the oxides of other metals that are located above it in the diagram. For example, in the Ellignham diagram, for the formation of chromium oxide lies above that of the aluminium, meaning that $Al_2O_3$ is more stable than $Cr_2O_3$ . Hence aluminium can be used as a reducing agent for the reduction of chromic oxide. However, it cannot be used to reduce the oxides of magnesium and calcium which occupy lower position than aluminium oxide.

3. The carbon line cuts across the lines of many metal oxides and hence it can reduce all those metal oxides at sufficiently high temperature. Let us analyse the thermodynamically favourable conditions for the reduction of iron oxide by carbon. Ellingham diagram for the formation of FeO and CO intersects around 1000 K. Below this temperature the carbon line lies above the iron line which indicates that FeO is more stable than CO and hence at this temperature range, the reduction is not thermodynamically feasible. However, above 1000 K carbon line lies below the iron line and hence, we can use coke as reducing agent above this temperature. The following free energy calculation also confirm that the reduction is thermodynamically favoured.

From the Ellingham Diagram at 1500 K,

$2Fe(s) + O_2(g) \rightarrow 2FeO(g) \quad \Delta G_1 = -350 \text{ kJ mol}^{-1}$
$2C(s) + O_2(g) \rightarrow 2CO(g) \quad \Delta G_2 = -480 \text{ kJ mol}^{-1}$

Reverse the reaction

$2FeO(s) \rightarrow 2Fe(s) + O_2(g) \; -\Delta G_1 = +350 \text{ kJ mol}^{-1}$

Now couple the reactions (2) and (3)

$2FeO(s) + 2C \; 2Fe(l, s) + 2CO(g) \; \Delta G_3 = -130 \text{ kJ mol}^{-1}$

Limitations of Ellingham diagram

1. Ellingham diagram is constructed based only on thermodynamic considerations. It gives information about the thermodynamic feasibility of a reaction. It does not tell anything about the rate of the reaction. More over, it does not give any idea about the possibility of other reactions that might be taking place.

2. The interpretation of $\Delta G$ is based on the assumption that the reactants are in equilibrium with the products which is not always true.

Electrochemical principle of metallurgy

Similar to thermodynamic principles, electrochemical principles also find applications in metallurgical process. The reduction of oxides of active metals such as sodium, potassium etc., by carbon is thermodynamically not feasible. Such metals are extracted from their ores by using electrochemical methods. In this technique, the metal salts are taken in a fused form or in solution form. The metal ion present can be reduced by treating it with some suitable reducing agent or by electrolysis.

Gibbs free energy change for the electrolysis process is given by the following expression

$$\Delta G^\circ = -nFE^\circ$$

Where n is number of electrons involved in the reduction process, F is the Faraday and E0 is the electrode potential of the redox couple.

If E0 is positive then the $\Delta G$ is negative and the reduction is spontaneous and hence a redox reaction is planned in such a way that the e.m.f of the net redox reaction is positive. When a more reactive metal is added to the solution containing the relatively less reactive metal ions, the more reactive metal will go into the solution. For example,

$$Cu(s) + 2Ag^+(aq) \rightarrow Cu^{2+}(aq) + 2Ag(s)$$

$$Cu^{2+}(aq) + Zn(s) \rightarrow Cu(s) + Zn^{2+}(aq)$$

### Electrochemical extraction of aluminium – Hall-Heroult process:

In this method, electrolysis is carried out in an iron tank lined with carbon which acts as a cathode. The carbon blocks immersed in the electrolyte act as a anode. A 20% solution of alumina, obtained from the bauxite ore is mixed with molten cryolite and is taken in the electrolysis chamber. About 10% calcium chloride is also added to the solution. Here calcium chloride helps to lower the melting point of the mixture. The fused mixture is maintained at a temperature of above 1270 K. The chemical reactions involved in this process are as follows.

Ionisation of alumina $Al_2O_3 \rightarrow 2Al^{3+} + 3O^{2-}$

Reaction at cathode $2Al^{3+}(melt) + 6e^- \ 2Al(l)$

Reaction at anode $6O^{2-}(melt) \rightarrow 3O_2 + 12e^-$

Since carbon acts as anode the following reaction also takes place on it.

$$C(s) + O^{2-}(melt) \rightarrow CO + 2e^-$$

$$C(s) + 2O^{2-}(melt) \rightarrow CO_2 + 4e^-$$

Due to the above two reactions, anodes are slowly consumed during the electrolysis. The pure aluminium is formed at the cathode and settles at the bottom. The net electrolysis reaction can be written as follows.

$$4Al^{3+}(melt) + 6O^{2-}(melt) + 3C(s) \rightarrow 4Al(l) + 3CO_2(g)$$

### Refining process

Generally the metal extracted from its ore contains some impurities such as unreacted oxide ore, other metals, nonmetals etc...Removal of such impurities associated with the isolated crude metal is called refining process. In this section, let us discuss some of the common refining methods.

### Distillation

This method is employed for low boiling volatile metals like zinc (boiling point 1180 K) and mercury (630 K). In this method, the impure metal is heated to evaporate and the vapours are condensed to get pure metal.

### Liquation

This method, is employed to remove the impurities with high melting points from metals having relatively low melting points such as tin (Sn; mp= 904 K), lead (Pb; mp=600 K), mercury (Hg; mp=234 K), and bismuth (Bi; mp=545 K). In this process, the crude metal is heated to form fusible liquid and allowed to flow on a sloping surface. The impure metal is placed on sloping hearth of a reverberatory furnace and it is heated just above the melting point of the metal in the absence of air, the molten pure metal flows down and the impurities are left behind. The molten metal is collected and solidified.

### Electrolytic refining:

The crude metal is refined by electrolysis. It is carried out in an electrolytic cell containing aqueous solution of the salts of the metal of interest. The rods of impure metal are used as anode and thin strips of pure metal are used as cathode. The metal of interest dissolves from the anode, pass into the solution while the same amount of metal ions from the solution will be deposited at the cathode. During electrolysis, the less electropositive impurities in the anode, settle down at the bottom and are removed as anode mud.

Let us understand this process by considering electrolytic refining of silver as an example.

Cathode : Pure silver

Anode : Impure silver rods

Electrolyte : Acidified aqueous solution of silver nitrate.

When a current is passed through the electrodes the following reactions will take place

Reaction anode $Ag(s) \rightarrow Ag^{+} (aq) + Le^{-}$
Reaction at Cathode $Ag^{+}(aq) + le^{-} \rightarrow Ag(s)$

During electrolysis, at the anode the silver atoms lose electrons and enter the solution. The positively charged silver cations migrate towards the cathode and get discharged by gaining electrons and deposited on the cathode. Other metals such as copper, zinc etc.,can also be refined by this process in a similar manner.

## Zone Refining

This method is based on the principles of fractional crystallisation. When an impure metal is melted and allowed to solidify, the impurities will prefer to be in the molten region. i.e. impurities are more soluble in the melt than in the solid state metal. In this process the impure metal is taken in the form of a rod. One end of the rod is heated using a mobile induction heater which results in melting of the metal on that portion of the rod. When the heater is slowly moved to the other end the pure metal crystallises while the impurities will move on to the adjacent molten zone formed due to the movement of the heater. As the heater moves further away, the molten zone containing impurities also moves along with it. The process is repeated several times by moving the heater in the same direction again and again to achieve the desired purity level. This process is carried out in an inert gas atmosphere to prevent the oxidation of metals. Elements such as germanium (Ge), silicon (Si) and galium (Ga) that are used as semiconductor are refined using this process.

## Vapour phase method

In this method, the metal is treated with a suitable reagent which can form a volatile compound with the metal. Then the volatile compound is decomposed to give the pure metal. We can understand this method by considering the following process.

## Mond process for refining nickel:

The impure nickel is heated in a stream of carbon monoxide at around 350 K. The nickel reacts with the CO to form a highly volatile nickel tetracarbonyl. The solid impurities are left behind.

$$Ni(s) + 4CO(g) \rightarrow [Ni(CO)_4]\ (g)$$

On heating the nickel tetracarbonyl around 460 K, the complex decomposes to give pure metal.

$$[Ni(CO)_4]\ (g) \rightarrow Ni(s) + 4CO(g)$$

## Van-Arkel method for refining zirconium/titanium:

This method is based on the thermal decomposition of metal compounds which lead to the formation of pure metals. Titanium and zirconium can be purified using this method. For example, the impure titanium metal is heated in an evacuated vessel with iodine at a temperature of 550 K to form the volatile titanium tetra-iodide. ($TiI_4$). The impurities are left behind, as they do not react with iodine.

$$Ti(s) + 2I_2(s) \xrightarrow[\Delta]{550K} Til_4(vapour)$$

The volatile titanium tetraiodide vapour is passed over a tungsten filament at a temperature aroud 1800 K. The titanium tetraiodide is decomposed and pure titanium is deposited on the filament. The iodine is reused.

$$Til_4(vapour) \xrightarrow[\Delta]{1800K} Ti(s) + 2I_2(s)$$

## Applications of metals

## Applications of Al

Aluminium is the most abundant metal and is a good conductor of electricity and heat. It also resists corrosion. The following are some of its applications.

- Many heat exchangers/sinks and our day to day cooking vessels are made of aluminium.
- It is used as wraps (aluminium foils) and is used in packing materials for food items,
- Aluminium is not very strong, However, its alloys with copper, manganese, magnesium and silicon are light weight and strong and they are used in design of aeroplanes and other forms of transport.
- As Aluminium shows high resistance to corrosion, it is used in the design of chemical reactors, medical equipments, refrigeration units and gas pipelines.
- Aluminium is a good electrical conductor and cheap, hence used in electrical overhead electric cables with steel core for strength.

## Applications of Zn

- Metallic zinc is used in galvanising metals such as iron and steel structures to protect them from rusting and corrosion.
- Zinc is also used to produce die-castings in the automobile, electrical and hardware industries
- Zinc oxide is used in the manufacture of many products such as paints, rubber, cosmetics,pharmaceuticals, plastics, inks, batteries, textiles and electrical equipment. Zinc sulphideis used in making luminous paints, fluorescent lights and x-ray screens.
- Brass an alloy of zinc is used in water valves and communication equipment as it is highlyresistant to corrosion.

## Applications of Fe

- Iron is one of the most useful metals and its alloys are used everywhere including bridges,electricity pylons, bicycle chains, cutting tools and rifle barrels.
- Cast iron is used to make pipes, valves and pumps stoves etc...
- Magnets can be made from iron and its alloys and compounds.

- An important alloy of iron is stainless steel, and it is very resistant to corrosion. It is used inarchitecture, bearings, cutlery, surgical instruments and jewellery. Nickel steel is used formaking cables, automobiles and aeroplane parts. Chrome steels are used for manufacturingcutting tools and crushing machines

Applications of Cu

Copper is the first metal used by the human and extended use of its alloy bronze resulted in anew era,'Bronze age'

Copper is used for making coins and ornaments along with gold and other metals.

Copper and its alloys are used for making wires, water pipes and other electrical parts

Applications of Au

- Gold, one of the expensive and precious metals. It is used for coinage, and has been used asstandard for monetary systems in some countries.

- It is used extensively in jewellery in its alloy form with copper. It is also used in electroplatingto cover other metals with a thin layer of gold which are used in watches, artificial limbjoints, cheap jewellery, dental fillings and electrical connectors.

- Gold nanoparticles are also used for increasing the efficiency of solar cells and also usedas catalysts.

The Iron Pillar – Delhi:

The Iron pillar, also known as Ashoka Pillar,is 23 feet 8 inches high, 16 inches wide andweighs over 6000 kg.

The surprise comes in knowing its age, some 1600 yearsold,an iron column should have turned into a pile of dust long ago.

Despite that, it has avoided corrosion for over the last 1600 yearsand stands as an evidence of the exquisite skills and knowledge ofancient Indians.
A protective film was created through a complicatedcombination of the presence of raw and unreduced iron in the pillar and cycles of the weather,which helped to create a thin, uniform layer of misawite on the pillar. Misawite is a compound ofiron, oxygen and hydrogen which does not rust and gives corrosion resistance.

# UNIT– 8. IONIC EQUILIBRIUM

Learning Objectives:

After studying this unit, the students will be able to

- Ø classify the substances into acids and bases based on Arrhenius, Lowry – Bronsted and Lewis concepts.
- Ø define pH scale and establish relationship between pH and pOH
- Ø describe the equilibrium involved in the ionisation of water.
- Ø explain Ostwald’s dilution Law and derive a relationship between the dissociation constant and degree of dissociation of a weak electrolyte.
- Ø recognise the concept of common ion effect and explain buffer action.
- Ø apply Henderson equation for the preparation of buffer solutio \
- Ø calculate solubility product and understand the relation between solubility and solubility product.
- Ø solve numerical problems involving ionic equilibria.

Peter Joseph William Debye:

Peter Joseph William Debye was Dutch-American physicist greatly contributed to the theory of electrolyte solutions. He also studied the dipole moments of molecules, Debye won the Nobel Prize in Chemistry (1936) for his contributions to the determination of molecular structure through his investigations on dipole moments and X-rays diffraction.

## INTRODUCTION

We have already learnt the chemical equilibrium in XI standard. In this unit, we discuss the ionic equilibria, specifically acid – base equilibria. Some of the important processes in our body involve aqueous equilibria. For example, the carbonic acid – bicarbonate buffer in the blood.

$$H_3O^+ (aq) + HCO_3^- (aq) \leftrightharpoons H_2CO_3 (aq) + H_2O(l)$$

We have come across many chemical compounds in our daily life among them acids and bases are the most common. For example, milk contains lactic acid, vinegar acetic acid, tea tannic acid and antacid tablet aluminium hydroxide / magnesium hydroxide. Acids and bases have many important industrial applications. For example, sulphuric acid is used in fertilizer industry and sodium hydroxide in soap industry etc… Hence, it is important to understand the properties of acids and bases.

In this unit we shall learn the definitions of acids and bases and study, their ionisation in aqueous solution. We learn the pH scale and also apply the principles of chemical equilibrium to determine the concentration of the species furnished in aqueous solution by acids and bases.

### 8.1 Acids and bases

The term ‘acid’ is derived from the latin word ‘acidus’ meaning sour. We have already learnt in earlier classes that acid tastes sour, turns the blue litmus to red and reacts with metals such as zinc and produces hydrogen gas. Similarly base tastes bitter and turns the red litmus to blue.

These classical concepts are not adequate to explain the complete behaviour of acids and bases. So, the scientists developed the acid – base concept based on their behaviour.

Let us, learn the concept developed by scientists Arrhenius, Bronsted and Lowry and lewis to describe the properties of acids and bases.

### 8.1.1 Arrhenius Concept

One of the earliest theories about acids and bases was proposed by swedish chemist Svante Arrhenius. According to him, an acid is a substance that dissociates to give hydrogen ions in water. For example, HCl, $H_2SO_4$ O etc., are acids. Their dissociation in aqueous solution is expressed as

$$\mathrm{HCl(g)} \overset{H^{2}O}{\leftrightharpoons} \mathrm{H^{+}\,(aq)+Cl^{-}\,(aq)}$$

The H+ ion in aqueous solution is highly hydrated and usually represented as $H_3O^+$ , the simplest hydrate of proton $[H(H_2O)^+$ . We use both $H^+$ and $H_3O^+$ to mean the same.

Similarly a base is a substance that dissociates to give hydroxyl ions in water. For example, substances like NaOH, $Ca(OH)_2$ etc., are bases.

$$\mathrm{Ca(OH)_2} \overset{H_2O}{\leftrightharpoons} \mathrm{Ca^{2+}\,(aq)+2OH^{-}\,(aq)}$$

Limitations of Arrhenius concept

i. Arrhenius theory does not explain the behaviour of acids and bases in non aqueous solvents such as acetone, Tetrahydrofuran etc...

ii. This theory does not account for the basicity of the substances like ammonia ($NH_3$) which do not possess hydroxyl group.

### 8.1.2 Lowry – Bronsted Theory (Proton Theory)

In 1923, Lowry and Bronsted suggested a more general definition of acids and bases. According to their concept, an acid is defined as a substance that has a tendency to donate a proton to another substance and base is a substance that has a tendency to accept a proton form other substance. In other words, an acid is a proton donor and a base is a proton acceptor.

When hydrogen chloride is dissolved in water, it donates a proton to the later. Thus, HCl behaves as an acid and $H_2O$ is base. The proton transfer from the acid to base can be represented as

$$HCl+H_2O \rightleftharpoons H_3O_{+}+Cl^{-}$$

When ammonia is dissolved in water, it accepts a proton from water. In this case, ammonia (NH3 ) acts as a base and H O2 is acid. The reaction is represented as

H O2 3 +NH NH +4 OH • + -

Let us consider the reverse reaction in the following equilibrium

$HCl \quad + \quad H_2O \quad \rightleftharpoons \quad H_3O \quad + Cl^-$

Proton donar (acid) Proton acceptor (Base) proton donar (acid) Proton acceptor (Base)

$H_3O^+$ donates a proton to $Cl^-$ to form HCl i.e., the products also behave as acid and base.

In general, Lowry – Bronsted (acid – base) reaction is represented as $Acid_1 + Base_2 \rightleftharpoons Acid_2 + Base_1$

The species that remains after the donation of a proton is a base ($Base_1$)and is called the conjugate base of the Bronsted acid ($Acid_1$) . In other words, chemical species that differ only by a proton are called conjugate acid – base pairs.

Conjugate acid - base pair

$HCl \quad + \quad H_2O \quad \rightleftharpoons \quad H_3O \quad + Cl^-$

Proton donar (acid) Proton acceptor (Base) proton donar (acid) proton acceptor (Base)

HCl and $Cl^-$ , $H_2O$ and $H_3O^+$ are two conjugate acid – base pairs. i.e., $Cl^-$ is the conjugate base of the acid HCl . (or) HCl is conjugate acid of $Cl^-$ . Similarly $H_3O^+$ is the conjugate acid of $H_2O$ .

Limitations of Lowry – Bronsted theory

- Substances like $BF_3$ , $AlCl_3$ etc., that do not donate protons are known to behave as acids.

8.1.3 Lewis concept

In 1923, Gilbert . N. Lewis proposed a more generalised concept of acids and bases. He considered the electron pair to define a species as an acid (or) a base. According to him, an acid is a species that accepts an electron pair while base is a species that donates an electron pair. We call such species as Lewis acids and bases.

A lewis acid is a positive ion (or) an electron deficient molecule and a lewis base is a anion (or) neutral molecule with at least one lone pair of electrons.

Let us consider the reaction between Boron tri fluoride and ammonia

Here, boron has a vacant 2p orbital to accept the lone pair of electrons donated by ammonia to form a new coordinate covalent bond. We have already learnt that in coordination compounds, the Ligands act as a lewis base and the central metal atom or ion that accepts a pair of electrons from the ligand behaves as a lewis acid.

| Lewis acids | Lewis bases |
|---|---|
| Electron deficient molecules such as $BF_3$ ,$AlCl_3$ ,$BeF_2$ etc... | Molecules with one (or) more lone pairs of electrons. $NH_3$ ,$H_2O$,R-O-H,R-O-R, R - $NH_2$ |
| All metal ions (or) atoms Examples: $Fe^{2+}$ ,$Fe^{3+}$ ,$Cr^{3+}$ ,$Cu^{2+}$ etc... | All anions $F^-$ ,$Cl^-$,$SCN^-$ ,$CN^-$,$SCN^-$ ,$SO_4^{2-}$ etc... |
| Molecules that contain a polar double bond Examples : $SO_2$, $CO_2$ ,$SO_3$ etc... | Molecules that contain carbon – carbon multiple bond Examples: $CH_2=CH_2$ ,$CH \equiv CH$ etc... |
| Molecules in which the central atom can expand its octet due to the availability of empty d – orbitals Example: $SiF_4$ ,$SF_4$ ,$FeCl_3$ etc.. | All metal oxides CaO,MgO,$Na_2O$ etc... |

| | |
|---|---|
| Carbonium ion $(CH_3)C_3$ + | Carbanion<br>$CH_3^-$ |

8.2 Strength of Acids and Bases

The strength of acids and bases can be determined by the concentration of $H_3O^+$ (or) $OH^-$ produced per mole of the substance dissolved in $H_2O$ . Generally we classify the acids / bases either as strong or weak. A strong acid is the one that is almost completely dissociated in water while a weak acid is only partially dissociated in water.

Let us quantitatively define the strength of an acid (HA) by considering the following general equilibrium.

$$\underset{\text{Acid1}}{HA} + \underset{\text{base 2}}{H_2O} \leftrightharpoons \underset{\text{acid 2}}{H_3O} + \underset{\text{base 1}}{A^-}$$

The equilibrium constant for the above ionisation is given by the following expression

$$K = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \quad \text{.......(8.1)}$$

We can omit the concentration of $H_2O$ in the above expression since it is present in large excess and essentially unchanged.

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \text{.......(8.2)}$$

Here, $K_a$ is called the ionisation constant or dissociation constant of the acid. It measures the strength of an acid. Acids such as HCl,$HNO_3$ etc... are almost completely ionised and hence they have high $K_a$ value ($K_a$ for HCl at $25^0$ C is $2\times10^6$ ) Acids such as formic acid ($K_a$=1.8 X $10^{-4}$ at $25^0$C), acetic acid (1.8X$10^{-5}$ at $25^0$C) etc.. are partially ionised in solution and in such cases, there is an equilibrium between the unionised acid molecules and their dissociated ions. Generally, acids with $K_a$ value greater than ten are considered as strong acids and less than one are considered as weak acids.

Let us consider the dissociation of HCl in aqueous solution,

$$\underset{\text{Acid1}}{HCl} + \underset{\text{base 2}}{H-OH} \leftrightharpoons \underset{\text{acid 2}}{H_3O^+} + \underset{\text{base 1}}{Cl^-}$$

As discussed earlier, due to the complete dissociation, the equilibrium lies almost 100% to the right. i.e., the $Cl^-$ ion has only a negligible tendency to accept a proton form $H_3O$ + . It means that the conjugate base of a strong acid is a weak base and vice versa.

The following table illustrates the relative strength of conjugate acid – base pairs.

| | | | |
|---|---|---|---|
| $HClO_4$ | Strong acids | $ClO_4^-$ | Very weak base |
| $HCl$ | | $Cl^-$ | |
| $H_2SO_4$ | | $HSO_4^-$ | |
| $HNO_2$ | | $NO_3^-$ | |

| | | | |
|---|---|---|---|
| $H_3O^+$ | Weak acids | $H_2O$ | Weak base |
| $HNO_2$ | | $NO_2^-$ | |
| HF | | $F^-$ | |
| $CH_3COOH$ | | $CH_3OO-$ | |
| $NH_3$ | Very weak acids | $NH_2^-$ | Strong base |
| $OH^-$ | | $O^{2-}$ | |
| $H_2$ | | $H^-$ | |

8.3 Ionisation of water

We have learnt that when an acidic or a basic substance is dissolved in water, depending upon its nature, it can either donate (or) accept a proton. In addition to that the pure water itself has a little tendency to dissociate. i.e, one water molecule donates a proton to an another water molecule. This is known as auto ionisation of water and it is represented as below.

$$\underset{\text{Acid1}}{HO\text{-}H} + \underset{\text{base 2}}{H_2O} \rightleftharpoons \underset{\text{acid 2}}{H_3O^+} + \underset{\text{base 1}}{OH^-}$$

Conjugate acid - base pairs

In the above ionisation, one water molecule acts as an acid while the another water molecule acts as a base.

The dissociation constant for the above ionisation is given by the following expression

$$K_a = \frac{[H_3O^+][OH^-]}{[H_2O]} \text{.......(8.3)}$$

The concentration of pure liquid water is one. i.e, $[H_2O]^2 = 1$

$$K = [H_3O^+][OH]\text{........(8.4)}$$

Here, $K_w$ represents the ionic product (ionic product constant) of water

It was experimentally found that the concentration of $H_3O^+$ in pure water is $1X10^{-7}$ at $25^0C$ . Since the dissociation of water produces equal number of $H_3O^+$ and $OH^-$ , the concentration of $OH^-$ is also equal to $1X10^{-7}$ at $25^0C$.

Therefore, the ionic product of water o at $25^0C$ is

$$K_w = [H_3O]^+[OH^-]\text{......(8.4)}$$
$$K_w = (1X10^{-7})(1X10^{-7})$$
$$= 1X10^{-14}.$$

Like all equilibrium constants, $K_w$ is also a constant at a particular temperature. The dissociation of water is an endothermic reaction. With the increase in temperature, the concentration of $H_3O^+$ and $OH^-$ also increases, and hence the ionic product also increases.

$K_w$ values at different temperatures are given in the following below

| Temperature ( $^oC$ ) | $K_w$ |
|---|---|
| 0 | $1.14 \times 10^{-15}$ |
| 10 | $2.95 \times 10^{-15}$ |
| 25 | $1.00 \times 10^{-14}$ |
| 40 | $2.71 \times 10^{-14}$ |
| 50 | $5.30 \times 10^{-14}$ |

In neutral aqueous solution like NaCl solution, the concentration of $H_3O^+$ is always equal to the concentration of $OH^-$ whereas in case of an aqueous solution of a substance which may behave as an acid (or) a base, the concentration of $[H_3O^+]$will not be equal to $[OH^-]$.

We can understand this by considering the aqueous HCl as an example. In addition to the auto ionisation of water, the following equilibrium due to the dissociation of HCl can also exist.

$$HCl+H_2O \leftrightharpoons H_3O^++Cl^-$$

In this case, in addition to the auto ionisation of water, HCl molecules also produces H3 O+ ion by donating a proton to water and hence $[H_3O^+]>[OH^-]$. It means that the aqueous HCl solution is acidic. Similarly, in basic solution such as aqueous $NH_3$ NaOH etc….. $[OH^–]>[H_3O^+]$.

8.4 The pH scale

We usually deal with acid / base solution in the concentration range 0.1 to 10 $M^{-7}$ . To express the strength of such low concentrations, Sorensen introduced a logarithmic scale known as the pH scale. The term pH is derived from the French word 'Purissance de hydrogene' meaning, the power of hydrogen. pH of a solution is defined as the negative logarithm of base 10 of the molar concentration of the hydronium ions present in the solution.

$$pH = - \log_{10} [H_3O^+] \text{........}(8.5)$$

The concentration of $H_3O^+$ in a solution of known pH can be calculated using the following expression.

$$[H_3O^+]=10^{-pH} \text{ (or) } [H_3O^+]= \text{antilog of } (-pH)............(8.6)$$

Similarly, pOH can also be defined as follows

$$pOH = - \log_{10}[OH^- ]......(8.7)$$

As discussed earlier, in neutral solutions, the concentration of $[H_3O^+]$ as well as $[OH^+]$ is equal to $1X10^{-7}M$ at $25^0C$ . The pH of a neutral solution can be calculated by substituting this $H_3O^+$concentration in the expression (8.5)

$$\begin{aligned} pH &= \log_{10}[H_3O^+] \\ &= \log_{10} 10^{-7} \\ &=-(-7)\log^{10}{}_{10} = +7(1) = 7 \end{aligned}$$

Similary, we can calculate the pOH of a neutral solution using the expression (8.7), it is also equal to 7.

The negative sign in the expression (8.5) indicates that when the concentration of $[H_3O^+]$ increases the pH value decreases. For example, if the $[H_3O^+]$ increases from to $10^{-7}$ to $10^{-5}M$ , the pH value of the solution decreases from 7 to 5. We know that in acidic solution, $[H_3O^+] > [OH^-]$ , i.e., $[H_3O^+] > OH^-$. Similarly in basic solution $[H_3O^+]<10^{-7}$ . So, we can conclude that acidic solution should have pH value less than 7 and basic solution should have pH value greater than 7.

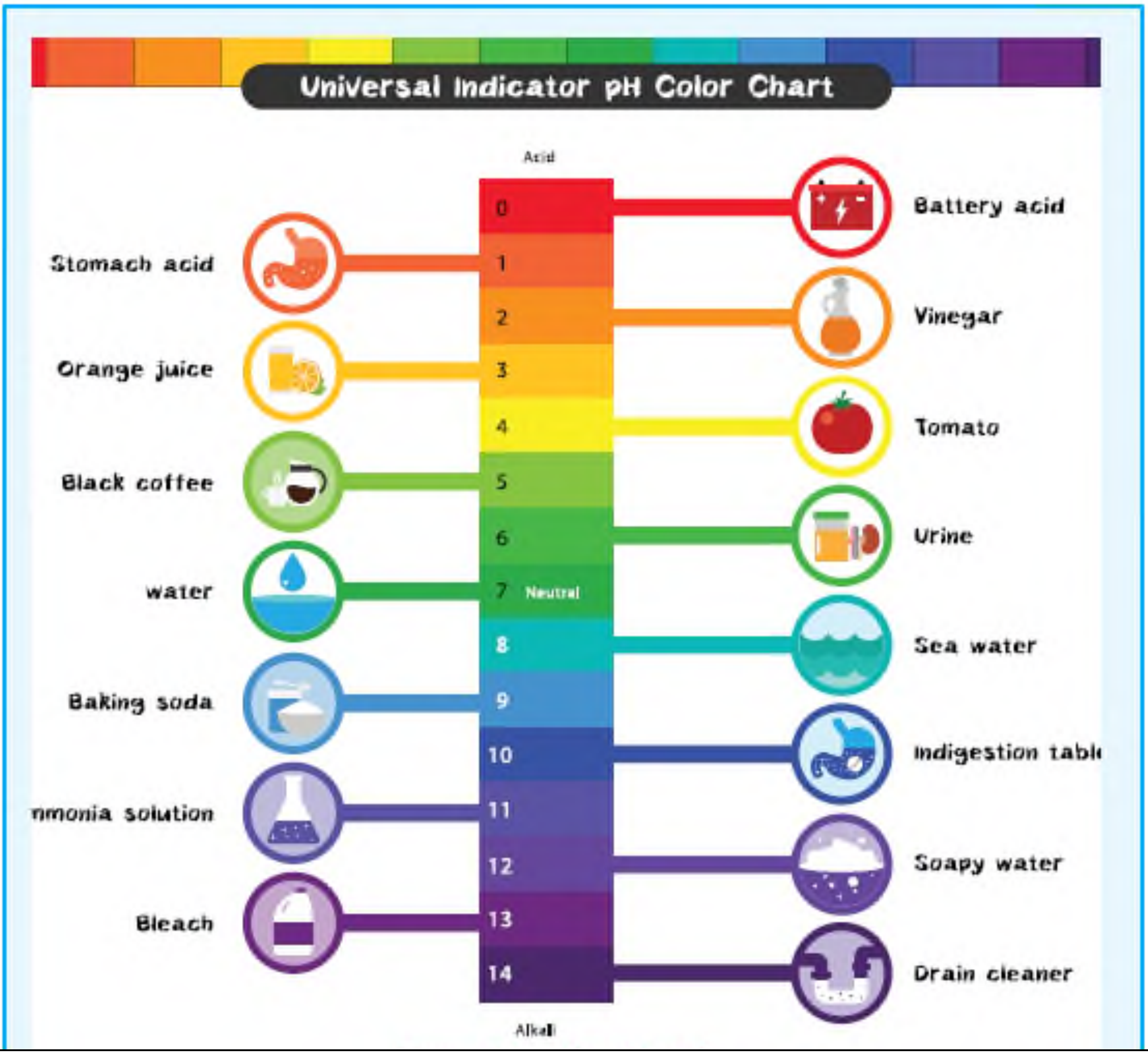


Figure 8.1 The pH scale

Adding equation (8.5) and (8.7)

$pH + pOH = log10[H_3O^+]\ log_{10}[OH^-]$

$= (-log_{10}[H_3O^+]+log_{10}[OH^-])$

$pH+pOH =-log_{10}[H_3O^+][OH^-]$ [Q log a+logb = logab]

We know that $[H_3O^+][OH^-]=K_w$

$pH+pOH= log_{10}K_w$

$pH+pOH=pK_w$.........(8.8)

at $25^0C$, the ionic product of water, $K_w=1X10^{-14}$

$pK_w= - log_{10}10^{-14} = 14log_{10}10$

$= 14$

(8.7) = At $25^0C$, pH + pOH= 14

## 8.5 Ionisation of weak acids

We have already learnt that weak acids are partially dissociated in water and there is an equilibrium between the undissociated acid and its dissociated ions.

Consider the ionisation of a weak monobasic acid HA in water.

$$HA+H_2O \rightleftharpoons H_3O^+A^-$$

Applying law of chemical equilibrium, the equilibrium constant Kc is given by the expression

$$K_C = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \text{……..(8.9)}$$

The square brackets, as usual, represent the concentrations of the respective species in moles per litre.

In dilute solutions, water is present in large excess and hence, its concentration may be taken as constant say K. Further $H_3O^+$ indicates that hydrogen ion is hydrated, for simplicity it may be replaced by $H^+$ . The above equation may then be written as,

$$K_C = \frac{[H^+][A^-]}{[HA]\ X\ k} \text{……..(8.10)}$$

The product of the two constants KC and K gives another constant. Let it be Ka

$$K_a = \frac{[H^+][A^-]}{[HA]} \text{……..(8.11)}$$

The constant Ka is called dissociation constant of the acid. Like other equilibrium constants, $K_a$ also varies only with temperature.

Similarly, for a weak base, the dissociation constant can be written as below.

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \text{……..(8.12)}$$

### 8.5.1 Ostwald's dilution law

Ostwald's dilution law relates the dissociation constant of the weak acid (K ) a with itsdegree of dissociation (α) and the concentration (c). Degree of dissociation (α) is the fractionof the total number of moles of a substance that dissociates at equilibrium.

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{total number of moles}}$$

We shall derive an expression for ostwald's law by considering a weak acid, i.e. acetic acid($CH_3$ COOH) . The dissociation of acetic acid can be represented as

$$CH_3COOH \leftrightharpoons H^+ + CH_3COO^-$$

The dissociation constant of acetic acid is,

$$Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \text{……..(8.13)}$$

| | $CH_3COOH$ | $H^+$ | $CH^3COO^-$ |
|---|---|---|---|
| Initial number of moles | 1 | - | - |
| Degree of dissociation of CH COOH | α | - | - |
| Number of moles at equilibrium | 1-α | α | α |
| Equilibrium concentration | (1-α)C | α C | α C |

Substituting the equilibrium concentration in equation (8.13)

$$K_a = \frac{(\alpha C)\,(\alpha C)}{(1-\alpha)\,C}$$

$$K_a = \frac{\alpha^2 C}{1-\alpha} \text{……..(8.14)}$$

We know that weak acid dissociates only to a very small extent compared to one, α is so small and hence in the denominator (1 - α)≈1. The above expression (8.14) now becomes,

$$K_a = \alpha^2 C$$

$$\alpha^2 = \frac{K_a}{C}$$

$$\alpha = \sqrt{\frac{K_a}{c}} \text{……….(8.15)}$$

Let us consider an acid with Ka value 4 ×10-4 and calculate the degree of dissociation of that acid at two different concentration 1×10-2M and 1×10-4M using the above expression (8.15)

For $1X10^{-2}$M,

$$\alpha = \sqrt{\frac{4 X 10^{-4}}{10^{2}}}$$

$$= \sqrt{4 X 10^{-2}}$$

$$= 2X10^{-1}$$

$$= 0.2$$

For $1X10^{-4}$M acid,

$$\alpha = \sqrt{\frac{4 X 10^{-4}}{10^{-4}}}$$

$$= 2$$

i.e, When the dilution increases by 100 times, (Concentration decreases from $1X10^{-2}$to $1X10^{-4}$M), the dissociation increases by 10 times.

Thus, we can conclude that, when dilution increases, the degree of dissociation of weak electrolyte also increases. This statement is known as Ostwald's dilution Law.

The concentration of $H^+(H_3O^+)$can be calculated using the Ka value as below.

[ H+ ]= αC ..............(8.16) (Refer table)

Equilibrium molar concentration of $[H^+]$ is equal to –C

$$\therefore [H+] = \sqrt{\frac{K_a \quad C}{C}} \qquad [\because \text{equation (8.15)}]$$

$$\sqrt{\frac{K_a C^2}{C}}$$

$$[H^+] = \sqrt{K_a C} \quad \text{……………..(8.17)}$$

Similarly, for a weak base

$$K_b = \alpha^2 C \text{ and } \alpha = \sqrt{\frac{K_b}{C}}$$

$$[OH^-] = \alpha C$$

Or

$$[OH^-] = \sqrt{K_b C} \quad \text{…………………….(8.18)}$$

## 8.6 Common Ion Effect

When a salt of a weak acid is added to the acid itself, the dissociation of the weak acid issuppressed further. For example, the addition of sodium acetate to acetic acid solution leads tothe suppression in the dissociation of acetic acid which is already weakly dissociated. In thiscase, $CH_3COOH$ and $CH_3COONa$ have the common ion,$CH_3COO^-$

Let us analyse why this happens. Acetic acid is a weak acid. It is not completely dissociated in aqueous solution and hence the following equilibrium exists.

$$CH_3COOH(aq) \leftrightharpoons H^+(aq)+CH_3COO^-(aq)$$

However, the added salt, sodium acetate, completely dissociates to produce $Na^+$ and $CH_3COO^-$ ion.

$$CH_3COONa(aq) \rightarrow Na^+ (aq)+CH_3COO^- (aq)$$

Hence, the overall concentration of $CH_3COO^-$ is increased, and the acid dissociation equilibrium is disturbed. We know from Le chatelier's principle that when a stress is applied to a system at equilibrium, the system adjusts itself to nullify the effect produced by that stress. So, inorder to maintain the equilibrium, the excess $CH_3COO^-$ ions combines with $H^+$ions toproduce much more unionized $CH_3COOH$ i.e, the equilibrium will shift towards the left. Inother words, the dissociation of $CH_3COOH$ is suppressed. Thus, the dissociation of a weak acid (CH3COOH) is suppressed in the presence of a salt (CH3COONa) containing an ioncommon to the weak electrolyte. It is called the common ion effect.

## 8.7 Buffer Solution

Do you know that our blood maintains a constant pH, irrespective of a number of cellularacid – base reactions. Is it possible to maintain a constant hydronium ion concentration insuch reactions? Yes, it is possible due to buffer action.

Buffer is a solution which consists of a mixture of a weak acid and its conjugate base (or) a weak base and its conjugate acid. This buffer solution resists drastic changes in its pH upon addition of a small quantities of acids (or) bases, and this ability is called buffer action. The buffer containing carbonic acid ($H_2CO$ 3) and its conjugate base $H_3CO^-$ is present in our blood. There are two types of buffer solutions.

1. Acidic buffer solution : a solution containing a weak acid and its salt.

Example : solution containing acetic acid and sodium acetate

2. Basic buffer solution : a solution containing a weak base and its salt.

Example : Solution containing NH4OH and $NH_4Cl$

### 8.7.1 Buffer action

To resist changes in its pH on the addition of an acid (or) a base, the buffer solution should contain both acidic as well as basic components so as to neutralize the effect of added acid (or) base and at the same time, these components should not consume each other.

Let us explain the buffer action in a solution containing $CH_3COOH$ and $CH_3COONa$
The dissociation of the buffer components occurs as below.

$$CH3COOH (aq) \leftrightharpoons CH3 - COO(aq) + H3O+(aq)$$

$$CH3COONa(s) \xrightarrow{H_2O(1)} CH3 – COO^-(aq) + Na^+(aq)$$

If an acid is added to this mixture, it will be consumed by the conjugate base $CH_3COO^-$ to form the undissociated weak acid i.e, the increase in the concentration of $H^+$ does not reduce the pH significantly.

$$CH3COO^- \ (aq) + H^+ \ (aq) \longrightarrow CH3COOH \ (aq)$$

If a base is added, it will be neutralized by $H3O^+$, and the acetic acid is dissociated to maintain the equlibrium. Hence the pH is not significantly altered.

$$OH^- \ (aq) + H_3O^+ ( \ aq) \longrightarrow H2O \ (1)$$

$H_2O(1)$

$$CH3COOH(aq) \leftrightharpoons CH3 - COO^-(aq+H_3O^+(aq)$$

$$OH^-(aq) + CH_3COOH( \ aq) \longrightarrow CH_3COO^-(aq) + H2O \ (1)$$

These neutralization reactions are identical to those reactions that we have already discussed in common ion effect.

Let us analyse the effect of the addition of 0.01 mol of solid sodium hydroxide to one litre of a buffer solution containing 0.8 M $CH_3COOH$ and 0.8 M $CH_3COONa$. Assume that the volume change due to the addition of NaOH is negligible. (Given: Ka for $CH_3COOH$ is1.8 X$10^{-5}$ ).

$H_2O$

$CH_3 \rightleftarrows COOH(aq) \qquad CH_3COO^-$

$(aq)+H^+(aq)$

$0.8\alpha$

$\alpha \qquad \alpha \qquad \longrightarrow$

$H_2O$

$CH_3COONa(aq) \qquad CH_3COO^- \ (aq)+Na^+(aq)$

$0.8 \qquad 0.8 \qquad 0.8$

The dissociation constant for $CH_3COOH$ is given by

$$K = \frac{[CH_3COO^-][H+]}{[CH_3COOH]}$$

$$H^+ = K_a = \frac{[CH_3COOH]}{[CH_3COO^-]}$$

The above expression shows that the concentration of $H^+$ is directly proportional to

$$\frac{[CH_3COOH]}{[CH_3COO^-]}$$

Let the degree of dissociation of CH3COOH α be then,

$[CH_3COOH]=0.8- \alpha$ and $[CH_3COO^-]= \alpha +0.8$

$$\therefore H^+ = K_a \frac{[0.8 - \alpha]}{[0.8 + \alpha]}$$

$\alpha<<0.8, \qquad 0.8-\alpha = 0.8$ and $0.8+\alpha = 0.8$

$$[H^+] = \frac{K_a(0.8)}{(0.8)} \Longrightarrow H^+ = K_a$$

Given that

$K_a$ for $CH_3COOH$ is $1.8 \times 10^{-5}$

$\therefore [H+] = 1.8 \times 10^{-5}$ ; $-\log(1.8 \times 10^{-5})$

$= 5 - \log 1.8$

$= 5 - 0.26$

Ph = 4.74

**Calculation of pH after adding 0.01 mol NaOH to 1 litre of buffer.**

$$CH_3\text{-}COOH(aq) \leftrightharpoons CH_3COO^-(aq) + H^+(aq)$$

$0.8\,\alpha \qquad \alpha \qquad \alpha$

$$CH_3COONa(aq) \longrightarrow CH_3COO^-(aq) + Na^+(aq)$$

$0.8 \qquad 0.8 \qquad 0.8$

$$CH_3COOH + OH^-(aq) \longrightarrow CH_3COO^-(aq) + H_2O\,(l)$$

$\therefore [CH_3COOH] = 0.8 - \alpha - 0.01 = 0.79 - \alpha$

$[CH_3COO^-] = \alpha + 0.8 + 0.01 = 0.81 + \alpha \qquad \alpha << 0.8;$

$0.79 - \alpha = 0.79$ and $0.81 + \alpha = 0.81$

$$\therefore [H^+] = (1.8 \times 10^{-5}) \times \frac{0.79}{0.81}$$

$[H+] = 1.76 \times 10^{-5}$

$\therefore pH = -LOG\,(1.76 \times 10^{-5})$

$= 5 - LOG\,1.76$

$= 5 - 0.25$

pH = 4.75

The addition of a strong base (0.01 M NaOH) increased the pH only slightly ie., from 4.74 to 4.75 . So, the buffer action is verified.

### 8.7.2 Buffer capacity and buffer index

The buffering ability of a solution can be measured in terms of buffer capacity. Vanslyke introduced a quantity called buffer index, â , as a quantitative measure of the buffer capacity. It is defined as the number of gram equivalents of acid or base added to 1 litre of the buffer solution to change its pH by unity.

$$\beta = \frac{dB}{d(pH)} \qquad \ldots\ldots\ldots\ldots.(8.19)$$

Here,

dB = number of gram equivalents of acid / base added to one litre of buffer solution.

d(pH) = The change in the pH after the addition of acid / base.

### 8.7.3 Henderson – Hasselbalch equation

We have already learnt that the concentration of hydronium ion in an acidic buffer solution depends on the ratio of the concentration of the weak acid to the concentration of its conjugate base present in the solution i.e.,

$$[H_3O^+] = K_a \frac{[acid]_{eq}}{[base]aq} \qquad \ldots\ldots\ldots\ldots\ldots..(8.20)$$

The weak acid is dissociated only to a small extent. Moreover, due to common ion effect, the dissociation is further suppressed and hence the equilibrium concentration of the acid is nearly equal to the initial concentration of the unionised acid. Similarly, the concentration of the conjugate base is nearly equal to the initial concentration of the added salt.

$$[H_3O^+] = K_a \frac{[\text{acid}]}{[\text{salt}]} \quad \ldots\ldots\ldots\ldots\ldots.(8.21)$$

Here [acid] and [salt] represent the initial concentration of the acid and salt, respectively used to prepare the buffer solution

Taking logarithm on both sides of the equation

$$\log [H_3O^+] = \log K_a + \log \frac{[\text{acid}]}{[\text{salt}]} \quad \ldots\ldots\ldots\ldots\ldots.(8.22)$$

reverse the sign on both sides

$$-\log [H_3O^+] = -\log K_a - \log \frac{[\text{acid}]}{[\text{salt}]} \quad \ldots\ldots\ldots\ldots\ldots.(8.23)$$

We know that

$$pH = -\log [H_3O^+] \text{ and } pK_a = -\log K_a$$

$$\Rightarrow \quad pH = pK_a - \log \frac{[\text{acid}]}{[\text{salt}]} \quad \ldots\ldots\ldots\ldots\ldots.(8.24)$$

$$\Rightarrow \quad pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]} \quad \ldots\ldots\ldots\ldots\ldots.(8.25)$$

Similarly for a basic buffer, $pOH = pK_b + \log \frac{[\text{salt}]}{[\text{base}]}$

## 8.8 Salt Hydrolysis

When an acid reacts with a base, a salt and water are formed and the reaction is called neutralization. Salts completely dissociate in aqueous solutions to give their constituent ions.

The ions so produced are hydrated in water. In certain cases, the cation, anion or both react with water and the reaction is called salt hydrolysis.

### 8.8.1 Salts of strong acid and a strong base

Let us consider the reaction between NaOH and nitric acid to give sodium nitrate and water.

$$NaOH\,(aq) + CH_3COOH(aq) \leftrightharpoons CH_3COONa(aq) + H_2O(l)$$

In aqueous solution, $CH_3COONa$ is completely dissociated as below

$$CH_3COONa\,(aq) \longrightarrow CH_3COO^-(aq) + Na^+(aq)$$

$CH_3COO^-$ is a conjugate base of the weak acid $CH_3COOH$ and it has a tendency to react with $H^+$ from water to produce unionised acid .

There is no such tendency for $Na^+$ to react with $OH^-$ .

$CH_3COO^-(aq) + H_2O(l) \leftrightharpoons CH_3COOH\ (aq) + OH\ (aq)$ and therefore $[OH^-]>[H^+]$, insuch cases, the solution is basic due to hydrolysis and the pH is greater than 7.

Let us find a relation between the equilibrium constant for the hydrolysis reaction (hydrolysis constant) and the dissociation constant of the acid.

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-][H_2O]}$$

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \quad \ldots\ldots\ldots..(1)$$

$$CH_3COOH\ (aq) \leftrightharpoons CH_3COO^-\ (aq) + H^+(aq)$$

$$K_a = \frac{[CH_3COOH][H^+]}{[CH_3COOH]} \quad \ldots\ldots\ldots..(2)$$

(1) X (2)

$K_h.K_a = [H^+][OH^-]$

we know that $[H^+][OH^-] = K_w$

$K_h.K_a = K_w$

Kh value in terms of degree of hydrolysis (h) and the concentration of salt (C) for the equilibrium can be obtained as in the case of ostwald's dilution law. $K = h^2C$. and i.e $[OH^-] = \sqrt{K_h .C}$

pH of salt solution in terms of Ka and the concentration of the electrolyte.

$pH + pOH = 14$

$pH = 14 - p\ OH = 14 - \{-\log [OH^-]\}$

$= 14 + \log [OH^-]$

$\therefore pH = 14 + \log (K_hC)^{½}$

$$pH = 14 + \log \left(\frac{KwC}{K_a}\right)^{½}$$

$pH = 14 + ( ½ \log K_w + ½ \log C – ½ \log K_a )$     $[ K_w = 10_{-14}$

$pH = 14-7 + ½ \log C + ½ pK_a$     $½ \log Kw = ½ X \log 10^{-14} = -14/ 2 (1) = -7$

$pH = 7 + ½ pK_a + ½ \log C.$     $- \log Ka = pK_a ]$

8.8.3 Hydrolysis of salt of strong acid and weak base

Let us consider the reactions between a strong acid, HCl, and a weak base, $NH_4OH$ 4 , to produce a salt, $NH_4Cl$ , and water

$$HCl\ (aq) + NH_4OH\ (aq) \leftrightharpoons NH_4Cl(aq) + H_2O(l)$$

$$NH_4Cl(aq) \longrightarrow NH_4^+ + Cl^-(aq)$$

$NH_4^+$ is a strong conjugate acid of the weak base $NH_4OH$ and it has a tendency to react with $OH^-$ from water to produce unionised $NH_4OH$ shown below.

$$NH_4^+(aq) + H_2O(l) \leftrightharpoons NH_4OH\ (aq) + H^+(aq)$$

There is no such tendency shown by $Cl^-$ and therefore $[H^+] > [OH^-]$ the solution is acidic and the pH is less than 7.

As discussed in the salt hydrolysis of strong base and weak acid. In this case also, we can establish a relationship between the Kh and Kb as

$$K_h . K_b = K_w$$

Let us calculate the $K_h$ value in terms of degree of hydrolysis (h) and the concentration of salt

$$K_h = h^2C \quad \text{and } [H^+] = \sqrt{K_h . C}$$

$$[H^+] = \sqrt{K_w / K_b . C}$$

$$Ph = - \log [H^+]$$

$$pH = - \log \left( \frac{K_w . C}{K_b} \right)^{½}$$

$$= - ½ \log K_w - ½ \log C + ½ \log K_b$$

$$pH = 7 - ½ pK_b – ½ \log C.$$

### 8.8.4 Hydrolysis of Salt of weak acid and weak base.

Let us consider the hydrolysis of ammonium acetate.

$$CH_3COONH_4(aq) \longrightarrow CH_3COO^- (aq) + NH_4^+ (aq)$$

In this case, both the cation ($NH_4^+$) and anion ($CH_3COO^-$) have the tendency to react with water

$$CH_3COO^- + H_2O \leftrightharpoons CH_3COOH + OH^-$$

$$NH_4^+ + H_2O \leftrightharpoons NH_4OH + H^+$$

The nature of the solution depends on the strength of acid (or) base i.e, if $K_a > K_b$ ; then the solution is acidic and pH < 7, if $K_a < K_b$ ; then the solution is basic and pH < 7, if $K_a = K_b$ a b; then the solution is neutral.

The relation between the dissociation constant (K ,K a b) and the hydrolysis constant is given by the following expression.

$$K_a . K_b . K_h = K_w$$

### pH of the solution

pH of the solution can be calculated using the following expression,

$pH = 7 + ½ pK_a – ½ pK_b$ .

### 8.9 Solubility Product

We have come across many precipitation reactions in inorganic qualitative analysis. For example, dil HCl is used to precipitate $Pb^{2+}$ ions as PbCl2 which is sparingly soluble in water. Kidney stones are developed over a period of time due to the precipitation of $Ca^{2+}$ (as calcium oxalate etc…). To understand the precipitation, let us consider the solubility equilibria that exist between the undissociated sparingly soluble salt and its constituent ions in solution.

For a general salt $X_m Y_n$ ;

$$X_m Y_n (s) \overset{H_2O}{\rightleftarrows} mX^{n+} (aq) + nY^{n-} (aq)$$

The equilibrium constant for the above is

$$K = \frac{[X^{n+}]^m [Y^{m-}]^n}{[X_m Y_m]}$$

In solubility equilibria, the equilibrium constant is referred as solubility product constant (or) Solubility product.

In such heterogeneous equilibria, the concentration of the solid is a constant and is omitted in the above expression

$$K_{sp} = [X^{n+}]^m [Y^{m-}]^n$$

The solubility product of a compound is defined as the product of the molar concentration of the constituent ions, each raised to the power of its stoichiometric co – efficient in a balanced equilibrium equation.

Solubility product finds useful to decide whether an ionic compound gets precipitated when solution that contain the constituent ions are mixed.

When the product of molar concentration of the constituent ions i.e., ionic product, exceeds the solubility product then the compound gets precipitated.

The expression for the solubility product and the ionic product appears to be the same but in the solubility product expression, the molar concentration represents the equilibrium concentration and in ionic product, the initial concentration (or) concentration at a given time 't' is used.

In general we can summarise as,

Ionic product > Ksp , precipitation will occur and the solution is super saturated.

Ionic product < Ksp , no precipitation and the solution is unsaturated.

Ionic product = Ksp , equilibrium exist and the solution is saturated.

### 8.9.1 Determination of solubility product from molar solubility

Solubility can be calculated from the molar solubility i.e., the maximum number of moles of solute that can be dissolved in one litre of the solution.

For a solute $X_m Y_n$ ,

$$X_m Y_n (s) \leftrightharpoons mX^{n+}(aq) + nY^{m-}(aq)$$

From the above stoichiometrically balanced equation we have come to know that 1 mole of $X_m Y_n$ (s) dissociated to furnish 'm' moles of and 'n' moles of $Y^{m-}$ if 's' is molar solubility of $X_m Y_n$, then

$[X^{n+}]=ms$ and $[Y^{n-}]=ns$

$\therefore K_{sp} = [X^{n+}]^m [Y^{m-}]^n$

$K_{sp} = [ms]^m [ns]^n$

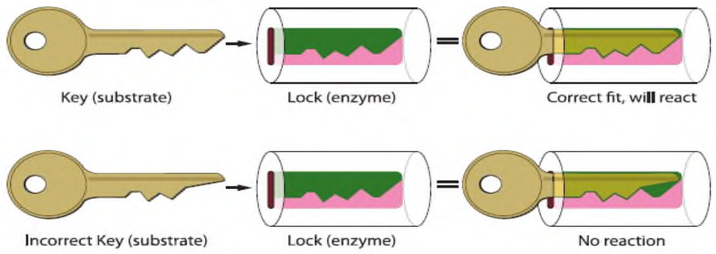
$K_{sp} = [m]^m [n]^n (s)^{m+n}$

Mechanism of enzyme action:

Enzymes are biocatalysts that catalyse a specific biochemical reaction. They generally activate the reaction by reducing the activation energy by stabilising the transition state. In a typical reaction enzyme E bind with the substrate molecule reversibly to produce an enzyme substrate complex. During this stage the substrate is converted into product and the enzyme becomes free and is ready to bind to another substrate molecule. More detailed mechanism is discussed in the unit XI surface chemistry.

$$\underset{\text{Enzyme}}{E} + \underset{\text{Substate}}{S} \rightarrow \underset{\text{Enzyme - substrate complex}}{[ES]}$$

$$[ES] \rightarrow E+P$$



Vitamins:

Vitamins are small organic compounds that cannot be synthesised by our body but are essential for certain function. Hence, it must be obtained through diet. The requirements of these compounds are not high, but their deficiency causes or excess can cause diseases. Unlike carbohydrates and lipids, they are energy sources. Each vitamin has a specific function in the living system, mostly as co enzymes.

The name ‘Vitamin’ is derived from ‘vital amines’, referring to the vitamins identified earlier are which are amino compounds. Vitamins are essential for the normal growth and maintenance of our health.

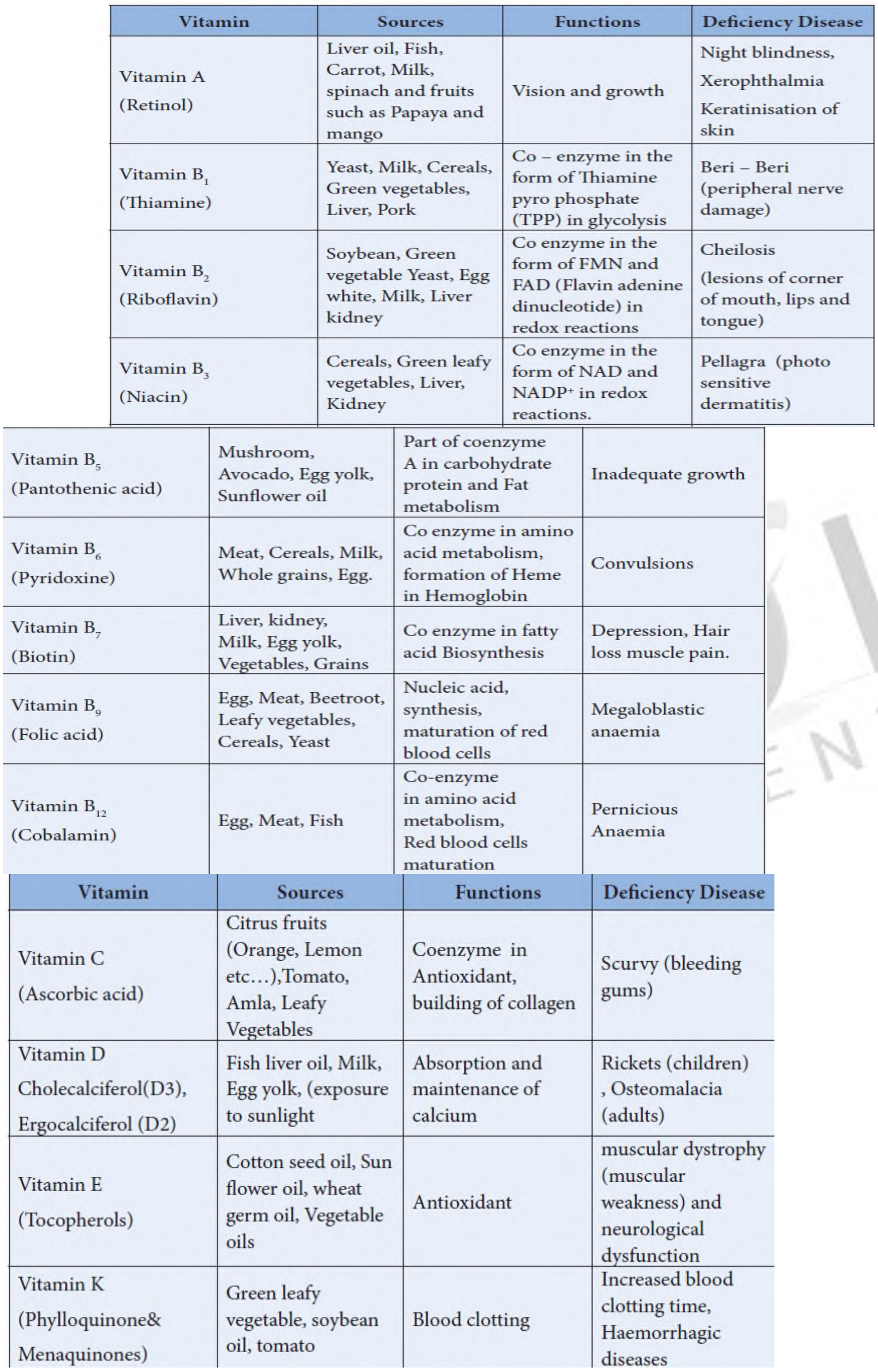
Classification of vitamins

Vitamins are classified into two groups based on their solubility in water and in fat.

Fat soluble vitamins: These vitamins absorbed best when taken with fatty food and are stored in fatty tissues and livers. These vitamins do not dissolve in water. Hence they are called fat soluble vitamins. Vitamin A, D, E & K are fat-soluble vitamins.

Water soluble vitamins: Vitamins B (B1, B2, B3, B5, B6, B7, B9 & B12) and C are readily soluble in water. On the contrary to fat soluble vitamins, these can’t be stored. The excess vitamins present will be excreted through urine and are not stored in our body. Hence, these twovitamins should be supplied regularly to our body. The missing numbers in B vitamins are once considered as vitamins but are no longer considered as such, and the numbers that were assigned to them now form the gaps.

Table 14.2: Vitamins, their Sources, Functions and their Deficiency disease



| Vitamin | Sources | Functions | Deficiency Disease |
|---|---|---|---|
| Vitamin A (Retinol) | Liver oil, Fish, Carrot, Milk, spinach and fruits such as Papaya and mango | Vision and growth | Night blindness,<br>Xerophthalmia<br>Keratinisation of skin |
| Vitamin B$_1$ (Thiamine) | Yeast, Milk, Cereals, Green vegetables, Liver, Pork | Co – enzyme in the form of Thiamine pyro phosphate (TPP) in glycolysis | Beri – Beri (peripheral nerve damage) |
| Vitamin B$_2$ (Riboflavin) | Soybean, Green vegetable Yeast, Egg white, Milk, Liver kidney | Co enzyme in the form of FMN and FAD (Flavin adenine dinucleotide) in redox reactions | Cheilosis<br>(lesions of corner of mouth, lips and tongue) |
| Vitamin B$_3$ (Niacin) | Cereals, Green leafy vegetables, Liver, Kidney | Co enzyme in the form of NAD and NADP$^+$ in redox reactions. | Pellagra (photo sensitive dermatitis) |
| Vitamin B$_5$ (Pantothenic acid) | Mushroom, Avocado, Egg yolk, Sunflower oil | Part of coenzyme A in carbohydrate protein and Fat metabolism | Inadequate growth |
| Vitamin B$_6$ (Pyridoxine) | Meat, Cereals, Milk, Whole grains, Egg. | Co enzyme in amino acid metabolism, formation of Heme in Hemoglobin | Convulsions |
| Vitamin B$_7$ (Biotin) | Liver, kidney, Milk, Egg yolk, Vegetables, Grains | Co enzyme in fatty acid Biosynthesis | Depression, Hair loss muscle pain. |
| Vitamin B$_9$ (Folic acid) | Egg, Meat, Beetroot, Leafy vegetables, Cereals, Yeast | Nucleic acid, synthesis, maturation of red blood cells | Megaloblastic anaemia |
| Vitamin B$_{12}$ (Cobalamin) | Egg, Meat, Fish | Co-enzyme in amino acid metabolism, Red blood cells maturation | Pernicious Anaemia |
| Vitamin C (Ascorbic acid) | Citrus fruits (Orange, Lemon etc…),Tomato, Amla, Leafy Vegetables | Coenzyme in Antioxidant, building of collagen | Scurvy (bleeding gums) |
| Vitamin D Cholecalciferol(D3), Ergocalciferol (D2) | Fish liver oil, Milk, Egg yolk, (exposure to sunlight | Absorption and maintenance of calcium | Rickets (children) , Osteomalacia (adults) |
| Vitamin E (Tocopherols) | Cotton seed oil, Sun flower oil, wheat germ oil, Vegetable oils | Antioxidant | muscular dystrophy (muscular weakness) and neurological dysfunction |
| Vitamin K (Phylloquinone& Menaquinones) | Green leafy vegetable, soybean oil, tomato | Blood clotting | Increased blood clotting time, Haemorrhagic diseases |

Nucleic acids

The inherent characteristics of each and every species are transmitted from one generation to the next. It has been observed that the particles in nucleus of the cell are responsible for the transmission of these characteristics. They are called chromosomes and are made up of proteins and another type of biomolecules called nucleic acids. They are mainly of two type's nucleic acids, the deoxyribonucleic acid (DNA) and ribonucleic acid (RNA). They are the molecular repositories that carry genetic information in every organism.

Composition and structure of nucleic acids

Nucleic acids are biopolymers of nucleotides. Controlled hydrolysis of DNA and RNA yields three components namely a nitrogenous base, a pentose sugar and phosphate group.

Nitrogen base

These are nitrogen containing organic compounds which are derivatives of two parent compounds, pyrimidine and purine. Both DNA and RNA have two major purine bases, adenine (A) and guanine (G). In both DNA and RNA, one of the pyrimidines is cytosine (C), but the second pyrimidine is thymine (T) in DNA and uracil (U) in RNA.

Double strand helix structure of DNA

In early 1950s, Rosalind Franklin and Maurice Wilkins used X-ray diffraction to unravel the structure of DNA. The DNA fibers produced a characteristic diffraction pattern.

The central X shaped pattern indicates a helix, whereas the
heavy black arcs at the top and bottom of the diffraction pattern reveal the spacing of the stacked bases.

The structure elucidation of DNA by Watson and Crick in 1953 was a momentous event in science. They postulated a 3-dimensional model of DNA structure which consisted of two antiparallel helical DNA chains wound around the same axis to form a right-handed double helix.

The hydrophilic backbones of alternating deoxyribose and phosphate groups are on the outside of the double helix, facing the surrounding water.

The purine and pyrimidine bases of both strands are stacked inside the double helix, with their hydrophobic and ring structures very close together and perpendicular to the long axis, thereby reducing the repulsions between the charged phosphate groups. The off set pairing of the two strands creates a major groove and minor groove on the surface of the duplex.

The model revealed that, there are 10.5 base pairs (36 A) per turn of the helix and 3.4 A between the stacked bases. They also found that each base is hydrogen bonded to a base in opposite strand to form a planar base pair.

Two hydrogen bonds are formed between adenine and thymine and three hydrogen bonds are formed between guanine and cytosine. Other pairing tends to destabilize the double helical structure. This specific association of the two chains of the double helix is known as
complementary base pairing. The DNA double helix or duplex is held together by two forces,

a) Hydrogen bonding between complementary base pairs

b) Base-stacking interactions The complementary between the DNA strands is attributable to the hydrogen bonding between base pairs but the base stacking interactions are largely non-specific, make the major contribution to the stability of the double helix.

Types of RNA molecules

Ribonucleic acids are similar to DNA. Cells contain up to eight times high quantity of RNA than DNA. RNA is found in large amount in the cytoplasm and a lesser amount in the nucleus. In the cytoplasm it is mainly found in ribosomes and in the nucleus, it is found in nucleolus. RNA molecules are classified according to their structure and function into three major

types

i. Ribosomal RNA (rRNA)
ii. Messenger RNA (mRNA)
iii. Transfer RNA (tRNA)

rRNA

rRNA is mainly found in cytoplasm and in ribosomes, which contain 60% RNA and 40% protein. Ribosomes are the sites at which protein synthesis takes place.

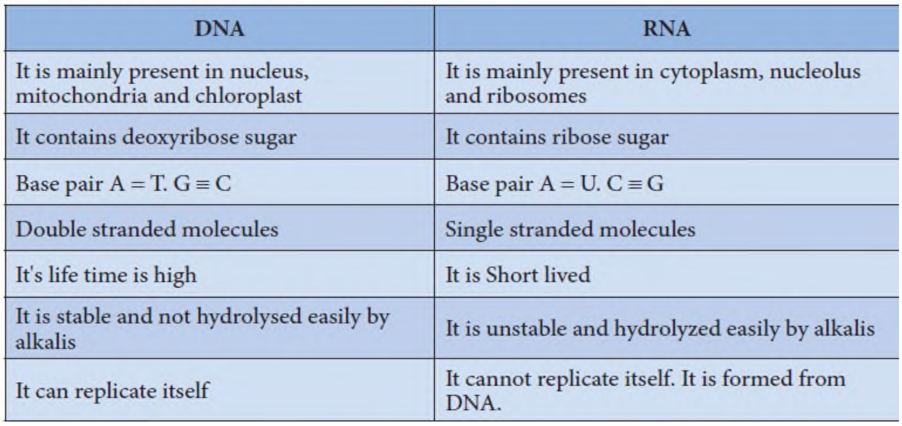
tRNA

tRNA molecules have lowest molecular weight of all nucleic acids. They consist of 73 – 94 nucleotides in a single chain. The function of tRNA is to carry amino acids to the sites of protein synthesis on ribosomes.

mRNA

mRNA is present in small quantity and very short lived. They are single stranded, and their synthesis takes place on DNA. The synthesis of mRNA from DNA strand is called transcription. mRNA carries genetic information from DNA to the ribosomes for protein synthesis

Table 14.3 Difference between DNA and RNA



| DNA | RNA |
|---|---|
| It is mainly present in nucleus, mitochondria and chloroplast | It is mainly present in cytoplasm, nucleolus and ribosomes |
| It contains deoxyribose sugar | It contains ribose sugar |
| Base pair A = T. G ≡ C | Base pair A = U. C ≡ G |
| Double stranded molecules | Single stranded molecules |
| It's life time is high | It is Short lived |
| It is stable and not hydrolysed easily by alkalis | It is unstable and hydrolyzed easily by alkalis |
| It can replicate itself | It cannot replicate itself. It is formed from DNA. |

## DNA finger printing

Traditionally, one of the most accurate methods for placing an individual at the scene of a crime has been a fingerprint. With the advent of recombinant DNA technology, a more powerful tool is now available: DNA fingerprinting (also called DNA typing or DNA profiling). It was first invented by Professor Sir Alec Jeffrey sin 1984. The DNA finger print is unique for every person and can be extracted from traces of samples from blood, saliva, hair etc…By using this method we can detect the individual specific variation in human DNA.

In this method, the extracted DNA is cut at specific points along the strand with restriction enzymes resulting in the formation of DNA fragments of varying lengths which were analysed by technique called gel electrophoresis. This method separates the fragments based on their size. The gel containing the DNA fragments are then transferred to a nylon sheet using a technique called blotting. Then, the fragments will undergo autoradiography in which they were exposed to DNA probes (pieces of synthetic DNA that were made radioactive and that bound to the fragments). A piece of X-ray film was then exposed to the fragments, and a dark mark was produced at any point where a radioactive probe had become attached. The resultant pattern of marks could then be compared with other samples. DNA fingerprinting is based on slight sequence differences (usually single base-pair changes) between individuals. These methods are proving decisive in court cases worldwide.

## Food additives:

Have you ever noticed the ingredients that is printed on the cover of the packed food materials such as biscuits, chocolates etc...You might have noticed that emulsifiers such as 322, 472E, dough conditioners 223 etc… are used in the preparation, in addition to the main ingredients such as wheat flour, edible oil, sugar, milk solid etc… Do you think that thesesubstances are necessary? Yes. These substances enhance the nutritive, sensory and practical value of the food. They also increase the shelf life of food. The substances which are not naturally a part of the food and added to improve the quality of food are called food additives.

Important categories of food additives

- Aroma compounds
- Food colours
- Preservatives
- Stabilizers
- Artificial Sweeteners
- Antioxidants
- Buffering substances
- Vitamins and minerals

Advantages of food additives:

1. Uses of preservatives reduce the product spoilage and extend the shelf-life of food
2. Addition of vitamins and minerals reduces the mall nutrient
3. Flavouring agents enhance the aroma of the food
4. Antioxidants prevent the formation of potentially toxic oxidation products of lipids and other food constituents

## Preservatives:

Preservatives are capable of inhibiting, retarding or arresting the process of fermentation, acidification or other decomposition of food by growth of microorganisms. Organic acids such as benzoic acid, sorbic acid and their salts are potent inhibitors of a number of fungi, yeast andbacteria. Alkyl esters of hydroxy benzoic acid are very effective in less acidic conditions. Acetic acid is used mainly as a preservative for the preparation of pickles and for preserved vegetables. Sodium metasulphite is used as preservatives for fresh vegetables and fruits. Sucrose esters with palmitic and steric acid are used as emulsifiers. In addition that some organic acids and their salts are used as preservatives. In addition to chemical treatment, physical methods suchas heat treatment (pasteurisation and sterilisations), cold treatment (chilling and freezing) drying (dehydration) and irradiation are used to preserve food.

Antioxidants:

Antioxidants are substances which retard the oxidative deteriorations of food. Food containing fats and oils is easily oxidised and turn rancid. To prevent the oxidation of the fats and oils, chemical BHT(butylhydroxy toluene), BHA(Butylated hydroxy anisole) are addedas food additives. They are generally called antioxidants. These materials readily undergo oxidation by reacting with free radicals generated by the oxidation of oils, thereby stop the chain reaction of oxidation of food. Sulphur dioxide and sulphites are also used as foodadditives. They act as anti-microbial agents, antioxidants and enzyme inhibitors.

Sugar Substituents:

Those compounds that are used like sugars (glucose, sucrose) for sweetening, but are metabolised without the influence of insulin are called sugar substituents. Eg. Sorbitol, Xylitol,

Mannitol.

Artificial sweetening agents:

Synthetic compounds which imprint a sweet sensation and possess no or negligible nutritional value are called artificial sweeteners. Eg. Saccharin, Aspartame, sucralose, alitame etc…