Lecture 1

Atomic Structure

Man has known the fact that matter is composed of very very small particles since ancient times. It is generally accepted that the concept that matter is discontinuous and composed of tiny particles was first given by the Greek philosophers of the fifth century BC, Leucippos and Democritos. It is notable that Plato and Aristotle did not believe in the existence of atoms and regarded the matter as continuous. Later in 100 BC a Roman poet Lucretius illustrated the idea of atom by his poetry. The word atom is from Greek words '*a*' meaning 'not' and '*tomos*' meaning divisible. Thus, the meaning of atom is the particle that is indivisible.

In 1808, John Dalton (1766-1844), an English schoolteacher put forward the concept of atom on the scientific grounds. He proposed that the elements of atoms that are indivisible.

Today, the atom is defined as the smallest particle of an element that can enter into chemical reactions.

Atom is not indivisible. It is, in fact, a tiny *organized system* consisting of smaller particles. These smaller particles that make up the atom are called subatomic particles. Subatomic particles of fundamental importance are electrons, protons and neutrons. These particles combine together in varying number to form atoms of different elements.

The number of protons in its atoms is the characteristic property of an element. All the atoms of an element have the same number of protons. The atoms of different elements have different number of protons. A neutral atom has as many electrons as protons. Number of neutrons is not fixed. Generally, it is equal to the number of protons in the lighter atoms, and much higher than the number of protons in the heavier atoms. Atoms of the same element can have different number of neutrons. Such atoms are called isotopes. Most elements have two or more isotopes.

DISCOVERY OF SUBATOMIC PARTICLES

Now, the question is how were electrons, protons, and neutrons discovered? There are a number of experiments that ultimately led to the discovery of these particles and their arrangement in the atom. These experiments include:

- Passage of electricity through solutions
- Discharge tube experiments
- Radioactivity
- Chadwick's experiment
- Spectroscopic studies

PASSAGE OF ELECTRICITY THROUGH SOLUTION –ELECTROLYSIS

There are numerous substances that pass electricity in solution or in their molten state. They are called electrolytes, and the process is called electrolysis. Electrolysis was thoroughly studied by an English scientist Michael Faraday (1791-1867), who in 1832-1833 found out the relationship between the quantity of electricity passed through the solution and the quantity of matter deposited at the electrodes as a result of the passage of electricity, and put forward his two famous laws.

Faraday's experimental results led George John Stone Stone Stoney in 1874 to conclude that electricity like matter is discontinuous and consists of particles. In 1891, he gave the name *electron* to this particle of electricity. (Electron is a Greek word for 'amber' which is electrified when rubbed with wool).

Discharge Tube Experiments

(Crookes tube Experiments)

Discharge tube experiments provided strong evidence for the existence of subatomic particles. A discharge tube is a glass tube having two electrodes sealed in at each end. It is connected to a high voltage battery to provide required voltage and to a vacuum pump to evacuate air or gas from the tube.

Since William Crookes, a British physicist, was the first of several scientists to construct discharge tubes, these are also known as Crookes tubes.

Working: At ordinary pressure, electricity does not pass through the tube since gases are non-conductor of electricity. As the gas or air from the tube is gradually evacuated with the vacuum pump, pressure decreases in the tube; a number of interesting phenomena are observed one after the other.

When the pressure is reduced to a very small value, around 0.01-0.001 torr, an electric discharge takes place producing a uniform glow inside the tube. Experiments have shown that it is due to a radiation emitted from the cathode, which travels towards the anode. Because the rays are emitted from cathode they are given the name cathode rays. Now the question is what are these cathode rays? The cathode rays are the streams of electrons emitted from the cathode. All electrons have the same charge and mass; they all are identical.

CONCLUSION

All atoms contain smaller particles called electrons. All electrons are identical. An electron is a negatively charged particle. Its charge is -1.6×10^{-19} coulombs. An electron is an extremely small material particle with a mass of 9.1×10^{-28} grams.

DISCOVERY OF PROTON

In 1886, E. Goldstein, a German physicist discovered that in addition to cathode rays, another type of rays is also produced in the discharge tube which travel in the direction opposite to that of cathode rays. The rays were given the name canal rays as they passed through the canals of the cathode. These rays were made up of positively charged particles. These particles are formed due to the *ionization* of the atoms or molecules of the gas present in the tube. In the discharge tube, cathode rays, the electrons, collide with the atoms or molecules of the gas in the tube and knock out one or more electrons from these atoms or molecules leaving them with a positive charge. When an atom or molecule loses one or more of its electrons, it acquires a net positive charge equal to the number of electrons lost. For example, hydrogen and helium may produce H^{+2} and He^{+} ions. They may also produce H^{+} and He^{2+} ions.

Thus, positive rays are the stream of positive ions of the gas present in the tube that are produced due to the ionization of their atoms or molecules.

Out of all positive ions obtained from different gases, the lightest ion was that of hydrogen. This ion, H^{+}, was named as *proton* (Greek *protos*, ‘first’) by Rutherford in 1920. It carries a charge equal to that of an electron but opposite in sign. The ions produced from all gases in the discharge tube have been found to have charge that is integral multiple of the charge of a proton (H^{+} ion). It shows that atoms contain one or more positively charged particles, the protons.

J.J. THOMSON’S MODEL OF ATOM

By the end of the nineteenth century it became all clear that atoms consist of negatively charged electrons and a positively charged part, but it was not clear how atoms are constructed. In 1898, J.J. Thomson suggested that an atom might be a positively charged sphere in which negatively charged electrons are embedded. This model of the atom is sometimes called the “plum pudding” model. Of course, it was based on insufficient information and soon found to be incorrect.

Today, it is known that neutron is a neutral particle with mass 1.008665 amu or 1.675×10^{-24} g. The nucleus of every atom contains neutrons alongwith protons except ordinary hydrogen, which has no neutron.

Rutherford’s Experiment

In 1909, Ernest Rutherford, with Hans Geiger and Ernest Marsden, performed a very important experiment. In their experiment they shot a stream of high-speed a-particles at very thin sheets of various materials such as gold. They observed that most of the a-particles (about 99.9%) passed through the sheet without any deflection. However, some particles deflected through various angles, and a few almost completely reversed their direction.

Rutherford’s atomic model: To explain the results of his experiment, Rutherford in 1911 proposed an atomic model. The main points of his model are as follows:

An atom consists of a nucleus which contains almost all mass and all positive charge of the atom. Around the nucleus, there are electrons which revolve around the nucleus just as the planets revolve around the sun.

Light

Atomic spectra have greatly helped us in understanding the electronic structure of the atom. The light emitted from an atom gives us information about the electronic structure of that atom.

Light has many forms such as visible or white light, ultraviolet light, infrared light, X-rays and y-rays etc. all these forms of light propagate through space as electromagnetic waves. Like all other waves, electromagnetic waves are described in terms of their velocity, frequency, wavelength, and amplitude. The wavelength, λ(lambda), is the distance between two successive crests or troughs of the wave. The frequency, v (nu), is the number of wave crests or troughs that pass a given point in one second. Light travels with a constant speed of 3.00 x 108 m/s, c. Frequency is inversely proportional to wavelength at constant velocity. Thus,

$$v = c/\lambda$$

All electromagnetic waves have the same speed in space but their wavelengths and frequencies vary. The wavelength of the visible or white light is about 400 to 750 nm, (4000 to 7500A0)

Continuous spectrum

A spectrum is a display of component colours (or wavelengths) of radiation on a screen or photographic plate. Visible light is composed of a mixture of electromagnetic waves of all wavelengths (frequencies) ranging from about 400 nm to 750 nm. When a narrow beam of visible light is passed through a glass prism it is spread out into a band of colours ranging from long-wavelength red light to short-wavelength violet light. A prism *refracts* light to different wavelengths through different angles and thus disperses the beam of light into its component wavelengths to form a continuous spectrum. A continuous spectrum contains all the wavelengths present in that range. All the colours are present in continuity and there is no demarcation or dark band between them.

Atomic Spectrum

When an element in its atomic form is heated, it emits radiation. If a beam of light emitted by a sample of an excited element is passed through a prism, a spectrum containing only a few lines (wavelengths) is obtained. This spectrum is known as a line spectrum. Since the light is emitted by atoms of an element, the spectrum is also called an atomic emission spectrum (or simply emission spectrum or atomic spectrum). The dark regions of the spectrum correspond to the wavelengths for which light is not emitted. On the other hand, if we pass a beam of white light through a sample of unexcited gas (any element in gaseous state) and the transmitted light is passed through a prism, the spectrum obtained is called an absorption spectrum. The absorption spectrum of an element is also a line spectrum. It is the photographic negative of the emission spectrum. The absorption spectrum of an element lacks those wavelengths that are present in its emission spectrum.

Significantly, each element displays a characteristic set of lines in its emission or absorption spectrum. An element emits the same wavelengths that it absorbs. Thus, the emission or absorption spectra can serve as "*fingerprints*" on the basis of which the elements can be identified.

Atomic Spectra of Hydrogen

Hydrogen is the simplest element. A number of scientists studied the emission of radiation from hydrogen atom. The atomic spectrum of hydrogen consists of several series of lines.

Planck’s Quantum Theory of Light:

In 1099, Max Planck proposed a revolutionary theory about the nature of light. The theory successfully explained several observations concerning the interaction of light and matter, which could not be explained by the wave theory of light. The theory is called Plank’s quantum theory of light. It states:

1) Light is emitted or absorbed by matter discontinuously in the form of discrete packets or bundles of energy called quanta (singular quantum). These quanta of light are also named as photons.
2) Each photon of light has a particular amount of energy which is proportional to the frequency of light.

Here E is the energy, v is the frequency, ? is the wavelength, c is the velocity of light, and h is the constant of proportionality called the Planck’s constant. Its value is 6.63 x 10^{-34} joule second.

The Planck’s quantum theory, thus, says that light is discontinuous and consists of discrete particles called photons. The light (energy) is absorbed or emitted by a substance in the form of these photons.

Bohr’s Atomic Model

Keeping in view the Rutherford’s atomic model, the Planck’s quantum theory of light, and the results of the studies of atomic spectra, Neils Bohr (1885 – 1962), a Danish physicist, in 1913 put forward his model of atomic structure. The postulates of this model are as follows:

1. Electrons revolve around the nucleus in certain *fixed orbits,* or *stationary states*. It means that the energy of the electrons is quantified, that is, an electron can have only certain discrete quantities of energy and none in between. The orbits are also called *energy levels.*
2. Only those orbits are possible for which the angular momentum (mvr) of an electron is the integral multiple of h/2?. That is,

   $$mvr = n \times h/2? \qquad \text{Where } n = 1,2,3,4,\ldots$$

   Where m is the mass, v the velocity, r the radius of the orbit of an electron, h is the Planck’s constant. n specifies the orbits. When n = 1, this is orbit number 1, when n = 2, this is orbit number 2, and so on.
3. As long as an electron moves in its own orbit, no emission or absorption of radiation occurs.
4. Emission or absorption of radiation takes place when an electron jumps from one orbit to another. An electron jumps from an orbit of lower energy (an inner orbit) to an orbit of higher energy (an outer orbit) as a result of the absorption of radiation. When an electron jumps from an orbit of higher energy to an orbit of lower energy, radiation is emitted. The energy of the light absorbed or emitted is equal to the difference of the energies of the orbits between which the electronic transition occurs.

   $$:.\ \Delta E = E2 - E1 = hv$$

Radii or Orbits: Different orbits have different radii. On the basis of Bohr’s atomic model, radii of the electronic orbits can be determined.

Ground State and Excited State

The ground state of an electron is the lowest energy state that an electron normally occupies. When energy is absorbed, the electron jumps to a higher energy state. This higher energy state is known as the excited state (higher energy state). The ground state of an electron is the stable state while the excited states are unstable states. As a result of absorption of energy when an electron jumps to an excited state, it immediately jumps back to the ground state with the emission of energy.

Wave Nature of Matter:

In 1924, a French physicist Louis de Broglie, using Planck's equation ($E = hv$) and Einstein's equation ($E = mc^2$), put forward a hypothesis that electron (and hence matter) possesses wave properties. That is, electron is a wave. Later, Davison and Germer in 1927 experimentally discovered the wave nature of electron. Subsequently, other particles, such as protons, neutrons and helium nuclei (a-particles) were also shown to exhibit wave properties.

The wave behaviour of matter can only be observed for very small particles. For big bodies the associated wavelength is much too small to be observed.

In short, under certain conditions, an electron resembles a particle while under some other conditions, it behave as if it is a wave. The electron and hence the matter possesses dual nature. However, it has been found that electrons can be treated as wave more effectively than as small particles.

Heisenberg Uncertainty Principle

In 1927, Werner Heisenberg (1901–1976), a German physicist, put forward a principle called the Heisenberg uncertainty principle (or Heisenberg indeterminacy principle). It states:

"It is impossible to determine with exact accuracy both the momentum and the position of an electron (or any other body) simultaneously."

It means the more accurately we know the momentum of an electron, the less accurately can we know its position and vice versa.

Thus, Bohr's model of an electron moving with a known velocity (or momentum, as it is mv), in a well-defined orbit (that is, with known position) cannot be correct. In other words, we cannot say where an electron lies around the nucleus.

Quantum Mechanics

The concepts given by Planck, Bohr, de Broglie, Heisenberg, and others ultimately led to the development of a new theory of the structure of atom, known as quantum mechanics or wave mechanics. Quantum mechanics replaced the classical mechanics (the Newtonian mechanics).

If the electron is a wave, then it should be possible to describe it with the help of some mathematical equations like the other waves. In 1926, Erwin Schrodinger (1887–1961) succeeded to develop an equation. This equation is the foundation stone of the quantum mechanics. It offers a mathematical approach to understanding the wave nature of matter.

The quantum mechanical treatment of an electron is highly mathematical as the Schrodinger equation is a very complex equation. Hydrogen is the only atom for which it has been solved. Each solution of this equation is described by a set of constant numbers called quantum numbers.

Quantum Numbers

The quantum mechanics explains the structure of atom with the help of four quantum numbers. These numbers are used to describe the distribution of electrons in space around the nucleus. The quantum numbers and their significance are given below:

1. Principal Quantum Number, *n*

The principal quantum number (n) describes the main energy level, or shell, that an electron occupies in an atom. n may be any positive integer:

$$n = 1, 2, 3, \ldots\ldots$$

When $n = 1$, it is the first main energy level, or the first shell. When $n = 2$, it is the second shell. And, so on. A main energy level or shell is the main region around the nucleus in which an electron may be present. Shells 1, 2, 3, 4,….. are also sometimes called K, L, M, N, …….shells.

2. Azimuthal (or subsidiary) Quantum Number, *l*

Azimuthal quantum number (l) describes subshells or sublevels in shells or main energy levels. It denotes the shape of the region in space an electron occupies. Its values are given by:

$$l = 0 \text{ to } (n - 1)$$

Thus, when $n = 1$, then

$$l = 0$$

When $n = 2$, then $l = 0, 1$

When $n = 3$, then $l = 0, 1, 2$

And, so on.

Thus, the values of l designate subshells or sublevels that electrons can occupy in a main shell. Each value of l is given a letter notation. Thus:

$$\begin{array}{lllllll} l = 0, & 1, & 2, & 3, & 4, & 5, & \ldots\ldots \\ \quad s, & p, & d, & f, & g, & h, & \ldots\ldots \end{array}$$

Thus, in the first shell ($n = 1$, $l = 0$), there is one subshell and it is *s*. In the second shell there are two subshells, *s* and *p*. in the third shell ($n = 3$), there are three subshells, *s*, *p* and *d*. In the fourth shell ($n = 4$), there are four subshells (*s*, *p*, *d*, and *f*). And, so on. Notice that the number of subshells in any given shell is simply equal to the value of n for that shell.

(The first four letters (*s*, *p*, *d*, *f*) find their historical origin in the study of the atomic spectra of the alkali metals. In these spectra four series of lines are observed and they are termed as the *s*harp, *p*rincipal, *d*iffuse and *f*undamental series. For $l = 4, 5, \ldots\ldots$ we just continue with the alphabet.)

Notice that the electrons in their ground state in atoms of all elements occupy only *s*, *p*, *d* and *f*.

3. Magnetic Quantum Number, *m*

It designates the spatial orientation of the region an electron occupies. This region is called an orbital. An orbital is the region around the nucleus in which the probability of finding an electron is maximum. Each subshell is composed of one or more orbitals. The values of m are given by:

$$m = -l, \ldots\ldots 0 \ldots\ldots +l$$

Thus, when $l = 0$, $m = 0$

When $l = 1$, $m = -1, 0, +1$

When $l = 2$, $m = -2, -1, 0, +1, +2$

When $l = 3$, $m = -3, -2, -1, 0, +1, +2, +3$

Values of m serve to determine the orientation of an orbital in space relative to the other orbitals.

In subshell *s*, there is only one orbital *s*. In subshell *p*, there are three orbitals, *px*, *py* ,*pz*. In subshell d, there are five orbitals, and in subshell f, there are seven orbitals.

4. Spin Quantum Number, s

It refers to the spin of an electron. Electron has a spin, that is, it rotates about its own axis. An electron can spin only in either of two directions, clockwise or anticlockwise. Therefore, *s* has only two values +1/2 and –1/2.

Atomic Orbitals:

From the above discussion we can conclude that in an atom there are various main energy levels or shells. Each shell has one or more sublevels or subshells. Each subshell consists of one or more orbitals. An orbital is the actual region where an electron is found. It can be defined as follows:

"An orbital is the region around the nucleus in which the probability of finding an electron is maximum."

Note that an orbital can have a maximum of two electrons.

SHAPES OF ATOMIC ORBITALS

Each *s* orbital in an atom is spherically symmetrical with respect to the nucleus. That is, an *s* orbital in shape is like a symmetrical sphere such as a football. Each *p* orbital is like a dumbbell. The three *p* orbitals (*px*, *py* and *pz*) are present perpendicular to one another. Subscripts x, y and z indicate the axis along which each of the three two-lobed *p* orbitals is directed. The *d* and *f* orbitals have complex shapes.

ELECTRONIC CONFIGURATION

The arrangement of electrons in shells, subshells and rbitals in an atom is called the electronic configuration. The electronic configuration of an atom is governed by the following rules and principles:

1. Pauli Exclusion Principle,

Since electrons are described by four quantum numbers, any two electrons in an atom must differ in at least one quantum number. Pauli Exclusion Principle states:

" In an atom no two electrons can have the same values of the four quantum numbers."

It can also be stated as:

"An orbital can accommodate no more than two electrons and these electrons must have opposite spins."

Take the example of helium, He, which has two electrons, both the electrons are in 1s orbital. We express this as 1s2. These two electrons have the same three quantum numbers, for both

$$n = 1$$
$$l = 0$$
$$m = 0$$

But, they differ in the fourth quantum number. If for one electron

$$s = + 1/2$$

then for the other $s = -1/2$

The two electrons having opposite spins are said to be "*paired*", while if there is only one electron in an orbital, it is called "*unpaired*".

(Pauli exclusion principle was put forward by a Swiss physicist Walgang Pauli (1900-1958) in 1925.)

2. Aufbau Principle

(Aufbau is from German aufbauen meaning "to build up"). This principle states:

"In an atom an electron tends to occupy the lowest energy orbital available."

As we go away from the nucleus, the energy of the shells increases. In writing electronic configuration, we start filling electrons from 1s. When it is completely filled, we go to 2s the to 2p and son on. Consider the following:

H (Z =1) $1s^1$
He (Z = 2) $1s^2$

Li	(Z= 3)	$1s^2, 2s^1$
Be	(Z=4)	$1s^2, 2s^2$
B	(Z=5)	$1s^2, 2s^2, 2p^1$
C	(Z=6)	$1s^2, 2s^2, 2p^2$
N	(Z =7)	$1s^2, 2s^2, 2p^3$
O	(Z =8)	$1s^2, 2s^2, 2p^4$
F	(Z=9)	$1s^2, 2s^2, 2p^5$
Ne	(Z=10)	$1s^2, 2s^2, 2p^6$
Na	(Z=11)	$1s^2, 2s^2, 2p^6, 3s^1$

3. (n+*l*) Rule

This rule states: *"The orbital with the lowest energy is the one for which the sum of n and l is lowest. When two orbitals have the same (n + l) value, the orbital with the lower n value has the lower energy.*

Take the example of potassium (K) that has 19 electrons. The first eighteen electrons have the following arrangement:

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6$$

Where will go the 19th electron, to orbital 3d or 4s? Let us apply ($n+l$) rule, for 3d

$$n + l$$
$$3 + 2 = 5$$

and for 4s

$$n + l$$
$$4 + 0 = 4$$

Thus, 4s has lower energy than 3d; the 19th electron will go to 4s.

$$\text{K } (Z = 19)\ 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$$

4. Hund's Rule

All the orbitals in a subshell have equal energy. How are then electrons filled in a subshell? Hund's rule states:

"As long as the orbitals of same energy available, electrons occupy the separate orbitals and have parallel spins."

Atomic Radius

The size of an atom is measured in terms of radius. It is not possible to determine the precise size of an atom since the outermost shell of an atom has no precise outer boundary. As we go away from the nucleus, the electron density decreases to a very small value but it does not become exactly zero even at a large distance from the nucleus. Moreover, we cannot isolate a single atom and measure its diameter the way we can measure the diameter of a football. We can estimate only the radius of a combined atom. Moreover, the size of the electronic cloud also depends upon its environment. In spite of all these difficulties, we talk about the atomic size because it is very useful in understanding many properties of elements. The atomic radius is defined as follows.

"The half of the bond length of a homonuclear diatomic molecule is called the atomic radius of the bonded atoms."

That is, if two atoms of the same element are covalently bonded, the half of the bond length will be the radius of each atom.

For Example, H-H bond length is 0.78 A. The one-half of this distance is 0.37 A. This is the atomic radius of hydrogen. Similarly, the CI-CI bond length is 1.98 A, the atomic radius of CI is 0.99 A. Other atomic radii can be found in a similar way. This atomic radius is the *covalent radius* since it is the radius of an atom involved in a covalent bond, and not the radius of a free atom.

If we know the length of a bond between two dissimilar atoms (A-B), and the radius of one of them, we can calculate the atomic radius of the other:

$$rA + rB = \text{A-B bond length}$$

Change of atomic radius in the periodic table

1. Atomic radius decreases as we go from left to right in the periodic table. It is because as we go from left to right in a period, the nuclear charge increases. This increasing nuclear charge pulls the valence electrons with increasing force and as a result the atomic radius decreases from left to right in the periodic table.

2. Atomic radius increases as we go from top to bottom in a group. It is because the number of shells increases in going from top to bottom. The increasing number of shells increases the atomic radius.

Ionic Radius

When one or more electrons are added to an atom, a negative ion, anion, is formed. While, when one or more electrons are removed from an atom, a positive ion, cation, is formed .In general, cations are always smaller than the neutral atoms from which they are formed, whereas, anions are larger than the neutral atoms from which they are formed.

The decrease in the size of a cation is due to two factors:

1) The removal of electron(s) from the outermost shell. Often all the electrons from the outermost shell are removed which means the removal of a whole shell.

2) The decrease in the total electron-electron repulsion. For example, radius of Na = 1.86A and that of Na^+ = 0.95 A.

The increase in the size of an anion is due to the added repulsion between the new electrons and the electrons already present. For example, radius of CI=0.99 A and of CI- = 1.81 A.

In a series of ions of different elements having the same number of electrons (isoelectronic ions) the size decreases with the increase in the nuclear charge.

Ionization Energy

Since electrons are attracted by the nucleus, energy must be supplied to remove an electron from an atom. This energy is called ionization energy or ionization potential, and defined as follows:

"The minimum amount of energy required to remove the most loosely bound electron from an isolated gaseous atom in its ground state is called the ionization energy,"

For example, the ionization energy of Na is 495.8 kJ/mol.

An atom has as many ionization energies as it has electrons. The energy required to remove the first electron is called the first ionization energy, the energy required to remove the second electron is known as the second ionization energy, and so forth. For example, for calcium the first ionization energy (IE) is 590 kJ/ mol.

The second ionization energy is 1145 kJ/ mol.

The ionization energy depends on the following factors

1. Atomic radius

The greater the atomic radius, the farther away is the outermost electron from the nucleus; the easier it is to remove it. Thus, lower will be the ionization energy.

2. Nuclear Charge

The greater the nuclear charge, the more attracted will be the electrons by the nucleus, and the higher will be the ionization energy.

3. Shielding effect

The intervening shells between the nucleus and the outermost electrons reduce the attraction between the nucleus and the outermost electrons. This effect is known as the *shielding* or *screening effect*. The greater the shielding effect, the easier it will be to remove the electron, and the lower will be the ionization energy. The shielding effect increases from top to bottom in the periodic table with the increase in the number of shells.

4. Type of orbital

The order of ionization energy with respect to orbitals is

$$s > p > d > f$$

It is most difficult to remove an electron from an s orbital because it is least diffused. The f is the most diffused orbital, so it is the easiest to remove an electron from f orbital.

Change of IP in the period table.

In the periodic table the ionization energy increases from left to right due to decrease in the atomic size and increase in the nuclear charge.

From top to bottom in a group, the ionization energy decreases due to increase in the atomic size and increase in the shielding effect.

Electron Affinity

Electron affinity can be defined as follows. When an electron enters an atom, energy is either released or absorbed. This energy is called electron affinity. Thus:

"The amount of energy evolved or absorbed when an electron is added to a gaseous atom in its ground state is called electron affinity."

Electron affinity shows the ability of an atom to accept one or more electrons. When a chlorine atom accepts an electron 348kJ/mol energy is released.

Cl(g) + e ----------------Cl(g)   EA= -348 kJ/mol

The halogens that have the most negative electron affinities readily form negative ions. By accepting one electron a halogen atom assumes the stable electronic configuration of the noble gas immediately following it.

In general, electron affinity becomes more and more negative in going from left to right in the periodic table as the nuclear charge increases and the atomic radius decreases.

Some elements gain more than one electrons to form anions. For example, oxygen gains two electrons to form a bivalent anion.

O(g) + e ---------------- O (g)   EA = -142 kJ/mol
O(g) + e ---------------- O(g)   EA = +780 kJ/mol

In the second step energy is absorbed. Electron affinities of anions are always positive. This is because of the repulsion between the negative ion and the incoming electron.

Problem: (a) Which element should easily form the cation: K (IP= 419kJ/mol or F (IP= 1680kJ/mol)?

(b) Which element should easily form anion: Na (EA= -53kJ/mol) or Br (EA= -324kJ/mol)?

Answer: (a) K, (b) Br.

Lecture 2

Matter and Energy

Fundamental Concepts of Chemistry: Matter and Chemistry

Chemistry is a branch of science that deals with matter and changes that occur in it. In chemistry we also study theories, laws and principles related to changes in matter. More precisely, in chemistry we study chemical and physical changes and properties of elements and compounds.

In this lecture our focus is on the basic concepts of chemistry. There are many concepts that are used in chemistry. The fundamental concepts include atom, molecule, ion, element, compound, mixture, symbols, formulas, equations, atomic number, mass number, atomic mass, molecular mass, mole, etc.

Matter:

Matter is any substance that has physical existence. That is, anything that has mass and volume. All that we see around us, or we can feel by touch are material substances. Mass is the quantity of matter that a substance contains in it. Volume is the space that a body occupies.

Physical states:

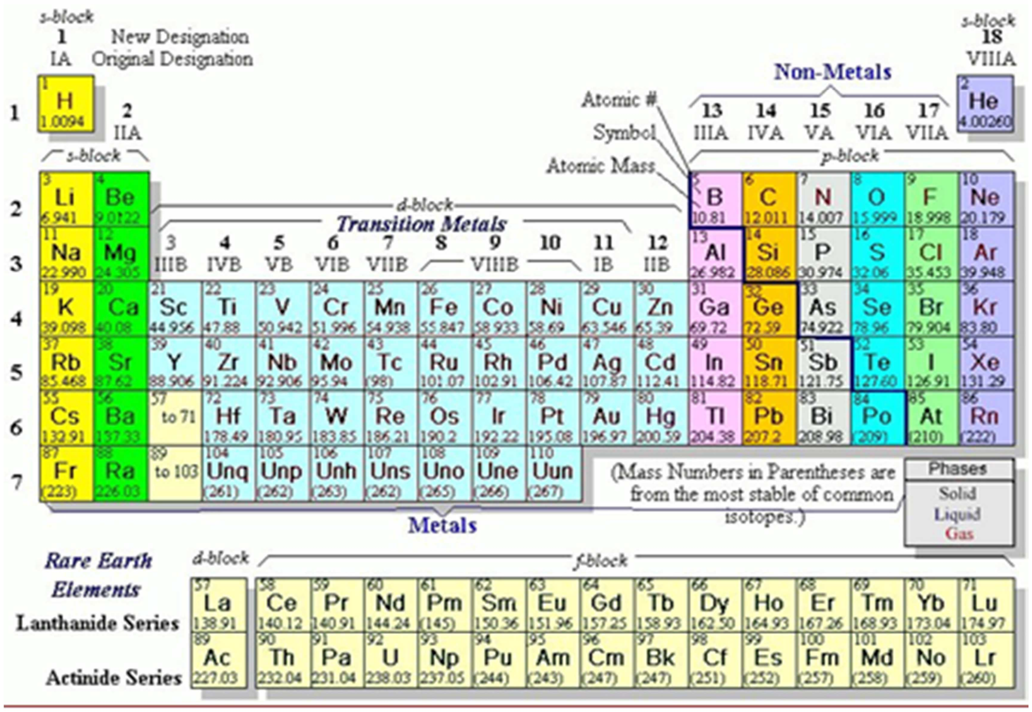
Matter exists in three physical states. These are: solid, liquid and gas. In solids, the particles are very close to one another. In gases, the particles are very away from one another. In liquids, the situation is intermediate. A substance can be changed from one physical state to another. Ice, liquid water and steam are three physical states of water.

Atom:

The atom is the smallest particle of an element that represents the elements in all chemical reactions. There are three types of fundamental particles in an atom.

1. Electrons
2. Protons
3. Neutrons

The electron is a very small particle. It has negative electric charge. The proton is a positively charged particle which is much heavier than electron. Neutron is an electrically neutral particle. It is the heaviest among the three particles. Protons and neutrons are found in the center of atom and collectively constitute a body called nucleus. Electrons revolved around the nucleus.



Atomic Mass:

An atom is a very small particle. But it also has mass. The quantity of this mass is very small. Atomic mass is the mass of one atom of an element and is defined as follows. The relative average mass of one atom of an element which tells us how heavy or light is that atom with respect to one atom of carbon-12. This unit is called amu or atomic mass unit.

One atomic mass unit is one-twelfth of the mass of carbon-12.

1 amu = 1/12 x(mass of one atom of C-12)

In this unit carbon-12 is chosen as standard. Carbon-12 is the most abundant isotope of carbon. For example: the atomic mass of hydrogen is 1.008amu.

Molecular mass:

By molecular mass we mean the mass of a molecule. It is the sum of atomic masses of all the atoms of all elements present in a molecule. We can calculate the molecular masses of water, sulfuric acid, and glucose as follows.

1. Water, H_2O; 1x2 + 16 = 18 amu
2. H_2SO_4: 1 x 2 + 32 +16 x 4 = 98 amu
3. $C_6H_{12}O_6$: 12 x 6 + 1 x 12 + 16 x 6 = 180 amu

Mole:

The amount of a substance that contains Avogadro’s number of particles is called a mole. It is the atomic mass, molecular mass or formula mass expressed in grams. For example, 18 grams of water is one mole of water. If you drink 9 grams of water, it means you have taken a half more of water. The Avodagro’s Number is the number of particles that is found in one mole of a substance. Its value is: 6.02×10^{23}. It is a huge number. If a person has eaten 180 g of glucose, he has eaten 6.02×10^{23} of glucose molecules.

Formula mass:

The Formula mass of a substance is the sum of the atomic masses of all the atoms present in the formula of that substance. For example, the formula mass of NaCl is 23+ 35.5 = 58.5.

Molecular mass:

The molecular mass of a substance is the sum of the atomic masses of all the atoms present in a molecule of that substance. For example, molecular mass of water, H_2O, is 1x2+16= 18.

Ion:

An electrically charged atom or molecule is called an ion. It has two types: cations or positive ions, and anions or negative ions. H^+ is a cation whereas Cl^- is an anion. Ions may be simple or compound. Simple ion consists of a single atom, but a compound ion is comprised of two or more atoms. For example, Na^+ is a simple ion but SO_4^{2-} is a compound ion.

Molecule:

An atom or group of bonded atoms which can exist independently. One molecule of helium (He) consists of one atom of helium. It is a monoatomic molecule. The molecules of other noble gases are also monoatomic. One molecule of water (H_2O) consists of three atoms. So it is a polyatomic molecule.

Atomic number:

The total number of protons in the nucleus of an atom is called atomic number. The atomic number of hydrogen is 1. The atomic number of oxygen is 8, sodium is 11 and iron is 26. All the atoms of an element have same atomic number.

Mass number:

The total number of protons and neutrons present in the nucleus of an atom is called the mass number of that atom. The mass number of carbon-12 is 12. It has 6 protons and 6 neutrons. Atoms of an element may differ in the mass number.

Isotopes:

The atoms of the same element having different mass number are called isotopes. Isotopes of an element have equal number of protons but different number of neutrons. Hydrogen element has three isotopes. They are called:

1. Ordinary hydrogen or protium,
2. Deuterium or heavy hydrogen, and
3. Tritium or radioactive hydrogen.

Ordinary hydrogen has no neutron. Deuterium has one neutron. Tritium has two neutrons.

Element:

An element is the simplest form of matter which cannot be converted into simper forms by any physical or chemical means. If in a collection of atoms, all atoms have the same atomic number, they all belong to the same element.

For example, Na, Fe, O etc. are elements. If you look at a periodic table, you will see elements in it. Elements are of many types. They have different physical states. Today, more than 110 elements are known. Of these 90 elements occur naturally. Other elements have been formed in nuclear reactors through nuclear reactions. Majority of the elements are metals, but many elements are non-metals. There are some elements which have properties in-between metals and non-metals. They are given the name metalloids.

Metals are elements which have high electropositivity. They easily lose electrons and have shining surfaces. For example: Cu, Ag, Au are metals. Non-metals are generally less electropositive and more electronegative.

Compound:

A compound is a substance that is formed by the chemical combination of two or more elements in a definite ratio. For example, water (H_2O) and common salt (NaCl) are compounds. At present, many millions of compounds are known.

Both the elements and compounds are pure substances. Elements are represented by symbols and compounds are shown by chemical formulas.

Mixture:

When two or more substances are mixed in any ratio in a manner that no chemical combination occurs is called a mixture. A mixture is a mixed substance formed by the physical combinations of two or more substances (elements or compounds). For example, air is a mixture of nitrogen, oxygen and some other gases. The mixtures are of two types.

1. Homogeneous mixtures, and
2. Heterogeneous mixtures

A homogeneous mixture has uniform composition. It is also known as a solution. For example, a mixture of salt (NaCl) and water is a homogeneous mixture. In a homogenous mixture, one thing is completely “dissolved” in another substance. On the other hand, a heterogeneous mixture does not have uniform composition. For example, a mixture of sand and water is a heterogeneous mixture.

Chemical reaction:

A chemical reaction is a chemical change that involves one or more elements or compounds. It is process in which one or more chemical bonds are broken or formed. In a chemical reaction, one or more substances undergo chemical change and form one or more new substances. The substances before the reaction are called reactants and the substances that are formed as a result of the reaction are called products.

A chemical reaction is shown by a “chemical equation”. A chemical equation consists of reactants, products and an arrow sign.

Reactants → Products

A chemical equation must be “balanced”. A balanced chemical equation is that in which the number of atoms of all elements involved in the reaction are equal on both sides of equation. That is, the number of atoms of an element in the reactants must be equal to the number of atoms of that element in the product. Look at the following equation. Is it balanced?

$H_2 + Cl_2 \rightarrow HCl$ (not balanced)

No. it is not balanced. Why? Because the number of hydrogen atoms in the reactants side is 2 while in the product side there is only 1 H atom. Similarly, number of Cl atoms is not equal on both the sides. How can you balance it? Write 2 before HCl in the product side. The equation now will be balanced.

$H_2 + Cl_2 \rightarrow 2HCl$ (balanced)

Lecture 3

Nature of Chemical Bonding

How atoms join with each other?

The existence of solids and liquids is a clear proof that atoms combine with one another. But, the question is why atoms combine with one another and how?

Isolated atoms are unstable and to gain stability they combine with one another. This combination is expressed by the term **chemical bond** (the word *bond* means linkage, attachment, connection, etc.). The chemical bond can be defined as follow:

"The chemical bond is a force which holds atoms together in a molecule or a compound"

It was in 1916 that W. Kossel (Germany) and G.N. Lewis (USA) independently proposed that atoms join together through the involvement of electrons. The noble gases (He, Ne, Ar, etc.) are stable, and have eight electrons in their outermost shells (except helium which has two electrons). It was thought that since the noble gases are stable, all elements tend to achieve the noble gas electronic configuration. This is known as the **octet rule**. (Octet: group of eight.) Now, how can atoms achieve eight electrons in their outermost shells? Kossel suggested that this is done by actual transfer of one or more electrons from one atom to another. Lewis proposed that atoms acquire noble gas electronic configuration by mutual sharing of electrons between two atoms. These views gave the two concepts of bonds: *ionic bond,* and *covalent bond.*

Ionic Bond or Electrovalent Bond

The concept of ionic bond was suggested by W. Kossel in 1916. Ionic bond is formed due to *transfer of electrons*. When electrons are transferred from one atom to another, the atom that loses electrons becomes a positive ion and the atom that gains electrons becomes a negative ion. These oppositely charged ions then attract each other and are attached with each other through the opposite electric charges. Thus, we can define the ionic bond as follows:

"The ionic bond is the bond which is formed between oppositely charged ions due to electrostatic force of attraction."

Take the example of NaCl. Sodium atom has one electron in its valence (outermost) shell. Chlorine atom has seven electrons in its outermost shell.

Sodium atom loses its valence electron and becomes a positive ion, while chlorine atom accepts one electron to form a negative ion. These ions attract each other due to their opposite changes to form ionic bond:

$$\mathrm{Na} \rightarrow \mathrm{Na^+} + e^-$$

$$\mathrm{Cl} + e^- \rightarrow \mathrm{Cl^-}$$

$$\mathrm{Na^+} + \mathrm{Cl^-} \rightarrow \mathrm{Na^+Cl^-} \rightarrow \mathrm{NaCl}$$

Energetics of Ionic Bond

Why an ionic bond is formed? The natural principle is that every system tends towards more stability. Atoms form bonds to acquire stability. For most cases we can understand stability as a state of less energy. Thus, in general, we can say that every system tends to acquire a state of lower energy. Let us study the energy changes in the formation of NaCl from gaseous sodium and chlorine atoms.

To remove the outermost electron from sodium atom the energy (the ionization energy) required is 494 kJ/mol. When a chlorine atom gains an electron, the energy (electron affinity) released is 348 kJ/mol.

This shows that the ionization energy of sodium is so high that the energy released when a chlorine atom accepts the electron is not sufficient to provide the energy needed to remove the electron from sodium. An additional 495-348 = 147 kJ energy is required to make possible the transfer of one mole of electrons from isolated sodium atoms to isolated chlorine atoms.

These sodium ions and the chloride ions combine together to form solid crystalline sodium chloride. During this step a high amount of energy (788 kJ/mol) is released.

$$Na^+(g) + Cl^-(g) \rightarrow NaCl(s) \quad \Delta H = -788\ kJ/mol$$

This energy is known as the **lattice energy**.

"The lattice energy is the amount of energy evolved when one mole of a crystalline ionic compound is formed from its gaseous ions."

The lattice energy here is high because one mole of sodium ions and one mole of chloride ions are arranged in the formation of crystal in such a way that one sodium ion is surrounded by six chloride ions and vice versa. Thus, it is the large lattice energy, which makes the formation of sodium chloride energetically favorable. The lattice energy is, in fact, the driving force behind the formation of sodium chloride from its elements.

In the same way we can understand the formation of any ionic compound. Ionic bond is formed between the elements having large difference of electronegativity, (usually higher than 1.7). In general the elements of group VIIA (halogens) form ionic bond with metals.

Characteristics of Ionic Compounds

1. Ionic Compounds are Non-molecular

An ion attracts the oppositely charged ions from all directions, so the ionic bond is non-directional. When a large number of cations and anions come closer to one another, they arrange themselves in such a way that one ion is surrounded by a number of oppositely charged ions. Each ion is surrounded by the greatest possible number of oppositely charged ions depending on the relative ionic radii of cations and anions. Thus, ionic bonds do not form freely existing particles called molecules. Therefore, ionic compounds do no consist of molecules.

2. Ionic Compounds are Solids

Under ordinary conditions, all ionic compounds are solids. It is because in ionic compounds, ions are held together by strong electrostatic forces of attraction.

3. Ionic compounds have high melting and boiling points

In ionic compounds, the oppositely charged ions are held in the crystal by strong electrostatic forces. Therefore, high energy is needed to overcome the strong electrostatic forces. Thus, the ionic compounds have high melting and boiling points.

4. Ionic compounds are soluble in polar solvents

Polar solvents like water have high *dielectric constants* (the ability of a solvent to decrease the attractive force between the ions dipped in it). Therefore, such solvents break the forces of attraction between the ions and get them dispersed in them. In nonpolar solvents ionic compounds are generally insoluble.

5. Ionic compounds are electrolytes

Ionic compounds conduct electricity in their solutions and in molten sates. This is because in solution or in molten state the ions become free from one another and can move under the effect of electric field.

Covalent Bond

The concept of covalent bond was given by G.N. Lewis in 1916. Covalent bond can be defined as follows:

"Covalent bond is the bond which is formed due to

sharing of electrons between tow atoms."

Take the example of a hydrogen molecule. Hydrogen atom has one electron in its valence shell:

$$\text{H } (Z = 1) \quad 1s^1$$

When two hydrogen atoms come close to each other, they share their electrons to form a covalent bond:

$$H^{\cdot} + H^{\cdot} \rightarrow H{:}H$$

This *shared pair* of electrons holds the two atoms together; each electron of the pair is attracted by both the nuclei. The shared pair of electrons is also known as *bonding pair* of electrons.

Covalent bond is a *unidirectional* bond and holds the bonded atoms to form a freely exiting particle called a molecule. Therefore, the covalent bond is generally shown by a small line drawn between the symbols of the bonded atoms. The line represents the bonding pair of electrons. Thus

H:H is represented as H–H

Type of Covalent Bond

A covalent bond between two atoms may be formed by mutual sharing of one, two or three pairs of electrons. Therefore, the covalent bonds are of three types.

Single Covalent Bond: The bond that is formed due to sharing of one pair of electrons between two atoms is called the single covalent bond. The H-H bond is a single covalent bond. Similarly, H-C1, Cl-C1, F-F Br-Br are single covalent bonds.

Double Covalent Bond: The bond that is formed due to sharing of two pairs of electrons between two atoms is called a double covalent bond. Each atom contributes two unpaired electrons that are paired with the electrons of the other atom. Take the example of O_2. An oxygen atom has the following electronic configuration.

$$O\ 1s^2, 2s^2, 2p_x{}^2, ap_y{}^1, 2p_z{}^1$$

It has two unpaired electrons, one in orbital $2p_y$ and other in $2p_z$. Two oxygen atoms share two pairs of electrons to form a double covalent bond:

$$O: + :O \rightarrow O::O$$

or

$$O=O$$

Similarly, ethene has a carbon-carbon double bond:

$$H_2C=CH_2$$

Triple Covalent Bond

When a bond is formed due to sharing of three pairs of electrons between two atoms, it is called a triple covalent bond. Take the example of N_2. A nitrogen atom ($z = 7$) has the following electronic configuration:

$$N\ 1s^2, 2s^2, 2p_x{}^1, ap_y{}^1, 2p_z{}^1$$

It has three unpaired elections. Two nitrogen atoms form a triple bond by sharing three pairs of electrons. Similarly, ethyne has a carbon-carbon triple bond.

Coordinate Covalent Bond

Coordinate covalent bond is a special type of covalent bond, which differs from the simple covalent bond in the *way* of formation:

"The covalent bond between two atoms in which both of the bonding electrons are donated by one of the atoms, is known as the coordinate covalent bond."

The H^+ ion has no electron, yet it forms a bond. For example, it forms a bond with the nitrogen of ammonia. It is because the nitrogen of ammonia has a non-bonding, or lone, pair of electrons which it donates to form a bond with hydrogen ion:

$H^+ + :NH_3 \rightarrow NH_4^+$

A coordinate covalent bond is also represented by an arrow sign showing the direction of the donation of electron pair.

The atom that donates the pair of electrons is called the donor, and the atom that accepts the pair of electrons is called the acceptor.

Coordinate covalent bond is also known as *dative* bond or *co-ionic* bond.

Characteristics of Covalent Compounds

1. Covalent compounds are molecular: The atoms bonded by covalent bonds form independently existing units known as molecules.

2. Covalent compounds may be solids, liquids or gases: The covalent compounds consist of molecules. In gases these molecules are free from one another and exert practically no force of attraction under ordinary conditions. In liquids and solids intermolecular forces of attraction, van der Waals forces, or hydrogen bonds hold the molecules together.

3. Non-electrolytes: In general, the covalent compounds are non-electrolytes**.** Exceptions include acids and bases.

4. Insoluble in water: In general, the covalent compounds are insoluble in polar solvents like water, and soluble in nonpolar solvents like organic liquids.

Electronegativity

A shared pair of electrons is attracted by both of the bonded atoms. For example in H:C1 both H and C1 attract the bonding pair. This power of an atom to attract the bonding pair of electrons is called electronegativity, which can be defined as follows:

"The ability of an atom to attract the shared pair of electrons towards it is known as electronegativity."

Fluorine is the most electronegative element. Its electronegativity is 4. Then comes oxygen whose electronegativity is 3.5.

Polar and Nonpolar Bonds

If two bonded atoms have equal electronegativity, the bonding electrons pair will be shared equally between the two atoms. In other words, the electron density of the bonding electron pair is distributed equally and symmetrically between the two atoms. Such a bond is known as a nonpolar bond. Thus;

"The bond between two atoms having equal electronegativity is a nonpolar bond."

For example, $C1-C1$, $O=O$, $N=N$ bonds are nonpolar bonds.

On the other hand, if the atoms forming a bond have different electronegativities, the bonding pair is shared unequally. The more electronegative atom acquires a greater share of the bonding electrons as compared to the less electronegative atom. Due to this the more electronegative atom acquires a partial negative charge and the less electronegative atom acquires a partial positive charge. These charges are of equal magnitude, and the overall charge is zero. Such a bond is known as a polar bond. It has negative and positive poles. Thus:

“The polar bond is the bond between two atoms having different electronegativities.”

Take the example of $H–C1$. Chlorine is more electronegative than hydrogen. Thus, the bonding pair of electrons is shared unequally, and chlorine has greater share of electrons than hydrogen. As a result, chlorine is partially negatively charged and hydrogen is partially positively charge.

Problem:

Which of the following molecules are polar and which are nonpolar?

$BeCl_2$, H_2S, CS_2, BF_3, NH_3, PCl_3

Answers:

$BeCl_2$ is a linear molecule, and is nonpolar.

H_2S is an angular molecule (like H_2O) with polar bonds, so it is polar.

CS_2 is a linear molecule (like CO_2), so it is nonpolar.

BF_3 is a trigonal planar molecule. Its bond moments cancel one another so the molecule is nonpolar.

$PC1_3$ is also a trigonal pyramidal molecule (like NH_3) and polar.

Bond length

“The distance between the nuclei of two bonded

atoms is called the bond length”.

The bond length of a single bond is longer than a double bond, which in turn is longer than a triple bond.

Bond Energy

When a bond is formed between two atoms a certain amount of energy is released during this process. When that bond is broken the same amount of energy is required to do so. This energy is known as bond energy

“The bond energy is the energy evolved when a bond is formed between two atoms.”

Or

“The bond energy is the energy required to break a bond between two atoms.”

The bond energy is also known as *bond dissociation energy*.

The Modern Concept of covalent Bonding

There are two important modern concepts of chemical bonding both are based on the quantum mechanics: valence bond theory (VBT), and molecular orbital theory (MOT). According to VBT

“a covalent bond between two atoms is formed due to the overlap of two half-filled orbitals, one from each atom.”

Molecular orbital theory (MOT) treats a molecule like an atom. An atom consists of atomic orbitals surrounding a nucleus. Likewise, a molecule consists of molecular orbitals surrounding two or more nuclei present in the molecule. Atomic orbitals are monocentric, they surround only one nucleus while the molecular orbitals are polycentric, and surround more than one nuclei.

Summary: A chemical bond is the force which holds atoms together. The bond may be ionic or covalent. Ionic bond is formed by the transfer of 1 or more electrons and covalent bond is formed by the sharing of electrons. In ionic bond there is complete transfer of electrons which result in formation of positive and negative ions which are called cations and anions these cations and anions are held together by the strong electrostatic force of attraction. So the ionic bond is very strong bond. The electrons which are present in the outer most shell of an element are called valence electrons. It the valence electrons which take part in bonding, for example there are one valence electrons in Na and seven in Cl.

Differentiation between ionic and covalent bond:

- Ionic compounds have ionic compounds while covalent compounds have covalent bonds.
- Since in ionic compounds, ions are held together through very strong electrostatic forces, ionic compounds are solids at room temperature. Whereas covalent compounds consist of molecules which are held together through weak inter molecular force, there for they may be solids, liquids or gases.
- Ionic compounds have higher melting and boiling points than covalent compounds.
- In general, ionic compounds are soluble in water and insoluble in organic solvents. While covalent compounds are generally insoluble in water and soluble in organic solvents.
- Ionic compounds don’t conduct electricity as such but do so in molten state. Covalent compounds don’t conduct electricity in general.

Explain bond formation in H2 and NaCl?

H_2 In H2 two hydrogen atoms are held together through a covalent bond. Each hydrogen atom contributed 1 electron. So there are two shared electrons this is known as a shared pair of electrons. It is this shared pair of electrons which holds two H atoms together.

$$H^{\cdot} + H^{\cdot} \rightarrow H{-}H$$

NaCl In NaCl there is ionic bond Na^+ is positive ion while Cl^- is negative ion, these ions are held together through very strong electrostatic force of attraction.

$$Na^+ + Cl^- \rightarrow NaCl$$

Lecture 4

Chemical Reactions

Chemical Reactions:

A chemical reaction is a chemical change in which one or more substances change into one or more other substances. In other words, a chemical reaction is a process in which one or more bonds are broken and one or more bonds are formed. For example, rusting of iron is a chemical reaction. Similarly burning of natural gas is a chemical reaction.

Chemical and physical change:

During a chemical change a new substance is formed while during a physical change no new substance is formed. For example, burning of wood is a chemical change while change of water into ice is a physical change. During a chemical change a chemical reaction occurs whereas during a physical change no chemical reaction occurs. Chemical change is generally a permanent change, while physical change is only a temporary change and can be reversed easily.

Chemical property of a substance is a property in which that substance undergoes a chemical change. For example, it is a chemical property of an acid to react with a base and form salt and water.

Exothermic and endothermic reactions:

When a chemical reaction takes place, change in energy also occurs. The reaction during which heat is evolved is called an **exothermic reaction**. On the other hand, the reaction during which heat is absorbed is called an **endothermic reaction.**

Heat of reaction:

When a chemical reaction occurs, certain amount of heat is either evolved or absorbed. This amount of heat which is evolved or absorbed during a chemical reaction is known as heat of reaction. It is also known as enthalpy of reaction and is denoted by ΔH. Its units are joules per mole or Kcal per mole.

Types of Reactions:

There are a number of types of reactions.

1. **Addition reactions:** the reactions in which two or more substance react to form a single substance. Ethene reacts with hydrogen to form ethane.

$$C_2H_4 + H_2 \rightarrow C_2H_6$$

2. **Substitution reaction:** the reactions in which one substance is replaced by another substance from a molecule:

$CH_3\text{-}Cl + NaOH \rightarrow CH_3\text{-}OH + NaCl$

This reaction is also known as double displacement reaction.

3. Elimination reaction: the reactions in which one or more atoms are eliminated from a molecule. For example, removal of H_2O from ethanol to form ethene.

$CH_3\text{-}CH_2\text{-}OH \rightarrow CH_2{=}CH_2 + H_2O$

4. Oxidation-Reduction Reactions

Many reactions involve transfer of electrons from one atom to another atom. These reactions are known as **oxidation-reduction reactions.** The loss of electrons from an atom is known as **oxidation**, while the gain of electrons by an atom is called **reduction.** Oxidation and reduction always take place simultaneously and the extent of oxidation is equal to the extent of reduction. That is, the loss of electrons is equal to the gain of electrons. The substance that undergoes oxidation is known as the **reducing agent**, and the substance that undergoes reduction is known as the **oxidizing agent.**

5. Combustion reactions: combustion means burning, and it is the reaction of a substance with oxygen. In a combustion reaction heat is produced. For example, the reaction of methane with oxygen is a combustion reaction.

$CH_4 + O_2 \rightarrow CO_2 + H_2O$

Generally in a combustion reaction, carbon dioxide and water are produced.

6. Neutralization reactions:

When an acidic solution is added to a basic solution in the right proportion, the properties of each are lost, and a salt and water are formed. This process is called **neutralization.**

"The reaction between an acid and a base that forms a salt and water is called neutralization".

For Example,

$HCI\ (aq) + NaOH\ (aq) \rightarrow NaCI\ (aq) + H_2O$

$HNO_3\ (aq) + NaOH\ (aq) \rightarrow NaNO_3\ (aq) + H_2O$

Chemical reactions may occur in solution or gaseous form. Generally, the chemical reactions are carried out in solution. Water and organic solvents are used for this purpose.

Rate of Reaction:

When a reaction occurs, one or more bonds are broken and then one or more bonds are formed. This process of bond breakage and formation takes some time. How much a reactant changes into a product in a given time is important. By the rate of reaction we mean the amount of reactant that is converted to product per unit time. It can also be defined on the bases of the appearance of a product. So, the rate of a reaction is the amount of product formed per unit time.

The rate of reaction is also called speed or velocity of reaction. It is measured in moles/seconds. Thus, the rate of a reaction is the amount of product which is formed in one second.

Rate of Reaction = concentration of product formed/time

On the basis of the rate of reactions, we can classify the reactions into the following categories.

- Very slow reactions: some reactions are very slow. For example, conversion of graphite into diamond in the earth crust is a very slow process.
- Slow reactions: some reactions occur with slow speed, e.g. rusting of iron is a slow process.
- Moderate reactions: most organic reactions occur with moderate speed.
- Fast reactions: many reactions occur with a fast speed. Strong acid strong base reactions are fast reactions.
- Very fast reactions: some reactions are very fast such as explosions.

Lecture 5

Organic Chemistry

Organic Chemistry:

Organic chemistry is a branch of chemistry that involves the study of carbon compounds. It deals with the structures, composition, and synthesis of organic compounds. Organic compounds are obtained from natural sources like plants, animals and microbes. They are also synthesized in laboratory. There are millions of organic compounds. They have wide variety of application such as in medicine, fertilizer, food, clothing, communication, transportation etc.

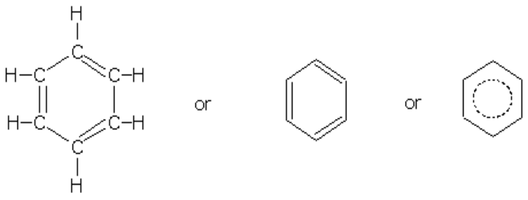
Catenation:

Carbon has a very unique ability that its large number of atoms can bond with each other to make chains of different lengths. This property of carbon to make chains is called catenation.

C-C C-C-C C-C-C-C C-C-C-C-C C-C-C-C-C-C-C

Hydrocarbons:

Hydrocarbons are the compounds of carbon and hydrogen. There are different classes of hydrocarbons such as aliphatic, aromatic, cyclic, acyclic, saturated and unsaturated, etc. Aromatic compounds are benzene and those which resemble benzene. They burn with black soot. They possess aromaticity and are comparatively more stable than expected. They are unsaturated compounds but are resistant to addition reactions. Their characteristic reactions are electrophilic substitution reactions. The structure of benzene is given below.



Classification of organic compounds:

There are millions of organic compounds and this makes it physically impossible to study each individual compound. To facilitate their study, organic compounds are classified into various groups and sub-groups.

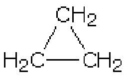
They may be broadly classified into the following classes:

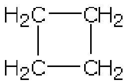
- Open chain or acyclic compounds
- Closed chain or cyclic compounds

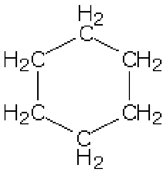
Open chain or acyclic compounds:

These compounds contain an open chain system of carbon atoms. The chains may be either straight chains (non-branched) or branched. The open chain compounds are also called aliphatic compounds. The name aliphatic is derived from the Greek word aleiphar meaning fats, as the earlier known compounds of this class were either obtained from animal or vegetable fats, or had fat like character.

$CH_3-CH_2-CH_2-CH_3$, $CH_3-CH_2-CH_2-CH_2OH$, $H_2C = CH_2$







Closed chain or cyclic compounds

These compounds contain one or more closed chains (rings) of atoms and are known as cyclic or ring compounds.

The aliphatic hydrocarbons are the organic compounds which contain no benzene ring. They may be open chain or closed chain. The closed chain compounds are also called cyclic compounds. The major classes of aliphatic hydrocarbons are alkanes, alkenes, alkynes and cycloalkanes, etc.

Functional groups:

An atom or group of atoms which imparts some specific properties to a compound is called a functional group. For example, -OH is functional group. It is known as hydroxyl group. The compounds which have this functional group show specific properties. They are phenols and alcohols.

Structural formula:

It is very common in organic chemistry that two or more compounds have same molecular formula. For example, both ethanol and dimethyl ether have same molecular formula, C_2H_6O. Why they are different? They are different because they have different arrangements of atoms in their molecules. The arrangement of atoms in molecule is represented by a formula which is known is the structural formula. The structural formula of a compound is the formula which shows the arrangement of atoms in its molecule. The structural formula of a compound shows which atom is attached with which atom.

Isomers and isomerism:

Two or more different compounds which have same molecular formula are called isomers. This phenomenon is known as isomerism. Ethanol and dimethyl ether are isomers. Similarly, n-butane and isobutene are isomers. They are two different compounds, and have same molecular formula (C_4H_{10}) but different structures. Isomerism is very common in organic compounds. There are many types of isomerisms.

Sources of organic compounds:

There are many sources of organic compounds. Plants, animals, petroleum, natural gas, coal are common sources of naturally occurring organic compounds. A huge number of compounds have been synthesized in laboratories by chemists. A great number of new compounds are being added continuously.

All organic compounds must contain carbon. Almost organic compounds also possess hydrogen. Many compounds also contain oxygen and/or nitrogen. Other common elements found in organic compounds are halogens, sulfur, and phosphorus.

Oxygen containing organic compounds:

Oxygen-containing organic compounds are very numerous. Many functional groups contain oxygen. Some examples are given below.

Alcohols:

Alcohols are common organic compounds. They contain –OH functional group. This is called hydroxyl group. Examples: Methanol, CH_3-OH ; ethanol, CH_3-CH_2-OH.

Both methanol and ethanol are liquids and are used as solvents.

Phenols:

Phenols also contain –OH functional group, but in a phenol the –OH group is attached to an aromatic carbon.

Aldehydes:

Aldehydes are those organic compounds which have aldehydic carbonyl functional group,-CHO. Formaldehyde, acetaldehyde, benzaldehyde are common aldehydes.

Ketones:

Ketones are those organic compounds which contain ketonic carbonyl functional group. This group is –CO–. There is a double bond between carbon and oxygen, C=O. Acetone is a common ketone (H_3C-CO-CH_3). It is a liquid and used as a solvent.

Carboxylic acid:

Carboxylic acids are compounds which contain carboxylic group, –COOH. Carboxylic acids are important organic compounds. Examples: formic acid, acetic acid, benzoic acid. Carboxylic acids are common in living organisms, proteins are composed of amino acids. Citric acid is found in citrus fruits. Milk contains lactic acid. Gapes have tartaric acid.

Carboxylic acids are weaker than mineral acids. Oils and fats are esters of glycerol with fatty acids.

Esters:

Esters are also common organic compounds. They are formed by combination of carboxylic acids and alcohols. Ethyl acetate is a common ester. Its formula is: CH_3-$COOCH_2$-CH_3. Fats and oils are esters of fatty acids with glycerol. Glycerol is a triol, i.e., it has three –OH groups.

Ethers:

Ethers are also a common class of organic compounds. They have C-O-C bonding. Dimethyl ether, and diethyl ether are common ethers. Diethyl ether is commonly called ether. It is anesthetic. It is used as a solvent in laboratory and industry.

Nitrogen containing organic compounds:

Nitrogen containing organic compounds are also very common. Amino acids contain nitrogen. Similarly DNA and RNA also contain nitrogen. Another important class of natural products called alkaloids also contains nitrogen. Common nitrogenous compounds have amino groups.

Amines:

Amines are nitrogenous organic compounds which contain amino group. Amines may be primary, secondary and tertiary. Examples: CH_3-NH_2 (Methyl amine), CH_3-NH-CH_3 (Dimethyl amine) and $(CH_3)_3N$ (Trimethyl amine).

Carbohydrates, proteins and lipids (Fats and oils) are naturally occurring common organic compounds. They are also part of our food.

Organic Reactions:

A chemical reaction is a chemical change. It is a process in which one or more bonds and broken and one or more bonds are formed. Coutless number of reactions occur involving organic compunds. But all these reaction belong to only a few types of reactions. Most common types of organic reactions are given below.

- Substitution reactions
- Elimination reactions
- Additions reactions

In substitution reactions, one group is replaced by another group.

$$OH^- + CH_3\text{-}Cl \rightarrow CH_3\text{-}OH + Cl^-$$

In the reaction Cl^- is replaced by OH^- group.

In elimination reactions, groups are eliminated from a molecule.

$$CH_3\text{-}CH_2\text{-}Cl \rightarrow H_2C{=}CH_2 + HCl$$

In this reaction HCl is eliminated from chloroethane and ethene is formed.

Addition reaction is reverse of elimination reaction. In an addition reaction, a molecule adds to another molecule. So, two molecules of reactants combine to form one molecule of product.

$$H_2C{=}CH_2 \quad + \quad HBr \quad \rightarrow \quad H_3C\text{-}CH_2\text{-}Br$$

Applications of Organic Compounds:

Organic compounds are very important chemical substances. They have a wide variety of applications in modern human life. Organic compounds are essential part of our food. The fibers and dyes are organic compounds. Similarly, fragrances and flavours are organic substances. Plastic and other polymers are also organic compounds.

Numerous organic compounds are used as medicines for different diseases. The number of such compounds is rapidly increasing.

Many fertilizers are also organic compounds. Similarly, soaps and detergents and other household materials are organic compounds.

Lecture 12

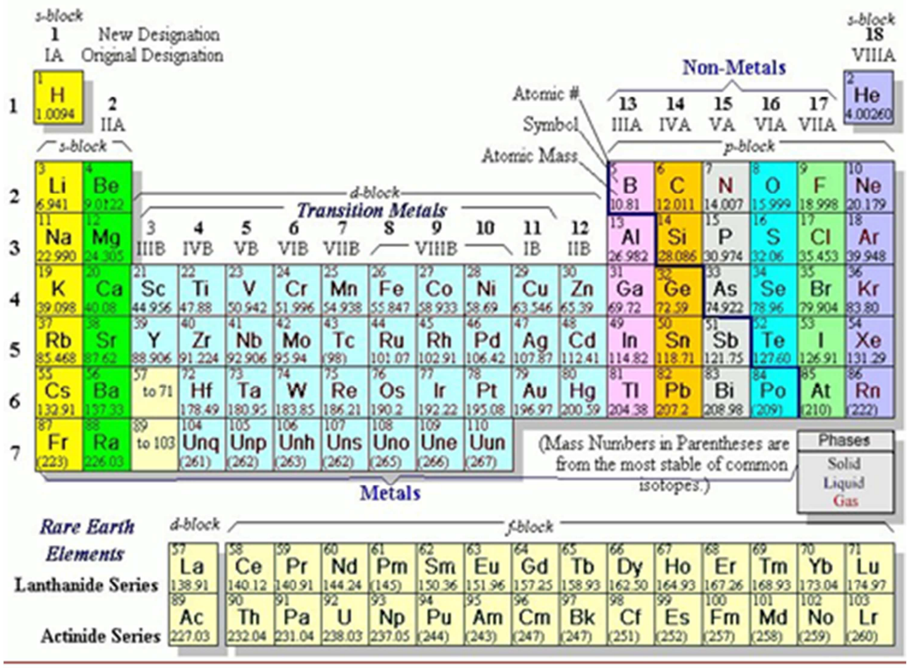
Metals

The modern classification of elements is based on the modern **periodic law**.

The modern periodic law states that the physical and chemical properties of elements are the periodic function of their atomic numbers.

When elements are arranged on the basis of the modern periodic law, we get modern periodic table.

In the modern periodic table the elements are arranged in the order of increasing atomic number. When the elements are arranged in the order of increasing atomic number, the elements with similar properties appear at definite intervals. When elements with similar properties are placed in the same column, we get groups or families of elements having similar properties. Thus, in the modern periodic table, we have vertical columns and horizontal rows. The horizontal rows are also called periods.



	1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18 VIIIA
1	1 H 1.0094																	2 He 4.00260
2	3 Li 6.941	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179
3	11 Na 22.990	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
4	19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.39	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
5	37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.91	54 Xe 131.29
6	55 Cs 132.91	56 Ba 137.33	57 to 71	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
7	87 Fr (223)	88 Ra 226.03	89 to 103	104 Unq (261)	105 Unp (262)	106 Unh (263)	107 Uns (262)	108 Uno (265)	109 Une (266)	110 Uun (267)								

(Mass Numbers in Parentheses are from the most stable of common isotopes.)

Lanthanide Series	57 La 138.91	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.93	66 Dy 162.50	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97
Actinide Series	89 Ac 227.03	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)

Periods in the periodic table:

Rows of elements are called periods. There are 7 period in the periodic table. The number of elements in a period increases as you move down the periodic table.

Groups in the periodic table:

Columns of elements in the periodic table are called groups. Elements within a group show similarity in properties. In a group, the elements have the same outer electron arrangement. The outermost electrons are called valence electrons. Why the elements belonging to the same group have similar properties? It is because they have the same number of valence electrons.

Representative elements: In the periodic table there are two sets of groups. The group A elements are called the representative elements. The group B elements are the non-representative elements. Representative elements are named after the first element of the group. So we have, lithium family, beryllium family, boron family, carbon family, nitrogen family, oxygen family, fluorine family or halogens, and helium family or noble gases. Group IA and IIA are also called alkali metals and alkaline earth metals respectively.

Transition metals:

The transition elements are located in groups IB to VIIIB. Copper, zinc, iron, silver, mercury and gold are examples of transition metals. These elements are very hard, with high melting points and boiling points. The transition metals are good electrical conductors and are very malleable.

Periodic properties:

There are a number of properties which change in a definite manner as we move from one end to the other end of periodic table. Such properties are called periodic properties. Periodic properties include: atomic and ionic radii, melting points and boiling points, metallic character, ionization potential, electron affinity, electronegativity, etc. take the example of electronegativity. The electronegativity of an element is the ability of the element with which it attracts the shared pair of electrons towards it. The electronegativity increases as we go from left to right in the periodic table. It decreases from top to bottom in a group.

Physical states of elements:

Most elements in the periodic table are solids. At room temperature all metals are solids except mercury. Only a few elements are liquids such as bromine and mercury. Some elements are gases. These are nonmetals. Nitrogen, oxygen, fluorine, chlorine and noble gases are found in gases state at room temperature.

Ores: An ore is a material that contains a metal in such quantities that it can be mined and worked commercially to extract that metal.

Metals are not found in free state. They are found in the form of minerals and ores.

The metal is usually contained in chemical combination with some other element in addition to various impurities. For example, iron is found in the form of ores such as hematite (Fe2O3), magnetite (Fe3O4), limonite ($FeO(OH).n(H_2O)$).

Properties of metals and nonmetals

(ref. (http://chemistry.about.com/od/periodictableelements/a/Metals-And-Nonmetals.htm)

Metal Physical Properties

- lustrous (shiny)
- good conductors of heat and electricity
- high melting point
- high density (heavy for their size)

- malleable (can be hammered)
- ductile (can be drawn into wires)
- usually solid at room temperature (an exception is mercury)
- opaque as a thin sheet (can't see through metals)
- metals are sonorous or make a bell-like sound when struck

Metal Chemical Properties

- have 1-3 electrons in the outer shell of each metal atom
- corrode easily (e.g., damaged by oxidation such as tarnish or rust)
- lose electrons easily
- form oxides that are basic
- have lower electronegativities
- are good reducing agents

Nonmetals

Nonmetal Physical Properties

- not lustrous (dull appearance)
- poor conductors of heat and electricity
- non-ductile solids
- brittle solids
- may be solids, liquids or gases at room temperature
- transparent as a thin sheet
- nonmetals are not sonorous

Nonmetal Chemical Properties

- usually have 4-8 electrons in their outer shell
- readily gain or share valence electrons
- form oxides that are acidic
- have higher electronegativities
- are good oxidizing agents

Metalloids or semimetals:

There are some elements which have properties between metals and nonmetals. They are called metalloids or semimetals. The metalloids or semimetals are located along the line between the metals and nonmetals in the periodic table. The metalloids are boron, silicon, germanium, arsenic, antimony, and tellurium.

- Electronegativities between those of metals and nonmetals
- Ionization energies between those of metals and nonmetals
- Possess some characteristics of metals/some of nonmetals
- Reactivity depends on properties of other elements in reaction
- Often make good semiconductors

Metals are generally good conductor of electricity. It is because metal has free electrons in it, according to modern bonding concepts metals have a special type of bond which is called metallic bond. The metal atom held together in a way there valence electrons are delocalized and free to move in the entire crystal. This is known as sea model. These free electrons help in conduction of electricity.

For example cooper wires are commonly used to conduct electricity because they have free electrons which conduct electricity.

On the other hand most nonmetals are poor conductor of electricity it is because they do not possess free electrons like metals. Some nonmetals do conduct electricity. For example, Graphite has layer structure and posses free electrons which conduct electricity.

Chemical properties:

Differences between Metals and Nonmetals

Metals	Nonmetals
Lose their valence electrons easily.	Gain or share valence electrons easily.
Form oxides that are basic.	Form oxides that are acidic.
Are good reducing agents.	Are good oxidizing agents.
Have lower electro negativities	Have higher electro negativities
Usually have 1-3 electrons in their outer shell.	Usually have 4-8 electrons in their outer shell.

Physical properties

How can you compare physical properties of Metals and Nonmetals? Some differences are given below:

Metals	Nonmetals
Good electrical conductors and heat conductors.	Poor conductors of heat and electricity.
Malleable - can be beaten into thin sheets.	Brittle - if a solid.
Ductile - can be stretched into wire.	Non-ductile.
Possess metallic luster.	Do not possess metallic luster.
Opaque as thin sheet.	Transparent as a thin sheet.

Lecture 13

Metallurgy of Copper & Aluminum

Almost all metals are found in the combined state as compounds on the crust of the earth. So we have to extract them. This process of metal extraction is called Metallurgy.

Metallurgy is the science and art of extracting a metal from its ores and carrying out different processes to bring metals into their useful forms. Thus, the various processes involved in the extraction of metals from their ores and refining them are broadly known as metallurgy.

Minerals: The natural materials in which the metals or their compounds occur in the earth are called minerals.

Ores: Those minerals from which the metals can be extracted profitably are called ores.

Gangue or Matrix: The rocky impurities, including silica and earthly particles, present in an ore are called gangue or matrix.

Metallurgy of Aluminium:

Aluminum is the most abundant metal. It is the third most abundant element in the earth crust (about 7%). Aluminium is a reactive metal and so does not occur free in nature. It occurs in clays in the form of aluminium silicates.

Ores of aluminium:

Aluminium has a number of ores. Some important ores are as follows:

1. Oxide Ores:

    Bauxite, $Al_2O_3.xH_2O$
    Corundum, Al_2O_3

2. Fluoride Ore:

    Cryolite, $3NaF.AlF_3$ or Na_3AlF_6

3. Silicate Ores:

Kaolin, $Al_2O_3.2SiO_2.2H_2O$
Potash mica, $K_2O.3Al_2O_3.6SiO_2.2H_2O$

Extraction of Aluminium:

(Ref: **http://www.s-cool.co.uk/gcse/chemistry/extraction-of-metals/revise-it/the-electrolysis-of-bauxite)**

Aluminium is commonly extracted from its ore bauxite. The bauxite (red-brown solid) - aluminium oxide mixed with impurities - is extracted from the earth. The extracted aluminium oxide is then treated with alkali, to remove the impurities. This results in a white solid called aluminium oxide or alumina. The alumina is then transported to huge tanks. The tanks are lined with graphite, this acts as the cathode. Also blocks of graphite hang in the middle of the tank, and acts as anodes. The alumina is then dissolved in molten cryolite - this lowers the melting point.

Electricity is passed and electrolysis begins. Electrolysis is the decomposition of a compound using electricity.

When dissolved, the aluminium ions and oxide ions in the alumina can move.

Reaction at Cathode:

$$4Al^{+} + 12e^{-} \longrightarrow 4Al(s)$$

Reaction at Anode:

$$3C + 6O^{2-} \longrightarrow 3CO_2 (g) + 12e^{-}$$

Purification of Bauxite:

Bauxite when obtained from the earth crust contains many ipurities such as ferric oxide, silica, and titanium oxide. These impurities are removed. Baeyer process is commonly used for the purification of bauxite. In this process, the ore is treated with concentrated NaOH solution called caustic soda. The following reaction takes place:

$$Al_2O_3 + 2NaOH \longrightarrow 2Na[Al(OH)_4](aq)$$

Then CO_2 is passed.

Reaction with CO_2

$$2Al(OH)_4^{-} + CO_2 \longrightarrow 2Al(OH)_3(s) + CO_3^{2-} + H_2O$$

The product is filtered and heated at 1000 °C. The process is called calcination. As a result of this process, pure alumina is obtained.

$$Al(OH)_3 + Heat \longrightarrow Al_2O_3 (s) + 3H_2O (g)$$

Now we have pure alumina.

Electrolysis of Alumina to obtain Aluminium:

The process used for the electrolysis of alumina is called Hall's process. Alumina is aluminium oxide, Al_2O_3. This is subjected to electrolysis. The cell used for electrolysis is a steel container whose inner surface is lined with graphite. The powdered alumina is mixed with fused cryolite and fluorspar. The melting point of alumina is very high, but it dissolves in molten cryolite at about 1000 °C. when electricity is passed, aluminium is deposited at the graphite cathode. From there it is drawn out in molten form**.** This aluminium is 99% pure. Further purification is carried out through a process called Hoope's method.

Refining of Aluminium:

In the Hoope's process, aluminium is purified by electrolytic method. For this purpose a box-like cell is used. The cell is operated in a manner that in it three layers are maintained. The lower layer consists of impure aluminum alloyed with copper. The middle layer consists of a solution of cryolite and barium fluoride. The upper layer consists of pure aluminium. These layers remain separated due to difference is specific gravity. The lower layer acts as anode where aluminium is oxidized and Al^{3+} ions move toward the upper layer which is negatively charged. This layer acts as cathode and when Al^{3+} ions reach in this layer they gain electrons and are deposited as aluminium metal there.

Reaction at Anode:

$$\mathbf{Al \rightarrow Al^{3+} + 3e^{-}}$$

Reaction at cathode:

$$\mathbf{Al^{3+} + 3e^{-} \rightarrow Al}\ \textbf{(pure aluminium)}$$

The aluminium obtained in this process is about 99.99% pure.

Metallurgy of Copper:

Copper is a common metal. It is used for a wide variety of purposes. It is a good conductor of electricity so its wires are used in electrical appliance and cables.

Over 360 ores of Copper are known. Some important ores are as follows:

Sulfide ores:

Copper pyrite or chalcopyrite, CuS.FeS or $CuFeS_2$
Chalcocite, Cu2S

Carbonate ores:

Malachite, $CuCO_3.Cu(OH)_2$
Azurite, $2CuCO_3.Cu(OH)_2$

Oxide ores: Cuprite, Cu_2O

Extraction of Copper:

Extraction of copper is good example of pyrometallurgy. In the metallurgy of copper the following steps are commonly used:

- Mining of ore from its mines
- Crushing and grinding of the ore
- Concentration of the ore and its purification
- Chemical process to obtain metal from the ore
- Purification of the metal
- Conversion of the metal into alloys

Important process employed in the extraction of copper:

- Concentration through Froth-flotation
- Roasting
- Smelting
- Reduction (Bessemerization)
- Refining

Concentration by Froth flotation method:

By concentration here we mean to free the ore from impurities. Copper is commonly extracted from copper pyrite. Copper pyrite is concentrated by a process called froth-floatation. Ore is crushed and ground to make a powder. This is placed in a large tank containing water and oil (such as pine oil). The mixture is stirred by blowing air through it. The ore is wetted by oil and rises to the surface from where it is skimmed off. The impurities (called gangue) are wetted with water settle down at the bottom.

Roasting:

By roasting here we mean heating in air strongly but below the melting point of the ore. As a result, impurities are converted into silicate slag. The slag floats at the surface from where it is removed. The ore undergoes the following reaction:

$$CuS.FeS + 4O_2 \longrightarrow Cu_2S\ (s) + 2FeO\ (s) + 3SO_2\ (g)$$

Smelting:

By smelting here we mean heating the product obtained from roasting strongly in a Reverberatory furnace. The product from the roasting is mixed with silica (SiO2) and heated at 1100 °C. Following reaction takes place in the furnace:

$$FeO + SiO_2 \longrightarrow FeSiO_3$$

Ferrous silicate is formed which is a slag. It is less dense that molten copper matte, Cu_2S, and so floats the surface from where it is removed.

Reduction (Bessemerization):

Molten copper(I) sulfide, Cu_2S, is put in Bessemer converter and heated strongly. As a result of this elemental copper is produced. The copper obtained is called the blistered copper.

$$2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$$
$$2Cu_2O(l) + Cu_2S(l) \longrightarrow 6Cu\ (l) + SO_2(g)$$

This copper is called blistered copper because it has blisters on it which are produced due to evolution of sulfur dioxide. When copper solidifies, sulfur dioxide escapes from it and produces blisters. Blistered copper is about 99% pure.

Refining of Copper:

Copper is refined by electrolytic process. In the electrolytic cell CuSO4 solution is used as an electrolyte. Impure copper is used to act as anode, while pure copper is used to act as a cathode. At anode, copper atoms lose electrons and become copper ions. These copper ions move through the solution and reach at the cathode. At cathode these copper ions gain electrons and deposit there a atoms. So in this way refined copper is obtained which is almost 100% pure.

Reaction at Anode:

$Cu \rightarrow Cu^{2+} + 2e^-$

Reaction at Cathode:

$Cu^{2+} + 2e^- \rightarrow Cu\ (s)$ pure copper

Lecture 14

Metallurgy of Iron

Ores:

An ore is the naturally occurring compound of a metal from which that metal can be extracted. In the earth crust, metals are generally found in the form of compounds which are found mixed with other substances these naturally occurring minerals of metals are called ores. For example; halite is an ore of Na and hematite and magnetite are the ores of Fe.

Alloys:

A material that has metallic properties and is composed of two or more chemical elements of which at least one is a metal (i.e. steel is an alloy of carbon in iron; stainless steel is an alloy of carbon, chromium and sometimes nickel in iron.)

Metallurgy:

It is the science and art of obtaining a metal from its ores. There are number of types of metallurgy.

In electrometallurgy, electricity is used to obtain a metal. Electrolysis is carried out of the molten or solution form of the ore and metal is obtained at the cathode. For example; Na is obtained by the electrolysis of NaCl by the Downs process.

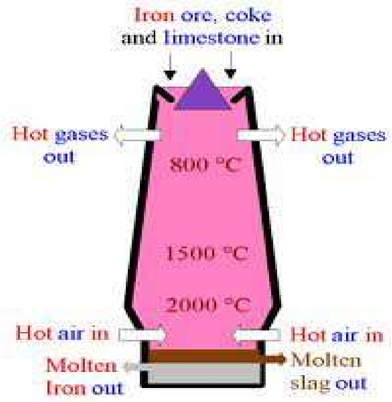
In pyrometallurgy strong heat is used to extract a metal from its ores. For example, Fe is extracted from its ores by heating at high temperature.

Iron is extracted through pyrometallurgy in a furnace called Blast Furnace. Commonly hematite and magnetite are used to obtain iron. A number of reactions occurs at high temperature in the blast furnace.

The reactions occurring in blast furnace are as follows.

- Reactions in blast furnace:

$Fe_2O_3 + CO \rightarrow 2Fe_3O_4 + CO_2\,(g)$
$Fe_3O_4 + CO \rightarrow 3FeO + CO_2\,(g)$
$FeO + CO \rightarrow Fe(l) + CO_2\,(g)$



Iron is a common metal. It has been known since prehistoric ages. Iron is soft, malleable, and ductile.

Occurrence:

Iron is a common metal. How it occurs?

- Metallic iron occurs in the free state in only a few localities in the world.
- In chemical compounds the metal is widely distributed.
- After aluminum, iron is the most abundant of all metals, and ranks fourth in abundance among all the elements in the earth's crust.
- It is found in meteorites, usually alloyed with nickel.
- Iron is found in the earth crust in the form of ores. Its principal ore is hematite and other important ores are magnetite, siderite, and limonite.
- Pyrite, FeS, the sulfide ore of iron, is not processed as an iron ore because it is too difficult to remove the sulfur.
- Small amounts of iron occur in combination in natural waters, in plants, and as a constituent of blood.

Physical properties of Iron metal:

What are the common physical properties of iorn?

- The atomic number of iron is 26, and atomic weight is 55.847.
- Pure iron melts at about 1535° C and boils at 2750° C.
- The specific gravity of iron is 7.86.
- It is a metal which is easily magnetized at ordinary temperatures, but at about 790° C the magnetic property of iron disappears.

Chemical Properties:

Describe some common properties of iron.

- ➢ Iron reacts with a number of elements. For example, it make compounds with the halogens (fluorine, chlorine, bromine, iodine), sulfur, phosphorus, carbon, and silicon.
- ➢ Iron reacts with acids and displaces hydrogen from dilute acids.

- It reacts with oxygen to form ferrosoferric oxide, Fe_3O_4.
- Rust: When exposed to moist air, iron undergoes deterioration or corrosion and forms a reddish-brown, flaky, hydrated ferric oxide commonly known as rust.
- When iron is dipped into concentrated nitric acid, it forms a layer of oxide that renders it *passive*—that is, it does not react chemically with acids or other substances.

Give some uses of iron:

- Iron has a wide variety of applications. It is used in processed forms, such as wrought iron, cast iron, and steel.
- Commercially pure iron is used for the production of galvanized sheet metal and of electromagnets.
- Many compounds of iron are used in different purposes. Ferrous sulfate (FeSO4), which is also called green vitriol or copperas. It is used as a mordant in dyeing, as a tonic medicine, and in the manufacture of ink and pigments.

Metallurgy of Iron: what are the reactions that take place in the Blast Furnace?

- Combustion of Coke

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} + \text{heat}$$
$$CO_{2(g)} + C_{(s)} \rightarrow 2CO_{(g)}$$

- Reduction of Fe_2O_3

$$2Fe_2O_{3(s)} + 3C_{(s)} \rightarrow 4Fe_{(l)} + 3CO_{2(g)}$$
$$Fe_2O_{3(s)} + 3CO_{(g)} \rightarrow 4Fe_{(l)} + 3CO_{2(g)}$$

- Calcination

$$CaCO_{3(s)} + \text{heat} \rightarrow CaO_{(s)} + CO_{2(g)}$$

- Slag formation

$$CaO_{(s)} + SiO_{2(s)} \rightarrow CaSiO_{3(l)} \text{ (slag)}$$
$$CaO_{(s)} + Al_2O_{3(s)} \rightarrow Ca(AlO_2)_{2(l)}$$

What are the Products which are formed in the Blast Furnace:

- Pig iron - 93-95% Fe, 3-5% C, 1% Si, 0.1- 0.3% P, <1% S
- Waste gases – CO_2 and CO
- Slag – $CaSiO_3$ and $Ca(AlO_2)_2$

Pig Iron:

Pig iron usually refers to the iron alloy with carbon content of the 2 to 4.3%, also known as cast iron. Besides carbon, pig iron also contains silicon, manganese and small amounts of sulfur and phosphorus. It cannot be forged, but can be cast. According to the presence of carbon under the different forms, pig iron can be divided into steel making pig iron, foundry pig iron and ductile iron.

What is cast iron?

This is pig iron melted with scrap Iron. It is the least pure of all forms of iron containing 93% Fe and 5% C.

The cast iron with carbon content of less than 0.2% is called wrought iron or pure iron. The cast iron with carbon content of 0.2-1.7% is called cast steel. So, cast steel is a kind of special cast iron. More than 2% of content is called pig iron.

What is wrought iron?

It is the purest form of iron produced when impurities are removed. It contains 0.5% impurities. Wrought iron is very soft, plastic and easily deformed, but its strength and hardness are lower, so not widely used.

What is steel?

Steel is a common form of iron which usually contains 0.1 to 2% carbon. Steel has many types. Since the pure iron metal is not very strong, impurities are added into it.

For example, carbon is added in iron to make steel which is much more stronger than iron.

Lecture 15

Corrosion and its Prevention

We all are aware of the rusting of iron. In the same manner most other metals also deteriorate with time. This process is called corrosion.

Corrosion occurs in all substances. It is the chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties. However, the term is commonly used with reference to metals. It can be broadly defined as follows.

“The deterioration of a metal as a result of its reaction with the environment is called corrosion”.

Chemically corrosion is an oxidation process that occurs at the surface of a metal. The rusting of iron, tarnishing of silver, the development of a green coating on copper are well known forms of corrosion. Corrosion is a great cause of the damage of metallic articles. Bridges, ships, vehicles, and other metallic things suffer from corrosion badly.

Sources of Corrosion:

Following are the common causes or sources of corrosion.

- Contact with atmosphere
- Submersion in water or water solutions
- Underground soil attack.
- Contact with chemicals.

There are two major factors which increase the rate of corrosion rapidly. They are;

- Temperature
- Moisture

Rate of corrosion:

Corrosion is a chemical process. It is an oxidation-reduction reaction that occurs at the surface of a metal. In this process the metal undergoes oxidation. Different metal corrode with different speeds. Gold is so stable that it does not corrode. Alkali metals like sodium and potassium corrode rapidly when exposed to atmosphere. Iron corrodes slowly, and silver, copper and tin corrode very slowly.

Rusting of Iron:

The corrosion of major concern is the rusting of iron. It is the cause of huge economic loss every year. From common person to big industries all suffer from corrosion in one way or the other. Now the question is what the rust is.

Rusting is a chemical reaction. When iron cones in contact with oxygen and moisture it is oxidized to hydrated ferric oxidized, $Fe_2O_3.xH_2O$. This is rust. This substance is porous and flaky. So it is removed away continuously. Thus the whole metal is eaten away.

Iron + Oxygen + Water ==> Hydrated Iron(III) oxide

Protection of iron form Rusting:

The protection of corrosion can be classified as follows:

- Active corrosion protection
- Passive corrosion protection
- Permanent corrosion protection
- Temporary corrosion protection

Active corrosion protection:

The aim of active corrosion protection is to influence the reactions which proceed during corrosion. It is possible to control the corrosion reaction in such a manner that corrosion is avoided. Examples of such an approach are the development of corrosion-resistant alloys and the addition of such materials to the metal which can inhibit corrosion.

Passive corrosion protection:

In passive corrosion protection, the metal is mechanically isolated from the damaging environment. For example by using protective layers, films or other coatings rusting can be avoided.

Permanent corrosion protection

The purpose of permanent corrosion protection methods is mainly to provide protection at the place of use. Machines are located, for example, in factory sheds and are thus protected from extreme variations in temperature, which are frequently the cause of condensation.

Prevention of Corrosion:

There are a number of methods which are used to avoid or slow down corrosion in a metal and rusting of iron in particular.

Protective metallic coating:

In this method a metal is coated with a thin layer of another metal which is resistant to corrosion. Rusting of iron can be prevented by coating it with tin, zinc or chromium. Tin plating is a well-known technique. In this technique, a layer of tin is applied on the surface of ion container. Tin cans are good example. When zinc is coated on iron, the process is called galvanizing, and the iron coated with zinc is called galvanized iron. However, zinc is not used in food cans because it readily reacts with acids found in food stuff and fruit juices.

Coating with paints:

Metal can be protected against corrosion by applying acoating of paints on their surfaces. For this purpose, any paint can be used. However, red lead and zinc chromate are commonly used. Grease, plastic emulsions, and enamels can also be used for this purpose. Oiling is a common household and small scale industrial method to protect small tools from rusting.

Cathode Protection:

Corrosion is actually an electrochemical process. During the corrosion reaction the metal plays the role of anode where oxidation occurs which eats out the metal. If we connect iron through a conductor to a more reactive metal in a manner that the electrical circuit is established, then oxidation will occur on the other metal and iron will be acting as cathode. This method will then protect iron from corroding. For example, if an underground iron pipe is connected to a zinc rod. The zinc rod will undergo corrosion and iron will not. This method can be used to protect ship and underground foundations of bridges from rusting.

Alloying:

Many metals can be made more resistant to corrosion by making their alloys. Steel, bronze, brass are metal alloys and are more stable than their pure metals.

Stain less steel is an alloy of iron. A wide variety of stainless steels are made today for different purposes. The common stain less steel has the following composition. C = 0.18 %, Cr = 18 %, Ni = 8 %, rest is iron or Fe. Stainless steel is used to make surgical instrument and cutlery etc.

Applications of Alloys:

Alloys are very important, as they have special properties and are more viable and useful than the pure metals. They have greater resistance to corrosion. For example, steel is mire resistance to corrosion than pure iron.

Many alloys also have useful magnetic properties. For example, **Alnico** has a strong magnetic properties. It is **Fe-Al-Ni-Co**.

Very hard steel is used to make jaws of rock crushers. It has Manganese and Vanadium.

Some alloys also have attractive colours, For example, Au-Cu is an alloy which has red or yellow colour.

Tin plating and methods of tin plating:

The art of applying tin on the surface of a metal is called tin plating. The purpose of tin plating is to protect the metal from corrosion. Tin plating of iron is very common.

There are a number of ways to coat tin on iron.

Electroplating is commonly used for large scale tin plating. This is an electrolytic process. For this purpose, an electrolytic cell is made in the cathode is made of iron sheet and tin is used as anode. The electrolytic solution contains a salt of tin such as tin sulfate or tin chloride. When electric current is passed, tin ions move to the iron cathode and are deposited on it. In this way a layer of tin is coated on the surface of iron sheet.

Another method to coat tin layer on iron surface is **hot-dip method**. In this method, sheets of iron are dipped in molten tin.

Classical method of tin plating is a manual technique. A metal tool or article is polished with tin with the help of a rag or brush. Traditionally, brass and copper utensils are tin plated by this method.

Stainless steel:

Steel is an alloy of iron. There are many types of steel. A very useful type of steel is the stainless steel. It is so called because it is resistant to corrosion or rusting. The composition of common stainless steel is as follows: chromium 18%, nickel 8% and carbon 0.18 %.

The stainless steel is hard and has a high tensile strength. Why it is resistant to rusting? This is due to the thin film of chromium oxide which is developed on the surface due to the reaction of chromium with oxygen. This is hard and tough film and does not corrode.

Applications of Stainless Steel:

- It is used to make cutlery
- It is used to make surgical instruments
- It is also used to make different household utensils and containers.
- It is also used to make automobiles parts, decoration aricles and electronic appliances.

Lecture 16

Periodic Table

In this lecture we will discuss two important elements, namely hydrogen and oxygen.

Hydrogen:

Hydrogen is unique element. Its atom is the smallest atom and has only 1 proton and 1 electron. It is generally placed at the top of group IA along with alkali metals but it is not a metal and it is not fully justified to place it in group IA.

Hydrogen is the most abundant element in the universe. The stars are mostly composed of hydrogen. In the earth crust hydrogen is found in the form of compounds. The most abundant compound of hydrogen is H_2O. Petroleum and natural gas also contains hydrogen. Hydrogen is also a part of organic compounds.

Isotopes of hydrogen: Hydrogen exists in the form of three isotopes. They are ordinary hydrogen or protium, heavy hydrogen or deuterium, and radioactive hydrogen or tritium.

Industrial Preparation of hydrogen:

On large scale hydrogen is prepared by a number of process. Some of them are discussed below.

- **Electrolysis of Water:**

In this method, electricity is passed through water containing a small amount of sulfuric acid. Hydrogen is obtained at cathode. At anode oxygen is obtained.

$2H_2O \rightarrow 2H_2 + O_2$

- **Coke and Steam Process:**

Coke (a form of carbon) is mixed with steam and strongly heated. Water gas is produced which is a mixture of carbon monoxide and hydrogen gas.

$$C + H_2O \xrightarrow{1200\,^\circ C} [CO + H_2]\ \text{Water gas}$$

How to separate H_2 from CO ?

1. Liquefaction process: the b.p. of CO = -192 °C and b.p. of H_2 = -253 °C. When this mixture is liquefied, CO first liquefies and thus separated leaving behind hydrogen gas.
2. Bosch Process: Then more steam is added and the mixture is heated strongly in the presence of ferric oxide. A mixture of carbon dioxide and hydrogen gas is obtained. This is known as Bosch process.

$$CO + H_2 + H_2O \xrightarrow[Fe_2O_3]{1000\ ^\circ C} CO_2 + 2H_2$$

How to separate CO_2?

Carbon dioxide is separated by passing the mixture through water under pressure. Carbon dioxide is dissolved in water and hydrogen is liberated.

- **Steam and hydrocarbon process:**

In this process a mixture of methane and steam is passed over a nickel catalyst at about 900 C under high pressure. A mixture of carbon monoxide and hydrogen gas is obtained.

$CH_4 + H_2O \rightarrow CO + 3H_2$

Carbon monoxide is separated by the method discussed above.

Laboratory Preparation:

In the laboratory, hydrogen gas can be prepared by the action of a dilute solution of a strong acid on reactive metals like zinc.

Action of dil. Acids on metals:

- $Zn + 2HCl \longrightarrow ZnCl_2 + H_2\ (g)$
- $Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2\ (g)$

Action of Water on CaH_2

$CaH_2 + 2H_2O \qquad Ca(OH)_2 + 2H_2\ (g)$

Chemical reactions of hydrogen:

1. Reaction with Oxygen: Burning of H_2

   $2H_2 + O_2 \longrightarrow 2H_2O + \text{Heat}$

2. Reaction with N_2

   $3H_2 + N_2 \longrightarrow 2NH_3$

3. Reaction with Sulfur

   $H_2 + S \longrightarrow H_2S$

4. Reaction with Phosphorus

   $3H_2 + 2P \longrightarrow 2PH_3$

5. Reaction with Chlorine

   $H_2 + Cl2 \longrightarrow 2HCl$

Applications of H_2

- Preparation of NH_3 (heating H_2 and N_2 at 500 °C using Fe_2O_3/Al_2O_3 as catalyst. The process is called Haber process.
- Preparation of HCl: Hydrogen gas is reacted with chlorine gas to obtain HCl.
- Preparation of methanol: heating water gas with ZnO_2/Cr_2O_3 catalyst:
  $CO + 2H_2 \longrightarrow CH_3OH$
- Hydrogenation of vegetable oils to ghee

Hydrides:

The binary compounds of hydrogen with other elements are called hydrides. Hydrogen reacts with almost all elements and forms binary compounds. Common examples are H_2O, NH_3, HX (X is a halogen), CH_4 and other hydrocarbons.

Ionic Hydrides: With alkali metals and calcium, hydrogen forms ionic hydrides.

$2Li + H_2 \rightarrow 2LiH$

$2Na + H_2 \rightarrow 2NaH$

$Ca + H_2 \rightarrow CaH_2$

They are ionic compounds and show typical properties of ionic compounds.

Covalent Hydrides: The hydrides of p-Block elements are covalent hydrides.

Common examples: CH_4, NH_3, H_2O, HCl, PH_3, H_2S, HBr, HI.

They are molecular. Have low b.p., m.p.

Metallic hydrides: The hydrides of transition metals are called metallic hydrides.

They are non-stoichiometric. They are interstitial compounds and they retain properties of the original metal.

Complex hydrides: common examples are $LiAlH_4$ $NaBH_4$

Nascent Hydrogen: The hydrogen at the time of its generatioin in a reaction is called nascent hydrogen. It is atomic hydrogen. It may react with any reactant available, or atomic hydrogen may produce hydrogen gas. For example:

$Zn + 2HCl \rightarrow ZnCl_2 + 2[H]$

$2[H] \rightarrow H_2$

Oxygen: Oxygen is a common element. In the earth crust, it is the most abundant element. Oxygen atom has 8 protons and 8 electrons. Common isotope of oxygen has 8 neutrons. Molecular formula of oxygen gas is O_2. Oxygen gas is about 20% of the air by volume. Oxygen is necessary for life. Most organic compounds also contain oxygen.

Characteristics of Oxygen:

- Abundance: most abundant in Earth crust, 50%
- In the air: 21% by volume
- Most abundant compounds: H_2O, SiO_2
- In the periodic table, group VIA,
- Electronegativity: 3.4.
- Electronic configuration:
- O_2 is paramagnetic

Allotropes of Oxygen: there are two allotropes of oxygen:

- Ordinary oxygen, dioxygen, oxygen gas, O_2
- Ozone, O_3

Formation of O^{2-} ions: oxygen has high electron affinity, so it absorbs electrons. Absorption of first electron is exothermic while that of the second electron is endothermic.

$$O + 2e^- \rightarrow O^{2-}$$

Preparation of Oxygen:

Laboratory preparation: By heating potassium chlorate using MnO_2 as catalyst: heated at 240°C

$$2KClO_3 \rightarrow 2KCl + 3O_2 (g)$$

Industrial preparation: On the industrial scale, oxygen is prepared by the following methods.

- **Electrolysis of water:** Electrolysis of water produces hydrogen and oxygen gases.
- **Liquefaction of air:** The major components of air are oxygen and nitrogen. Their boiling points are given below.

b.p. of O_2 = -183°C

b.p. of N_2 = -196°C

So these gases can be separated by liquefaction.

Chemical properties:

Oxygen is a reactive element and reacts with almost all metals and non-metals, the compounds the oxygen formed with other elements are of different types.

1. Reaction with C, S, P, H_2 oxides are formed.

$$C + O2 \rightarrow CO2$$

$S + O2 \rightarrow SO2$

$P4 + 5O2 \rightarrow P4O10$

$2H2 + O2 \rightarrow 2H2O$

2. With sodium

The following reaction occurs at room temperature:

$4Na + O_2 \rightarrow 2Na_2O$ sodium oxide

At higher temperature:

$2Na + O_2 \rightarrow Na_2O_2$ sodium peroxide

3. With potassium

Potassium reacts with oxygen to for superoxide:

$K + O_2 \rightarrow KO_2$ potassium superoxide

4. With Mg, Ca and Ba

$2Ca + O_2 \rightarrow 2 CaO$

5. Reaction with Fe

$2Fe + O_2 \rightarrow 2FeO$

$4FeO + O_2 \rightarrow 2Fe_2O_3$

6. Reaction with CH4 (Combustion)

CH4 and other hydrocarbons burn:

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O + \text{Heat}$

Oxides: The binary compounds of oxygen:

The binary compounds of oxygen with other elements called oxides. Oxides are of three types.

1. Normal oxides; in which the oxidation number of oxygen is -2.
2. Peroxides; in which the oxidation number of oxygen.
3. Super oxides; in which the oxidation number of oxygen is -1/2

Normal oxides are very conmen. H_2O, CO_2, NO_2 are its examples. H_2O_2 is hydrogen per oxide.

KO_2 is potassium super oxide.

Types of Oxides:

1. Covalent oxides or acidic oxides. They are oxides of nonmetals, CO2, H2O, NO2, SO2, etc. When dissolved in water, they form acids:

CO2 + H2O → H2CO3

SO2 + H2O → H2SO3

SO3 + H2O → H2SO4

2. Basic oxides: The basic oxides are the oxides of metals. They react with water to form bases:

Na2O + H2O → 2NaOH
CaO + H2O → Ca(OH)2
BaO + H2O → Ba(OH)2

Interesting chemistry of KO_2: How O_2 gas is produced in rescue masks? It is done by the reaction of K_2O with water:

$$4KO_2 + 2H_2O \rightarrow 4KOH + 3O_2$$

$$2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$$

Applications of Oxygen gas:

1. Oxidizing agent: it is used in steel making, and is used to burn impurities.
2. To bleach pulp and paper (oxidation of coloured compounds usually gives colourless products).
3. Medical use (to ease breathing difficulties)
4. To produce oxy-acetylene flame
   2C2H2 + 5O2 → 4CO2 + 2H2O
5. To produce oxy-hydrogen flame

Compounds of Oxygen: Sulfuric Acid

Preparation of H2SO4 by Contact Process involves the following reactions:

1. S + O2 → SO2
2. $2SO_2\ O_2 \rightarrow 2SO_3$ Catalyst: V_2O_5
3. $SO_3 + H_2SO_4 + H_2S_2O_7$
4. $H_2S_2O_7 + H_2O \rightarrow 2H_2SO_4$

Lecture 17

Properties and Trends in Periodic Table

Nitrogen is a common element, it occurs in the form of element and compounds. Nitrogen gas is composed of N_2 molecules. Nitrogen gas is found 78% by volume in air. Nitrogen molecule N_2 is very stable because there is a triple bond which binds nitrogen atoms together. In the triple bond, 1 bond is sigma and other 2 bonds are pi bonds.Nitrogen compounds are numerous; examples include ammonia, urea and nitric acid. Many organic compounds also contain nitrogen. Naturally occurring minerals of nitrogen are saltpeters KNO_3 and $NaNO_3$.

Laboratory preparation of nitrogen gas: By heating NH_4NO_2 which is prepared by the action of ammonium chloride with sodium nitrite:

$$NH_4Cl + NaNO_2 \rightarrow NH_4NO_2 + NaCl$$

$$NH_4NO_2 \rightarrow N_2 + 2H_2O$$

Large scale obtaining: On large scale nitrogen gas is obtained by liquefaction of air:

b.p. of O_2 = -183°C

b.p. of N_2 = -196°C

Chemical Properties:

1. Reaction with oxygen:
   $N_2 + O_2 \rightarrow 2NO$ heating at 1500-2000 °C
2. Heating with Mg, Ca, B
   Nitrides are formed: BN (boron nitride), Ca_3N_2 (calcium nitride)
3. Reaction with H_2 (Haber Process) produces ammonia (NH_3).

Applications of Nitrogen gas:

1. Nitrogen is used to prepare ammonia which is then used to prepare nitric acid and fertilizer.
2. It is used as an inert gaseous blanket to exclude O_2 to a processing and packaging of foods.
3. Liquid nitrogen is used as a coolant to freeze foods rapidly.

Ammonia, NH_3

Ammonia is a base. It is because it has a lone pair of electrons which can be donated to a proton, thus ammonia is electron pair donor or it is an proton acceptor.

$$N_2 + H^+ \longrightarrow NH_4^+$$

Ammonia is a binary compound of nitrogen and hydrogen. Its molecular formula is NH_3. It is prepared on industrial scale by the method called Haber process. In this process nitrogen is reacted with hydrogen in the presence of catalyst Fe2O3/ Al2O3.

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

The reactants are heated at 500 ^{0}C.

Laboratory preparation of ammonia:

In the laboratory ammonia can be prepared by the action of base on ammonium chloride.

1. $NH_4Cl + NaOH \longrightarrow NH_3 + NaCl + H_2O$
2. $NH_4Cl + Ca(OH)_2 \longrightarrow NH_3 + H2O + CaCl_2$

Nitric Acid, HNO_3

Nitric acid is an important compound of nitrogen. It is one of the common acids used extensively in laboratories and industries.

Preparation of Nitric acid:

Nitric acid is prepared industrially by a method known as **Ostwald's method**.

In this method nitric acid is prepared by the oxidation of ammonia.

There are three main steps:

1. Oxidation of ammonia to nitric oxide
2. Oxidation of nitric oxide to NO_2.
3. Reaction of NO_2 with water to produce nitric acid.

Chemical reactions are shown by the chemical equations as follows:

$$4NH_3 + 5O_2 \longrightarrow 4NO + 6H_2O$$

$$2NO + O_2 \longrightarrow 2NO_2$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + NO$$

Lecture 18

Halogens (VII)

The elements of group VII are called halogens, which mean salt formers. Halogens include the following elements:

1. Fluorine (F)
2. Chlorine (Cl)
3. Bromine (Br)
4. Iodine (I)
5. Astatine (At)

Atomic Numbers of Halogens are given below along with the name of the element:

1.	F	Fluorine (9)
2.	Cl	Chlorine (17)
3.	Br	Bromine (35)
4.	I	iodine (53)
5.	At	Astatine (85

Occurrence: halogens occur in the form of different compounds in the earth crust.

1. Salts e.g., NaCl, Br^- , I^-
2. Fluorspar, CaF_2
3. Cryolite, Na_3AlF_6,
4. Fluorapatite, $Ca_5(PO_4)_3F$

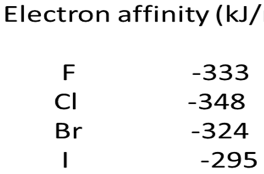
Halogens form diatomic molecules: F_2 Cl_2 Br_2 I_2

Physical States: In their elemental forms, halogens occur as diatomic molecules. They have different physical states. Fluorine and chlorine are gases, bromine is a liquid and iodine is a solid.

Electronegativity: The electronegativity of an element is the ability of the element to attract the shared pair of electrons toward it. The halogens are very electronegative elements. Fluorine has the highest electronegativity among all the elements. The electronegativity values of halogens are given below:

1.	F	4.0
2.	Cl	3.0
3.	Br	2.8
4.	I	2.5

Electron affinity: The electron affinity of an element is the energy absorbed or evolved when an electron enters into an atom of the element. A halogen atom absorbs an electron to make a negative ion (anion). During this process energy is evolved. Electron affinity values of halogens are given below:



	Electron affinity (kJ/mol)
F	-333
Cl	-348
Br	-324
I	-295

Chlorine gas (Cl_2)

In this lecture we will study chlorine as a typical halogen. Chlorine is a yellowish green coloured gas.

Laboratory preparation: In the laboratory, chlorine gas is prepared by the action of hydrochloric acid on manganese dioxide.

$$4HCl + MnO_2 \rightarrow MnCl_2 + 2H_2O + Cl_2(g)$$

Industrial preparation:

On the industrial scale chlorine gas is prepared by sodium chloride.

1. Electrolysis of molten NaCl (Downs Cell Process):

It may be prepared by the electrolysis of molten NaCl. For this purpose a special electrolytic cell is used which is called Downs cell and the process thus is called the Downs cell process. The melting point of NaCl is 801°C, which is a very high temperature. To lower the melting point of NaCl, calcium chloride is added. The electrolytic mixture in the Downs cell contains 40% NaCl and 60% $CaCl_2$. Chlorine gas is obtained at anode.

$$2NaCl \rightarrow 2Na + Cl_2(g)$$

2. Electrolysis of Brine (Castner-Kellner Cell Process): In this method aqueous solution of sodium chloride (common salt) is electrolyzed. The aqueous solution of NaCl is called brine. Chlorine gas is obtained at the anode. In the Castner-Kellner cell Moving mercury cathode is used. Sodium is discharge at the mercury electrode and forms sodium amalgam. The sodium amalgam is taken into another compartment where it react with water to produce NaOH and hydrogen gas. Mercury is recirculated.

$$2NaCl + 2H_2O \rightarrow 2NaOH + H_2(g) + Cl_2(g)$$

Physical properties:

1. Chlorine is a greenish yellow gas.
2. It has pungent smell.
3. Chlorine is a toxic gas. If it comes in contact, it produces inflammation of lungs, throat and nose.
4. Its boiling point is -34.6 C, and melting point is -101.6C.
5. It is fairly soluble in water.

Chemical properties of Chlorine gas:

Chlorine is a reactive gas. It reacts with many metals and non-metals. It also reacts with compounds.

Reactions with metals:

$2Na + Cl_2 \rightarrow 2NaCl$

$2K + Cl_2 \rightarrow 2KCl$

$2Sb + 3Cl_2 \rightarrow 2SbCl_3$

$2Fe + 3Cl_2 \rightarrow 2FeCl_3$

$Sn + 2Cl_2 \rightarrow SnCl_4$

Reactions with non-metals

$P_4 + 6Cl_2 \rightarrow 4PCl_3$

$P_4 + 10Cl_2 \rightarrow 4PCl_5$

$2S + Cl_2 \rightarrow S_2Cl_2$

Reaction with hydrogen:

$H_2 + Cl_2 \rightarrow 2HCl$

Reactions with Compounds

Reaction with Ammonia:

$2NH_3 + 3Cl_2 \rightarrow N_2 + 6HCl(g)$

$6NH_3 + 6HCl \rightarrow 6NH_4Cl(s)$

Oxidation of FeCl2 to FeCl3

$2FeCl_2 + Cl_2 \rightarrow 2FeCl_3$

Chlorine replaces bromine and iodine from their compounds. It is a stronger oxidizing agent than bromine and iodine.

$2NaBr + Cl_2 \rightarrow 2NaCl + Br_2$

$2KI + Cl_2 \rightarrow 2KCl + I_2$

Photochemical reactions: chlorine also undergoes photochemical reactions. In these reaction a photon of light breaks the chlorine molecule into chlorine free radicals which are chlorine atoms. The chlorine radicals then react with other compounds such as methane.

$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl$

Chlorine as a bleaching agent:

Chlorine reacts with water to form HCl and HOCl. HOCl then breaks up to form atomic or nascent oxygen. The atomic oxygen is very reactive and is a strong oxidizing agent. It reacts with the spots and removes them. This is called bleaching action.

$H_2O + Cl_2 \rightarrow HCl + HOCl$

$2HOCl \rightarrow 2HCl + 2[O]$ Nascent Oxygen

Uses of Chlorine:

Chlorine is a useful element. It is used for a variety of purposes.

- For sterilizing drinking water
- To prepare PVC (Polyvinyl chloride) plastic
- To prepare CCl_4 and $CHCl_3$
- To prepare HCl
- To prepare bleaching powder, $CaOCl_2.H_2O$

Hydrochloric Acid (HCl)

One of the important compounds of chlorine is HCl **which** hydrogen chloride. It is a gas. When it is dissolved in water, we obtain hydrochloric acid. Hydrochloric acid is a commonly used acid. Hydrogen chloride can be prepared by a number of methods.

Laboratory preparation: In laboratory HCl can be prepared by the action of sulfuric acid on sodium chloride.

$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl(g)$

Industrial preparation: On industrial scale, HCl is prepared by the reaction of chlorine with hydrogen gas.

$H2 + Cl2 \rightarrow 2HCl$

Chemical reactions of HCl:

- Reaction with a base, NaOH or KOH

$HCl + NaOH \rightarrow NaCl + H2O$

$HCl + KOH \rightarrow KCl + H2O$

- Reaction with ammonia

$HCl + NH3 \rightarrow NH4Cl$

- Reaction with calcium oxide

$2HCl + CaO \rightarrow CaCl2 + H2O$

- Reaction with sodium carbonate

$2HCl + Na2CO3 \rightarrow 2NaCl + CO2 + H2O$

Lecture 20

Properties of Solutions

Mixture:

A mixture is a “mixed” substance which obtained on mixing two are more substances without undergoing any chemical reaction.

Types of mixtures: Mixtures are of two types:

- Homogenous Mixtures
- Heterogeneous. Mixtures

Homogeneous mixture

A Homogeneous mixture has uniform composition throughout its body. They are known as solutions. For example, when sugar or salt is dissolved in water it forms a solution in which the sugar or salt and water are uniformly mixed (the sugar or salt is dissolved uniformly in water). Another common example is air.

Heterogeneous mixture

A Heterogeneous mixture is that which does not have uniform composition. e.g. granite which consists of quartz, feldspar and mica and you can identify each of the substances separately in the mixture.

Heterogeneous mixtures can be suspensions or colloids.

Solution:

“A solution is a homogenous mixture of atoms, ions or molecules of two or more substances.”

A homogenous mixture is that which has uniform composition throughout its body. In other words, it has only one phase. Suppose, we stir some sugar into a glass of water. The grains of sugar disappear and we have a clear liquid that looks just like pure water. The sugar molecules have dispersed among the water molecules, and sugar and water thus form a solution.

Types of solution

Solutions can be classified on the basis of their state: solid, liquid, or gas. Thus there are nine types of solutions. The most common type of solutions is a solid dissolved in liquids. The liquid is mostly water.

Solvent and Solute

The solvent is the component of a solution that is visualized as dissolving another component called a solute. Usually the component present in the larger quantity is called the solvent, and the component present in the smaller quantity is called the solute.

Concentration and its units

By concentration we mean the relative amounts of the components of a solution. It tells us the ratio of the quantity of one component to the quantity of the other or to the total quantity of solution. It has many units. Some common units are discussed below.

Percentage

The ratio of the mass of the solute to the mass of the solution multiplied by 100 is called mass percentage.

$$\text{Mass Percentage of a solute} = \frac{\text{Mass of the solute}}{\text{Mass of solution}} \times 100$$

Example

A solution contains 25 grams of sugar in 150 grams of water. What is the %age by mass of sugar in the solution? (14.3%)

For liquid-liquid solutions, it is sometimes more convenient to express the concentration in the units of percentage by volume:

$$\text{Volume Percentage of a liquid} = \frac{\text{Volume of the liquid}}{\text{Total volume}} \times 100$$

Example

A solution of 10 ml acetone and 50 ml water was prepared. Calculate the percentage by volume of acetone. (16.67%)

Molarity (M)

Molarity is the most common unit of concentration used in chemistry.

“Molarity or the molar concentration is the number of moles of solute dissolved per dm^3 of solution”. (1 dm^3 is equal to 1 Liter)

Thus

$$\text{Molarity} = \frac{\text{Number of moles of solute}}{\text{Volume of solution in liters}}$$

Example: 15g of NaOH were dissolved in enough water to prepare 100 cm^3 solution. Calculate the molarity of NaOH. (3.75 mol/dm^3)

Molarity (m)

"Molarity is the number of moles of solute dissolved per kilogram of solvent".

Example: 15 g of NaOH was dissolved in 100 g of water. Calculate the molality of NaOH.

(3.75 mol/Kg)

Molality is independent of temperature as it is mass-to-mass ratio, while molarity is temperature dependent as it is mass to volume ratio.

Solubility and Saturation

This is an important question that how much a solute at maximum can be dissolved in a given quantity of a solvent. The maximum amount of a solute dissolved in a given amount of a solvent is called **solubility** of that solute. It can be precisely defined as follows:

"The solubility of a solute in a given solvent is the concentration of that solute in its saturated solution at a specific temperature".

Solubility can be expressed in any of the units of concentration. However, it is commonly expressed in grams per dm^3.

"A saturated solution is the solution which can dissolve no more amount of the solute, at the given temperature".

If we start slowly adding sugar (sucrose) to water taken in a beaker. At first it dissolves rapidly, but then gradually the dissolution process becomes slow. The continued addition of sugar eventually brings the solution to saturation, after which any additional sugar simply falls to the bottom of the container where it remains undissolved. At this point, there is an equilibrium between the excess undissolved solute and the dissolved one.

This solution of sugar is said to be saturated, and the concentration of sugar in this solution is called its solubility.

Dissociation of Solutes

When sugar dissolves in water, the solute particles that are dispersed through out the resulting solution are sugar molecules. On the other hand many solids (electrolytes) undergo dissociation or ionization when dissolve. For example, NaCl forms sodium and chlorine ions in solution.

The solubility of NaCl at 25^oC have been estimated to be 5 mol/dm^3 or 292.5 g/dm^3.

Sparingly Soluble Substances

The substances that have very low solubility are known as **sparingly soluble** or slightly soluble substances. Example, AgCl.

Hydration

When an ionizable substance (an acid, base or salt) is added to water to form a solution, it breaks up into ions. The ions are surrounded or encaged by water molecules due to attraction between the ions and water molecules. This process is known as hydration.

Water is a polar molecule in which the hydrogen atoms are partially positively charged and the oxygen atom is partially negatively charged. Being polar, water molecules surround the ions dipped in it. Thus, in water solution all cations and anions are hydrated. The cations are attracted by the negative ends (oxygen) of water molecules and the anions are attracted by the positive ends of the water molecules (hydrogens).

Water of hydration

Water can become incorporated in solid compounds by occupying specific crystal sites in the solid without being strongly bonded to a specific atom. This water is called water of hydration or water of crystallization. The compounds having water of hydration are called hydrates. Some examples are $CaSO_4.2H_2O$, $CuSO_4.5H_2O$, $CaC1_2.6H_2O$. Many hydrates lose their water of hydration upon heating and form anhydrous compounds. For example, crystalline copper sulfate pentahydrate (blue) changes into anhydrous copper sulfate (white) on heating.

Hydrolysis

“The reaction of water with an anion or a cation or both of a salt causing a change in the pH is called hydrolysis”.

Colloids:

Colloids form the dividing line between solutions and heterogeneous mixture. They are not true solution. In colloids the disperse particles are larger than typical molecules. In colloids we don’t have solute or solvent. Rather, we have dispersed phase and dispersion medium colloids scattered light. This is called Tyndal effect.

Solution	Colloid
i. This is the homogeneous and stable mixture of a solute in solvent.	i. This is the heterogeneous and stable mixture of particles in the solvent.
ii. Particle sizes of solutes are very small does not visible under light microscope.	ii. Particles are larger sized and visible through the light microscope.
iii. Solute evenly distributed does not show. Brownian movement, tyndal effect etc.	iii. Particles are remaining scattered does not steeled down longer perion. They show Brownian motion and exhibit tyndal effect.

What is a saturated solution?

A saturated solution is that solution which cannot dissolve more solute at a given temperature. If in such a solution you add more solute at that temperature, it will not dissolve and will settle down at the bottom. Thus, the solution which can not dissolve more solute at a particular temperature is called a saturated solution.

What is solubility?

The amount of solute needed to form a saturated solution in a given quantity of solvent at specific temperature is called the solubility of that solute in that solvent at temperature. In other words solubility is the maximum amount of solute that will dissolve in a given amount of solvent at a particular temperature.

How molarity is different from molality?

Molarity is a unit of concentration. It is the number of moles of solute present per litter of solution.

Molality is another unit of concentration. It is the number of moles of solute present per Kg of solvent. So, molarity is mass per volume whereas molality is mass per mass. Therefore, molarity varies with temperature but there is no effect of temperature on molality.

Lecture # 21

Acids, Bases

Arrhenius concept of acid and base:

According to Arrhenius theory an acid is substance which produces H^+ ions when dissolved in water, examples; HCl, HNO_3 etc.

$$HCl \rightarrow H+ \quad + \quad Cl^-$$

According to this theory a base is a substance which produces OH^- when dissolved in water. Examples include NaOH and KOH.

$$NaOH \rightarrow Na^+ \quad + \quad OH^-$$

When an acid and a base react, they cancel each other. This reaction is known as neutralization and in neutralization reaction a salt and water is formed. Example;

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{NaOH} \longrightarrow \underset{\text{Salt}}{NaCl} + \underset{\text{Water}}{H_2O}$$

Some bases	Their uses
Ammonia (NH_3)	Production of fertilizers (ammonium and nitrate salts), used in the manufacture of nitric acid, neutralize the acid (in the petroleum industry) and prevent premature coagulation in natural / synthetic latex.
Aluminium hydroxide ($Al(OH)_3$)	Manufacture other aluminium compound and to make gastric medicine (antacid)
Calcium hydroxide ($Ca(OH)_2$)	To make cement, limewater, neutralize the acidity of soil and application of sewage treatment.
Sodium hydroxide	Used in the manufacturing of soaps, detergents, and cleaners.

Lowry-Bronsted concept of acid and base:

According to Lowry-Bronsted concept, an acid is a proton donor and a base is a proton acceptor.

When acid-base reaction occurs, another set of acid and base is formed. They are call d

conjugate acids and bases.

Example: When HCl is dissolved in water the following reaction occurs.

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

Hydronium ($H3O^+$) ion is a **conjugate** acid whereasCl^- ion is conjugate base.

Reaction of acids with metals:

$Al + HCl \longrightarrow AlCl_3 + H_2$

$Mg + H_2SO_4 \longrightarrow MgSO_4 + H_{2s}$

$Fe + H_2SO_4 \longrightarrow FeSO_4 + H_2$

Acid-base reactions:

$NaOH + HNO_3 \longrightarrow NaNO_3 + H_2O$

$KOH + CH_3COOH \longrightarrow CH_3COOK + H_2O$

Reactions of acids with metal oxides:

$Al_2O_3 + 6HCl \longrightarrow 2AlCl_3 + 3H_2O$

$3K_2O + 2H_3PO_4 \longrightarrow 2K_3PO_4 + 3H_2O$

Acid and Base Strength

According to **Arrhenius definitions**, an acid furnishes H^+ ions and a base furnishes OH^- ions in their aqueous solutions. For example:

$HCI(g) \rightarrow H^+ (aq) + CI^- (aq)$

$NaOH (s) \rightarrow Na^+ (aq) + OH^- (aq)$

However, all acids, and all bases are not equally strong. The strength of an acid or a base is estimated by a number of parameters, such as:

1. Degree of dissociation
2. Percent degree of dissociation
3. Dissociation constant

Degree of dissociation

It tells us how fast an acid or base undergo dissociation of ionization when they are put in water. Degree of dissociation is the ratio of the number of the moles or molecules dissociated and the total number of the moles or molecules initially taken. Thus

$$\text{Degree of Dissociation} = \frac{\text{Number of moles dissociated}}{\text{Total Number of moles taken}}$$

The higher the degree of dissociation of an acid or a base, the stronger they are. The maximum value of the degree of dissociation is 1.

Percentage Degree of Dissociation

Percent degree of dissociation is obtained by multiplying the degree of dissociation by 100.

Strong acids and bases are almost 100% dissociated in water, while weak acids and bases are not 100% dissociated. HCI, HNO_3, NaOH and KOH are almost 100% dissociated in dilute water solution, while CH_3COOH is only 1.4% and NH_4OH is again 1.4% dissociated.

Dissociation Constant (Ka and Kb)

According to Lowry-Bronsted concept an acid is a proton donor. Thus, in general, an acid, HA, forms the following equilibrium in water:

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

The equilibrium constant expression for this reaction is:

$$K_c = \frac{[A^-][H_3O^+]}{[HA][H_2O]}$$

Water is present in large amount so its concentration is almost constant. Thus, the product Kc $[H_2O]$ is also constant and known as the dissociation constant of an acid and is given the symbol K_a.

$$K_a = \frac{[A^-][H^+]}{[HA]}$$

Strong acids, such as HCI, HNO_3 have very large values of dissociation constants. While weak acids have very small values of Ka, for example:

CH_3COOH	K_a	=	1.8×10^{-5}
HCN	K_a	=	4.9×10^{-10}
H_2O	K_a	=	1.0×10^{-14}

According to Lowry-Bronsted concept a base is a proton acceptor. Thus, in general, a base, B, reacts with water as follows:

$B + H_2O \rightleftharpoons BH^{+} + OH^{-}$

pH and pOH

Pure water is only about 2×10^{-7} percent dissociated (self-dissociation) into ions at $25^{o}C$.

$H_2O \rightleftharpoons H^{+} (aq) + OH^{-} (aq)$

Then, the equilibrium constant, Kc, is

$$Kc = \frac{[H^+][OH^-]}{[H_2O]}$$

Since water is in excess, $[H_2O]$ is constant:

$$K_c\,[H_2O] = [H^+][OH^-] = K_w$$

Thus, $K_w = [H^+][OH^-]$

K_w is known as **ionic product** of water. Its value has been experimentally found as:

$$K_w = 1\text{x}10^{-14}\ \text{mol}^2\ \text{dm}^{-6}$$

Or $K_w = 1 \text{ x } 10^{-14}\ \text{mol}^2\ \text{lit}^{-2}$

In pure water (or in a neutral aqueous solution)

$$[H^+] = [OH^-] = 10^{-7}\ \text{mol/dm}^3$$

The H^+ ion concentration in solution can range from more than 10 mol/dm^3 to less than $1\text{x}10^{-15}$ mol/dm^3. The pH scale was devised as a convenient way of expressing such a wide range of concentration. The pH is defined as follows:

> *"The pH of a solution is the negative logarithm to the base*
>
> *10 of the hydrogen ion (or hydronium ion) concentration".*

Mathematically,

$$\text{pH} = -\log_{10}[H^+]$$

or $\text{pH} = -\log_{10}[H_3O^+]$

The concept of the pH was proposed in 1909 by the Danish chemist Soren Sorenson (1868-1939).

In the same way we can also define pOH.

$$\text{pOH} = -\log[OH^-]$$

$$\text{pH} = \text{p}K_\text{a} + \log\frac{[\text{A}^-]}{[\text{HA}]}$$

Table: 7.1 pH, pOH, (25oC), and H+ ion, oH ion concentration

	[H+], M	pH	[OH], M	pOH	
More acidic ↑	10	-1	10-15	15	More acidic ↑
	1	0	10-14	14	
	10-1	1	10-13	13	
	10-2	2	10-12	12	
	10-3	3	10-11	11	
	10-4	4	10-10	10	
	10-5	5	10-9	9	
Neutral	10-7	7	10-7	7	Neutral
More basic ↑	10-8	8	10-6	6	More basic ↑
	10-9	9	10-5	5	
	10-10	10	10-4	4	
	10-11	11	10-3	3	
	10-12	12	10-2	2	
	10-13	13	10-1	1	
	10-14	14	1	0	
	10-15	15	10	-1	

At 25 ^{o}C,

[H+][OH-] = 1 x 10^{-14}

pH + pOH = 14

Thus,

The pH of a neutral solution is 7, the pH of acids is less than 7 while that of bases is higher than 7.

Problem:

What is the pH of a 0.016 mol/dm^3 solution of NaOH?

Solution:

NaOH is a strong base and dissociates almost 100% to form OH$^-$ ions, thus

$$\begin{aligned}[OH^-] &= [NaOH] \\ &= 0.016\ \text{mol/dm}^3\end{aligned}$$

Therefore,

$$\begin{aligned}pOH &= -\log [OH^-] \\ &= -\log 0.016 \\ &= 1.8 \\ pH + pOH &= 14 \\ pH &= 14 - pOH \\ &= 14 - 1.8 \\ &= 12.2\end{aligned}$$

Measurement of pH

The pH of a solution can be determined by two general methods:

1. Indicators 2. pH meters

Indicators

Indicators are chemical compounds which change colour with pH and thus give an approximate value of the pH of a given solution. There are a number of indicators. A special indicator is the universal indicator, which is a mixture of several indicators that has several colour changes over a wide range of pH.

pH Meters

A pH meter is an electrical instrument that employs two electrodes to measure the potential difference between the solution to be tested and a standard solution of known pH. This potential difference is related to the pH of the solution being tested. The pH is read directly from the dial of the instrument.

Common Indicators:

To determine the end-point in an acid-base titration or to determine the pH of a solution, various compounds are used, that are called indicators. Broadly speaking, *“an indicator is any* *compound which changes colour with the change in pH".* An acid-base indicator is a weak acid (or base) whose colour is different from that of its conjugate base (or acid). Take the example of phenolphthalein (C20H13O4H):

$$C_{20}H_{13}O_4H\ (aq) \rightarrow C_{20}H_{13}O_4^-\ (aq) \quad + \quad H^+\ (aq)$$

(colourless) (red) conjugate base

Table: Some indicators and their colour changes

Indicators	Approximate pH range	Corresponding coloru change
Methyl orange	3.1 – 4.4	Orange to yellow
Bromophenol blue	3.8. - 4.6	Yellow to blue
Methyl red	4.4 – 6.2	Red to yellow
Phenolphthalein	8.0 – 10.0	Colourless to red

A paper strip impregnated with a universal indicator is often used. This is known as pH paper. When a part of this strip is dipped in a solution, the paper shows a colour from which the pH can be judged.

Neutralization

When an acidic solution is added to a basic solution in the right proportion, the properties of each are lost, and a salt and water are formed. This process is called **neutralization.**

"The reaction between an acid and a base that forms

a salt and water is called neutralization".

For Example,

$HCI\ (aq) + NaOH\ (aq) \rightarrow NaCI\ (aq) + H_2O$

$HNO_3\ (aq) + NaOH\ (aq) \rightarrow NaNO_3\ (aq) + H_2O$

Buffers or Buffer Solutions

Normally, solutions change their pH when an acid or a base is added to them. For example, pure water, when kept open, changes its pH from neutral to acidic due to the absorption of CO_2 from air forming carbonic acid (H_2CO_3).

However, there are certain solutions, which tend to maintain their pH. These are known as

buffers or **buffer solutions**.

Definition:

"A buffer solution is a solution which undergoes only a slight change of pH when an acid or a base is added to it".

A buffer offers resistance against any change in its pH. Most commonly:

"A buffer solution is a solution of a weak acid and a salt of it, or a buffer solution is a solution of a weak base and a salt of it."

For example, a solution of acetic acid and sodium acetate forms a buffer: (CH_3COOH + CH_3COONa) solution and a solution of ammonium hydroxide and ammonium chloride forms a buffer: (NH_4OH + NH_4CI) solution

Buffers maintain their pH upon addition of acids or bases by shifting equilibrium position.

Buffers play a very important role in many chemical and biological processes. For example, the control of the pH is very important in the treatment of sewage in electroplating, and in the manufacturing of photographic materials. Maintaining a constant pH is essential for many metabolic processes; the pH of the blood has to be close to 7.4 and the pH of saliva is close to 6.8.

Oxidation and Reduction

Many reactions involve transfer of electrons from one atom to another atom. These reactions are known as **oxidation-reduction reactions.** The loss of electrons from an atom is known as **oxidation**, while the gain of electrons by an atom is called **reduction.** Oxidation and reduction always take place simultaneously and the extent of oxidation is equal to the extent of reduction. That is, the loss of electrons is equal to the gain of electrons. The substance that undergoes oxidation is known as the **reducing agent**, and the substance that undergoes reduction is known as the **oxidizing agent.**

Oxidation Number

A very important question is how to decide whether a given reaction is an oxidation- reduction reaction or not. To recognize such reactions, we can use the concept of **oxidation number**, also known as oxidation state:

"The oxidation number of an atom is an apparent charge that is assigned to it on the basis of certain rules."

For compounds, the oxidation number may be defined as follows:

"Oxidation number of an atom in a compound is the apparent charge on the atom if both electrons of each bond are arbitrarily assigned to the atom of higher electronegativity".

The oxidation number is not the real electrical charge. It is the charge that *would be* associated with a particular atom if we assign both the electrons of each bond to the atom of higher electronegativity. The oxidation number is the measure of the extent or degree of oxidation of an element in its compounds.