

**A.D. M COLLEGE FOR WOMEN (A)., NAGAPATTINAM**

**PG & RESEARCH DEPARTMENT OF CHEMISTRY**

**STUDY MATERIAL**

**III-B.SC CHEMISTRY**

**SEMESTER – VI**

**NUCLEAR, INDUSTRIAL CHEMISTRY**

**&**

**METALLIC STATE**

**BY**

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## **UNIT I : NUCLEAR CHEMISTRY I**

Introduction – composition of nucleus and nuclear forces.

Nuclear stability – o/p ratio, mass defect, binding energy, packing fraction and magic numbers, shell and drop models.

Isotopes – detection and separation. Isotopic constitution of elements and whole number rule. Deviation of atomic weights from whole numbers. Isobars, isotones and isomers.

## **UNIT II : NUCLEAR CHEMISTRY II**

Radioactivity- Radioactive emanations. Disintegration theory – modes of decay – Group displacement law – Rate of disintegration – Half life and average life – Radioactive series, Geiger Nuttal rule. Detection and measurements -Wilson cloud chamber & Geiger Muller Counter.

Nuclear transformations use of projectiles nuclear reactions fission and fusion. Nuclear reactors. Applications of radio isotopes – Medicine, Agriculture, Industry & Carbon dating – Radio active waste disposal

## **UNIT III : INDUSTRIAL CHEMISTRY**

Fossil fuels – varieties of coal and petroleum – petroleum refineries in India. Gaseous fuels – natural, gobar, coal, water, semi water and producer gases. Liquefied Petroleum Gases (LPG)

Safety matches – Introduction, Raw materials and manufacturing methods.

Paints and varnishes- Definition, types and composition.

## **UNIT IV : METALLIC STATE**

Metallic state – packing of atoms in metal (BCC,CCP,HCP). Theories of metallic bonding- Electron gas Pauling and Band theories. Structure of alloys substitutional and interstitial solid solutions – humerothery ratios crystal defects.

Semi conductors – Extrinsic and Intrinsic – n-type and p-type conductors. Structure and uses in electronic industry.

## **UNIT V : INORGANIC POLYMERS & SILICATES**

Inorganic polymers – coordination polymers, metal alkyls, phosphonitric polymers.

Silicates – Classification into discrete an ions, one, Two and three dimensional structure with typical examples. composition, properties and uses of beryl, asbestos, talc, mica, zeolites and ultramarines.

## UNIT- I

### NUCLEAR CHEMISTRY I

#### **Introduction : Nuclear Chemistry**

Nuclear chemistry is the study of the physical and chemical properties of elements which are influenced by changes in the structure of the atomic nucleus. It also deals with the energy released from nuclear reactions and its uses. It is also termed as radiochemistry which includes the study of the formation of the elements in the universe, the design of radioactive drugs for diagnostic medicine and many other applications.

Nuclear chemistry is a fascinating branch of science that delves into the heart of matter, the nucleus of atoms. It explores the transformations and properties of the nucleus, encompassing radioactivity, nuclear reactions, and the synthesis of new elements.

#### **Nuclear Structure and Forces:**

The nucleus, composed of protons and neutrons, is the densest part of an atom. Protons and neutrons are bound together by the incredibly strong nuclear force, overcoming the repulsive electrostatic force between protons.

Nuclear chemistry is the sub-field of chemistry dealing with radioactivity, nuclear processes, and transformations in the nuclei of atoms, such as nuclear transmutation and nuclear properties.

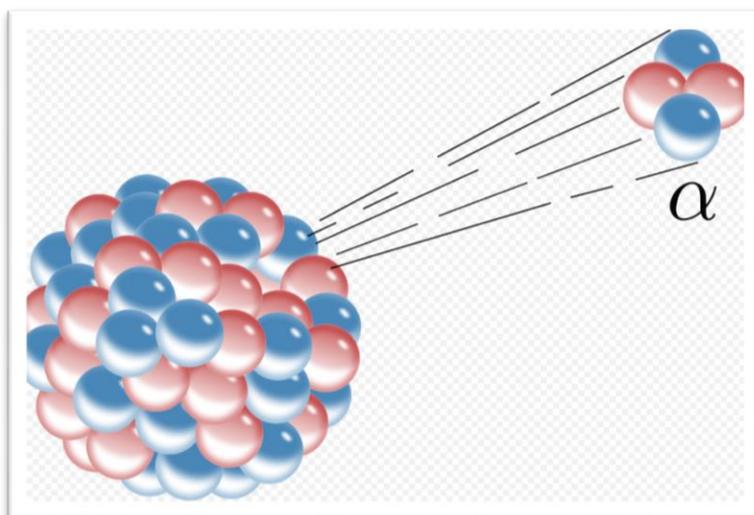
It is the chemistry of radioactive elements such as the actinides, radium and radon together with the chemistry associated with equipment (such as nuclear reactors) which are designed to perform nuclear processes. This includes the corrosion of surfaces and the behavior under conditions of both normal and abnormal operation (such as during an accident). An important area is the behavior of objects and materials after being placed into a nuclear waste storage or disposal site.

It includes the study of the chemical effects resulting from the absorption of radiation within living animals, plants, and other materials. The radiation chemistry controls much of radiation biology as radiation has an effect on living things at the molecular scale. To explain it another way, the radiation alters the biochemicals within an organism, the alteration of the bio-molecules then changes the chemistry which occurs within the organism; this change in

chemistry then can lead to a biological outcome. As a result, nuclear chemistry greatly assists the understanding of medical treatments (such as cancer radiotherapy) and has enabled these treatments to improve.

It includes the study of the production and use of radioactive sources for a range of processes. These include radiotherapy in medical applications; the use of radioactive tracers within industry, science and the environment, and the use of radiation to modify materials such as polymers.

It also includes the study and use of nuclear processes in *non-radioactive* areas of human activity. For instance, nuclear magnetic resonance (NMR) spectroscopy is commonly used in synthetic organic chemistry and physical chemistry and for structural analysis in macro-molecular chemistry.



Alpha decay is one type of radioactive decay, in which an atomic nucleus emits an alpha particle, and thereby transforms (or "decays") into an atom with a mass number decreased by 4 and atomic number decreased by 2.

### **COMPOSITION OF NUCLEUS**

The nucleus, that dense heart of an atom, packs a punch when it comes to composition. Here's a breakdown of its key players:

The Main Cast:

- Protons: These positively charged particles carry the atomic number ( $Z$ ) and define the element. Think of them as the identity cards of your nucleus.

- **Neutrons:** These neutral particles add to the nuclear mass without affecting the charge. The number of neutrons (N) can vary, resulting in different isotopes of the same element.

### **Supporting Characters:**

- **Nucleons:** This term collectively refers to both protons and neutrons, highlighting their role as the building blocks of the nucleus.
- **Mass Number (A):** This number equals the total number of nucleons ( $A = Z + N$ ). It essentially tells you how heavy the nucleus is.

### **The Power Dynamic:**

- **Nuclear Force:** This incredibly strong force, much stronger than the electrostatic repulsion between protons, binds the nucleons together, keeping the nucleus from exploding. It's like super glue for the subatomic world.
- **Stability:** The balance between protons and neutrons determines the stability of a nucleus. Some nuclei are happy just sitting there, while others need to shed particles or rearrange themselves through radioactive decay to achieve stability.

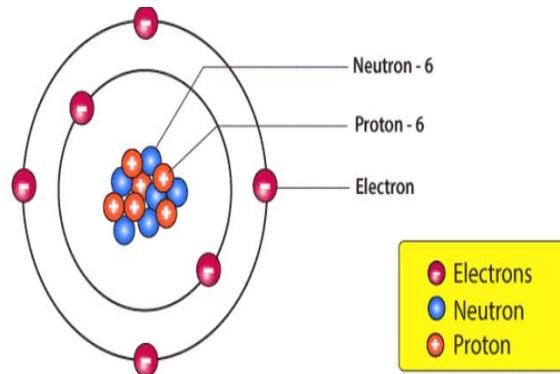
### **Beyond the Basics:**

- **Quarks:** While protons and neutrons were once considered elementary particles, they are now known to be made up of even smaller particles called quarks. This adds another layer of complexity to the composition of the nucleus.
- **Exotic Nuclei:** Scientists are constantly pushing the boundaries, studying nuclei with extremely high or low numbers of protons and neutrons, shedding light on the limits of nuclear stability.

### **Nucleus of an Atom – Composition**

The Nucleus of an atom consists of a tightly packed arrangement of protons and neutrons. These are the two heavy particles in an atom and hence 99.9% of the mass is concentrated in the nucleus. Of the two, the protons possess a net positive charge and hence the nucleus of an atom is positively charged on the whole and the negatively charged electrons revolve around the central nucleus. Since the mass concentration at the nucleus of an atom is immense the nuclear forces holding the protons and the neutrons together are also large. The protons are in such close vicinity to each other inside the tiny nucleus and therefore the electrostatic forces of repulsion also act inside the nucleus. Nuclear energy relies

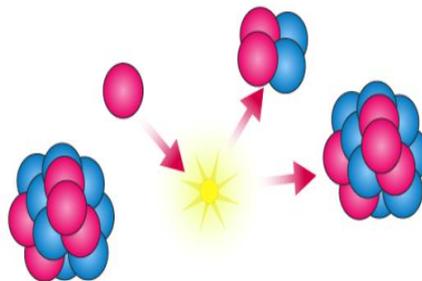
on nothing but releasing the energy trapped in the nucleus of an atom. The total number of protons in a nucleus is equal to the number of electrons revolving around the nucleus and hence the atom, on the whole, is electrically neutral.



## NUCLEAR FORCES

The nuclear force is one of the four fundamental forces of nature, the others being gravitational and electromagnetic forces. In fact, being 10 million times stronger than the chemical binding forces, they are also known as the strong forces. In this section, we will discuss this force in detail. *We can define nuclear force as:*

The nuclear force is a force that acts between the protons and neutrons of atoms.

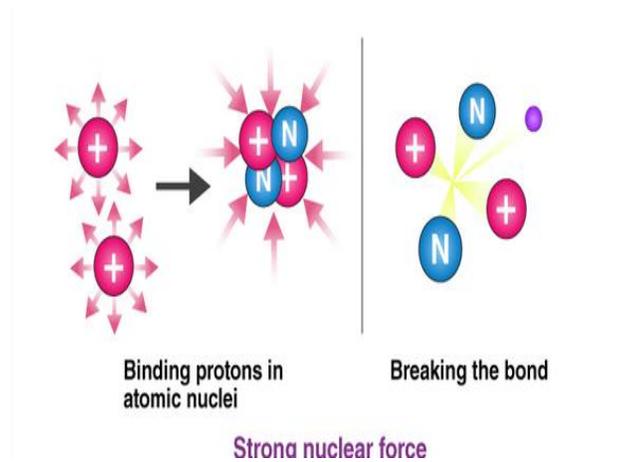


The nuclear force is the force that binds the protons and neutrons in a nucleus together. This force can exist between protons and protons, neutrons and protons or neutrons and neutrons. This force is what holds the nucleus together.

The charge of protons, which is  $+1e$ , tends to push them away from each other with a strong electric field repulsive force, following Coulomb's law. But nuclear force is strong enough to keep them together and to overcome that resistance at short range.

## Properties of Nuclear Force

- It is attractive in nature but with a repulsive core. That is the reason that the nucleus is held together without collapsing in itself.
- The range of a nuclear force is very short. At 1 Fermi, the distance between particles in a nucleus is tiny. At this range, the nuclear force is much stronger than the repulsive Coulomb's force that pushes the particles away. However, if the distance is anything more than 2.5 Fermi, nuclear force is practically non-existent.
- The nuclear force is identical for all nucleons. It does not matter if it is a neutron or proton, once the Coulomb resistance is taken into consideration, nuclear force affects everything in the same way.
- At a distance of less than 0.7 Fermi, this force becomes repulsive. It is one of the most interesting properties of nuclear force, as this repulsive component of the force is what decides the size of the nucleus. The nucleons come closer to each other to the point that the force allows, after which they cannot come any closer because of the repulsive property of the force.



## Nuclear Force Examples

The most obvious example of Nuclear Force, as discussed earlier, is the binding of protons, which are repulsive in nature because of their positive charge.

- On a larger scale, this force is responsible for the immense destructive power of nuclear weapons. The release of energy when a nuclear weapon is detonated is due to strong nuclear forces. It is also used in Nuclear power plants to generate heat for the purpose of generating energy, such as electricity.

- A weaker nuclear force can transform a neutron into a proton and a proton into a neutron. These forces occur in many reactions such as radioactive decay, burning of the sun, radiocarbon dating etc.

Nuclear forces" is a broad term, so to give you the most helpful information, I need a bit more context.

What specifically about nuclear forces are you interested in? Here are some potential areas I can help you with:

- **Basics of nuclear forces:**

- Definition and explanation of the strong and weak nuclear forces
- How they bind protons and neutrons together in the nucleus
- Their role in nuclear stability and radioactive decay

- **Applications of nuclear forces:**

- Nuclear power generation and fission reactions
- Nuclear fusion and its potential for energy production
- Medical applications like radiation therapy

- **Advanced topics in nuclear physics:**

- Quantum chromodynamics (QCD) and the nature of the strong force
- Electroweak theory and the unification of the electromagnetic and weak forces
- Open questions and challenges in nuclear physics research

Please let me know what you're interested in learning, and I'll do my best to provide you with accurate and informative information.

## **NUCLEAR STABILITY**

Nuclear stability refers to the stability of a nucleus of an atom. A stable nucleus does not decay spontaneously. Radioactive elements contain unstable nuclei and decay spontaneously emitting various radiations.

Nuclei of atoms contain protons and neutrons. Positively charged protons repel each other due to electrostatic repulsion between them. This electrostatic repulsion is overcome by the strong nuclear force, the attractive force present between nucleons. Neutrons are important for stabilising the nucleus. If the attractive force between nucleons is less than the electrostatic repulsion then it makes the nucleus unstable and results in decay.

It defines the stability of an isotope of the elements. Nucleons with high binding energy are more stable. Stability of an isotope can be determined by calculating the ratio of neutrons to protons present in a nucleus ( $N/Z$ ). Elements having atomic number less than 20, mostly have proton and neutron ratio 1:1. The number of neutrons increases as the atomic number increases. Most of the stable nuclei have neutrons to protons ratio more than 1. Only  $^1\text{H}$  and  $^3\text{He}$  have neutrons to protons ratio less than one but are stable.

The first 80 elements of the periodic table have stable isotopes. All the elements with the atomic number more than 82 are unstable and radioactive, irrespective of the number of neutrons.

Nuclear stability is a fascinating topic in physics and chemistry, referring to the ability of an atomic nucleus to resist spontaneous decay. Stable nuclei remain intact indefinitely, while unstable nuclei undergo radioactive decay, emitting particles and energy in the process.

Here are some key points about nuclear stability:

#### **Forces at play:**

- **Strong nuclear force:** This short-range but powerful attractive force binds protons and neutrons together within the nucleus.
- **Electrostatic repulsion:** Protons, being positively charged, repel each other. This repulsive force increases with the number of protons.

#### **Factors affecting stability:**

- **Neutron-to-proton ratio:** Generally, nuclei with a neutron-to-proton ratio closer to 1 are more stable for lighter elements. Heavier elements require a higher ratio of neutrons for stability.
- **Magic numbers:** Certain "magic numbers" of protons and neutrons (e.g., 2, 8, 20) correspond to exceptionally stable nuclei, due to the way they fill energy shells within the nucleus.
- **Binding energy per nucleon:** This measures the strength of the nuclear force holding each nucleon (proton or neutron) in the nucleus. Nuclei with higher binding energy per nucleon are generally more stable.

### **Visualization:**

- The "valley of stability" on a chart of nuclides shows the region where stable nuclei are concentrated.
- The chart reveals that most stable nuclei have a neutron-to-proton ratio close to 1 for lighter elements, gradually increasing with atomic number.

### **Consequences of instability:**

- Unstable nuclei decay through various processes like alpha decay, beta decay, and gamma emission.
- Radioactive decay releases energy and particles, making unstable isotopes useful for applications like medical imaging and nuclear power.

The terms "ortho" and "para" refer to the nuclear spin states of diatomic molecules, while nuclear stability deals with the ability of a nucleus to resist radioactive decay. These two concepts are not directly related to each other.

## **NUCLEAR BINDING ENERGIES**

### **N/P RATIO**

The ratio between the number of neutrons present in the nucleus of an element and the number of protons present in the same nucleus is called the N/P ratio.

### **Nuclear spin states (ortho and para):**

In diatomic molecules like hydrogen ( $H_2$ ), the nuclei can have their spins aligned in either the same direction (parallel) or opposite directions (antiparallel).

Parallel spin state is called ortho (o- $H_2$ ).

Antiparallel spin state is called para (p- $H_2$ ).

These spin states affect the molecule's rotational energy levels and hence its physical and chemical properties.

o- $H_2$  has slightly higher energy than p- $H_2$  due to magnetic repulsion between the parallel spins.

At high temperatures, o-H<sub>2</sub> and p-H<sub>2</sub> are equally populated (o:p ratio = 3:1). As the temperature decreases, the o-H<sub>2</sub> population gradually decreases due to conversion to p-H<sub>2</sub> (a process called ortho-para conversion).

At room temperature, the equilibrium o:p ratio is about 75:25.

### **Nuclear stability:**

Nuclear stability is determined by the balance between attractive strong nuclear force and repulsive electrostatic force within the nucleus.

Stable nuclei have a specific ratio of neutrons (n) to protons (p). This ratio increases with the atomic number (number of protons).

For lighter elements, a roughly equal n/p ratio is sufficient for stability.

For heavier elements, a significantly higher n/p ratio is needed due to the increasing electrostatic repulsion between protons.

Nuclei that deviate significantly from the stable n/p ratio are unstable and undergo radioactive decay to reach a more stable configuration.

### **Relationship between ortho-para ratio and nuclear stability:**

There is no direct relationship between the ortho-para ratio of a molecule and the nuclear stability of its atoms.

Ortho-para conversion is a purely physical process involving changes in the rotational energy states of the molecule and does not affect the nuclear structure or stability.

The n/p ratio of an element, which determines its nuclear stability, is a fixed property independent of the spin state of its molecules.

In summary, while both ortho-para ratio and nuclear stability are important concepts in chemistry and physics, they are unrelated to each other. Ortho-para conversion deals with the rotational energy states of molecules, while nuclear stability concerns the balance of forces within the nucleus.

## MASS DEFECTS

Mass defect is the difference between the actual atomic mass and the predicted mass calculated by adding the mass of protons and neutrons present in the nucleus. The actual atomic mass is less than the predicted mass calculated by adding the masses of nucleons. This additional mass is accounted for by binding energy that is released when a nucleus is formed. When a nucleus is formed, some of the mass is converted to energy and this results in the mass defect. Due to this reason, the actual mass of an atomic nucleus is less than the mass of particles it is made up of.

### Mass Defect

The actual mass of the atomic nucleus is always less than the mass of protons and neutrons present in the nucleus. When a nucleus is formed, energy is released. This energy is removed in the form of a reduction in total mass. This missing mass is known as the 'mass defect' and it accounts for the energy released.

The mass defect ( $\Delta M$ ) can be calculated by subtracting the original atomic mass ( $M_A$ ) from the sum of the mass of protons ( $m_p = 1.00728$  amu) and neutrons ( $m_n = 1.00867$  amu) present in the nucleus.

### Mass defect formula:

$$\Delta M = (Zm_p + Nm_n) - M_A$$

$\Delta M$  – mass defect

$M_A$  – mass of the nucleus

$m_p$  – mass of a proton, i.e. 1.00728 amu

$m_n$  – mass of a neutron, i.e. 1.00867 amu

$Z$  – number of protons

$N$  – number of neutrons

## **Nuclear Binding Energy**

Nuclear binding energy is the energy required to split an atomic nucleus into its components. It is the energy equivalent to the mass defect.

Binding energy can be calculated by Einstein's formula,  $E = mc^2$ .

Where  $c$  is the speed of light. In nuclei, the binding energy is so high that it holds a considerable amount of mass.

The actual mass is less than the sum of individual masses of the constituent neutrons and protons in every situation because energy is ejected when the nucleus is created. This energy consists of mass which is ejected from the total mass of the original components and is called a mass defect. This mass is missing in the final nucleus and describes the energy liberated when the nucleus is made.

Mass defect is determined as the difference between the atomic mass observed ( $M_o$ ) and expected by the combined masses of its protons ( $m_p$ , every proton has a mass of 1.00728 AMU) and neutrons ( $m_n$ , 1.00867 AMU).

## **Bond Energy or Bond-dissociation Energy**

We are talking about bond energy and bond-dissociation energy, which are basically measures of the binding energy between the atoms in a chemical bond. Bond energy is the energy that is used to disassemble a molecule into its constituent atoms. It appears in the form of chemical energy released during chemical explosions, the burning of chemical fuel and other processes.

## **Applications**

Binding energy is also applied in determining whether fusion or fission will be favourable. For elements that are lighter than iron-56, the fusion releases energy since the nuclear binding energy rises with the hike in mass. Elements that are heavier than iron-56 release energy on fission since the lighter elements consist of higher binding energy. Hence, there exists a peak at iron-56 according to the nuclear binding energy curve.

## **BINDING ENERGY**

**Binding energy** is typically defined as the smallest amount of energy that is required to remove a particle from a system of particles. In other words, it is the

energy that is used to separate a system of particles into single units. We study about binding energy mostly in atomic physics and chemistry as well as in condensed matter physics. In nuclear physics, the term binding energy is used to describe separation energy.

Binding energy is necessary to split subatomic particles in atomic nuclei or the nucleus of an atom into its components, namely: neutrons and protons or collectively known as nucleons. The binding energy of nuclei is a positive value because every nucleus needs net energy to isolate them into neutron and proton. Binding energy is also applicable to atoms and ions bound together in crystals.

### **Types of Binding Energy**

Binding energy is of several types, and each operates over a different distance and energy scale. An important point to note here is that if the size of a bound system is small, then its associated binding energy will be higher. We will look at the types in brief below.

#### **Electron Binding Energy – Ionization Energy**

Electron binding energy, which is commonly known as ionization energy, is the energy required to remove an electron from its atomic orbital. The electron binding energy is mostly derived as a result of the electromagnetic interaction that occurs between the electron and the nucleus, the other electrons of the atom, molecule or solid that is usually mediated by photons.

#### **Atomic Binding Energy**

The atomic binding energy of the atom is the energy that is used to break down an atom into free electrons and a nucleus. We can say that it is the sum of the ionization energies of all the electrons that belong to a particular atom. The atomic binding energy is derived from the electromagnetic interaction between the electrons with the nucleus, which is mediated by the photons.

#### **Nuclear Binding Energy**

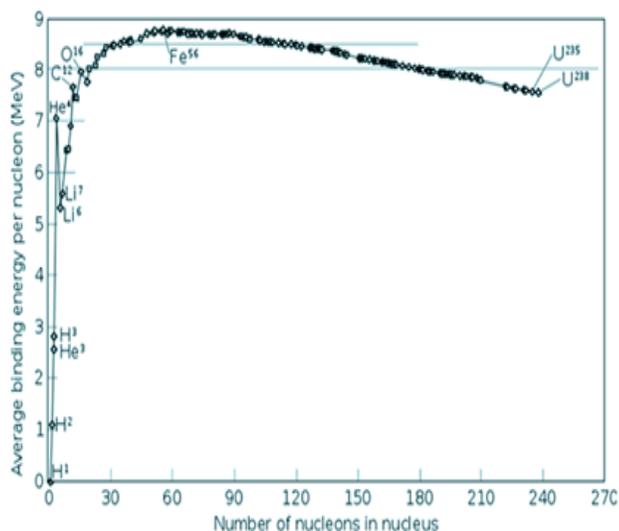
Nuclear binding energy is basically the energy required to dismantle a nucleus into free unbound neutrons and protons. It is the energy equivalent of the mass defect, the difference between the mass number of a nucleus and its measured

mass. Nuclear binding energy is derived from the residual strong force or nuclear force, which again is mediated by 3 types of mesons.

Nuclear binding energy can be determined once the mass defect is calculated, usually by converting mass to energy by applying  $E = mc^2$ . When this energy is calculated, which is of joules for a nucleus, you can scale it into per-mole quantities and per-nucleon. You need to multiply by Avogadro's number to convert into joules/mole and divide by the number of nucleons to convert to joules per nucleon.

Nuclear binding energy is also applied to situations where the nucleus splits into fragments that consist of more than one nucleon, wherein the binding energies of the fragments can be either negative or positive based on the position of the parent nucleus on the nuclear binding energy curve. When heavy nuclei split or if the new binding energy is known when the light nuclei fuse, either of these processes results in the liberation of binding energy.

## BINDING ENERGY



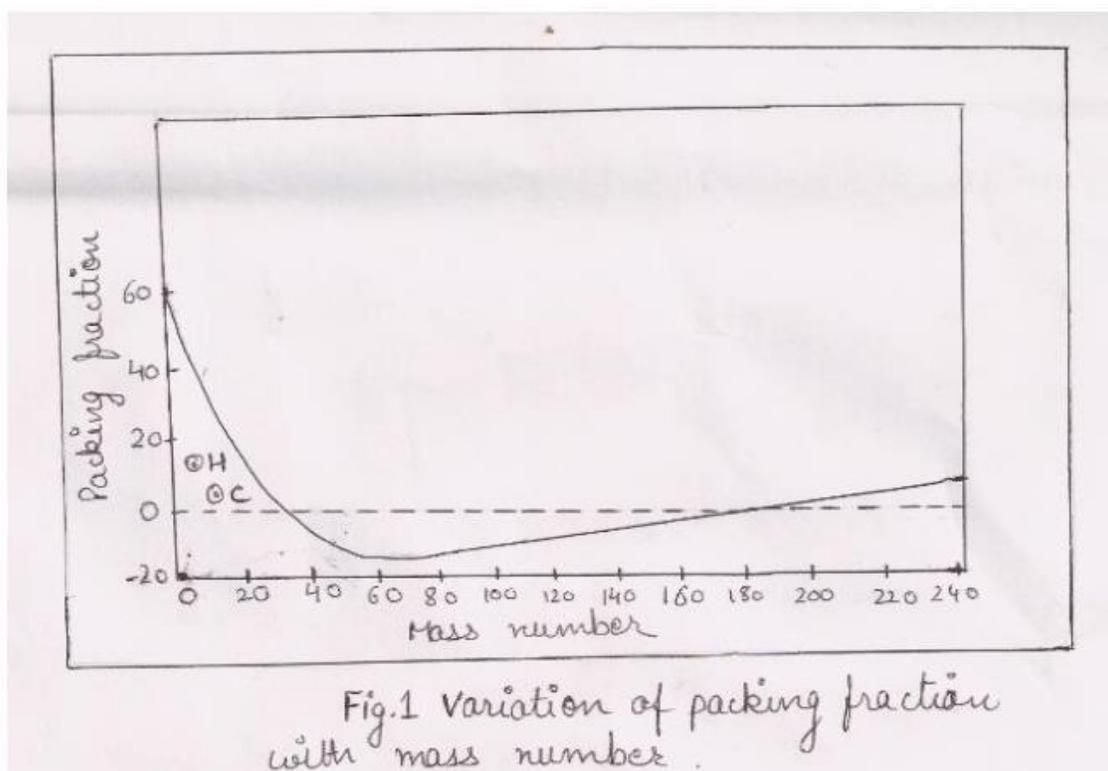
## PACKING FRACTION

Packing fraction is defined as a way of expressing the variation of isotopic mass from whole mass number (atomic mass).

$$\text{Packing fraction} = \frac{\text{Isotopic mass} - \text{Mass number}}{\text{Mass number}} * 10^4$$

This fraction can have positive or can have negative sign. A positive packing fraction describes a tendency towards instability. A negative packing fraction means isotopic mass is less than actual mass number. This difference is due to the transformation of mass into energy in the formation of nucleus. A plot of packing fraction against corresponding mass no's of various elements is as shown.

From figure it is clear that the elements which have less atomic mass (hydrogen, helium, carbon) do not fall on this curve. Therefore, these are stable atoms. Oxygen is highly stable. The packing fraction beyond mass number 200 becomes positive and increases with increase in mass number. It increases instability of these elements.



### Even and odd rule

In nuclear physics, properties of a nucleus depend on evenness or oddness of its atomic number  $Z$ , neutron number  $N$  and, consequently, of their sum, the mass number  $A$ . Most importantly, oddness of both  $Z$  and  $N$  tends to lower the nuclear binding energy, making odd nuclei generally less stable. This effect is not only experimentally observed, but is included in the semi-empirical mass formula and explained by some other nuclear models, such as the nuclear shell

model. This difference of nuclear binding energy between neighbouring nuclei, especially of odd- $A$  isobars, has important consequences for beta decay.

Also, the nuclear spin is integer (mostly 0) for all even- $A$  nuclei and non-integer (half-integer) for all odd- $A$  nuclei.

**Even vs. odd mass number ( $A$ ).**

	<b>Even</b>	<b>Odd</b>	<b>Total</b>
Stable	151	101	252
Long-lived	25	9	34
All primordial	176	110	286

The neutron-proton ratio is not the only factor affecting nuclear stability. Adding neutrons to isotopes can vary their nuclear spins and nuclear shapes, causing differences in neutron capture cross sections and gamma spectroscopy and nuclear magnetic resonance properties. If too many or too few neutrons are present with regard to the nuclear binding energy optimum, the nucleus becomes unstable and subject to certain types of nuclear decay. Unstable nuclides with a nonoptimal number of neutrons or protons decay by beta decay (including positron decay), electron capture, or other means, such as spontaneous fission and cluster decay.

## **MAGIC NUMBERS**

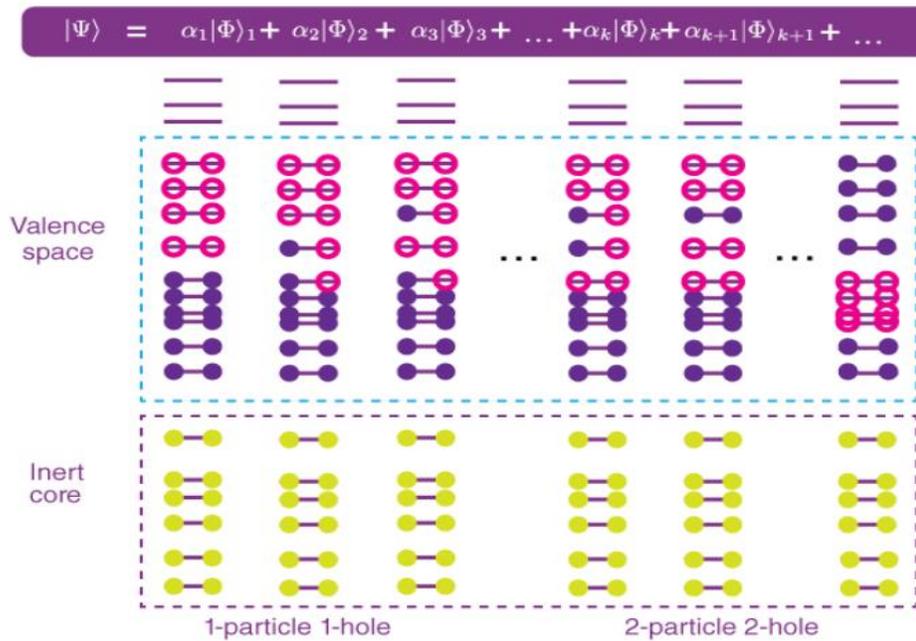
The number of electrons present in the neutral atoms constituting the relatively unreactive noble gases exactly correspond to the atomic magic numbers. The magic numbers for nuclei are 2, 8, 20, 28, 50, 82, and 126.

### **Shell Model**

The nuclear shell model is a model of the atomic nucleus. It uses the Pauli exclusion principle to explain the nucleus structure in terms of energy levels. In order to study the complete nucleus structure, various nuclear shell models were proposed. The first shell model was introduced in the year 1932 by Dmitry Ivanenko and later on developed by various physicists – Maria Goeppert Mayer, Eugene Paul Wigner, and J.Hans.D. Jensen in the year 1949.

### **Nuclear Shell Model**

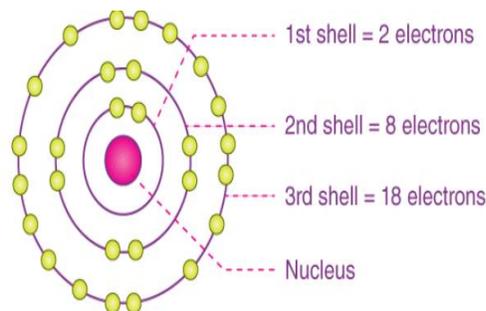
It basically explains the distribution of energy levels into different atom shells and nucleus atom shells. A shell is described as the energy level where particles having the same energy exist. In this model, all the nuclear particles are paired one-to-one, neutron with a neutron, and proton with a proton. The paired neutrons and protons in nuclear energy levels are filled when the number of neutrons or protons is equal to 2, 8,20,28,50,82, or 126. These are the magic numbers that show the most stable nuclei.



The unpaired ones are responsible for the properties of a nucleus and valence electrons are responsible for different chemical properties of elements. With the help of the shell model, we can accurately predict the properties of nuclei such as angular momentum. But, for nuclei which are in a highly unstable state, the shell model needs to be modified or replaced with other models such as the collective model, liquid-drop model, and compound nucleus model.

### Shell Model of the Atom

It explains the arrangement of different electrons present around the nucleus of an atom as per energy levels.



**Atomic Number** = number of electrons in an atom

The atomic shell model explains the structure of atoms. The negatively charged fundamental particles which are known as electrons are considered to occupy diffuse shells in the space that surrounds the positively charged nucleus. The shell which is closest to the nucleus is the first shell.

The shells are designated as:

K	First shell
L	Second shell
M	Third shell and so on

The sequence in which the electrons occupy the shell is given as:

2, 8, 18, 32, 50, 72, 98.

The atomic shell model also helps in understanding the chemical properties of the atoms.

The maximum number of electrons that can occupy the energy level in an atom is found by using the following formula:

$$\text{Electron capacity} = 2n^2$$

Where n is the principal quantum number.

Following is the table for the shell levels and their electron capacity:

Energy Level	Shell Designation	Maximum no. of electrons
1	K	2
2	L	8
3	M	18

4	N	32
5	O	50
6	P	72

## LIQUID-DROP MODEL

**liquid-drop model** in nuclear physics, a description of atomic nuclei in which the nucleons (neutrons and protons) behave like the molecules in a drop of liquid. If given sufficient extra energy (as by the absorption of a neutron), the spherical nucleus may be distorted into a dumbbell shape and then split at the neck into two nearly equal fragments, releasing energy. Although inadequate to explain all nuclear phenomena, the theory underlying the model provides excellent estimates of average properties of nuclei. Russian-born American physicist George Gamow formulated the model in 1929, and Austrian physicists Lise Meitner and Otto Frisch used it in 1938 to explain nuclear fission.

## ISOTOPES

Isotopes are members of a family of an element that all have the same number of protons but different numbers of neutrons. The number of protons in a nucleus determines the element's atomic number on the Periodic Table. For example, carbon has six protons and is atomic number 6.

Isotopes can be defined as the variants of chemical elements that possess the same number of protons and electrons, but a different number of neutrons. In other words, isotopes are variants of elements that differ in their nucleon (The total number of protons and neutrons) numbers due to a difference in the total number of neutrons in their respective nuclei.

Isotopes are primarily represented in two different ways:

- By writing the name of the element followed by a hyphen and the mass number of the isotope. For example, uranium-235 and uranium-239 are two different isotopes of the element uranium.
- By following the AZE notation (also known as the standard notation). This involves writing the symbol of an element and prefixing the atomic number in subscript and the mass number in superscript. For example, the uranium-235 isotope can be represented as  $^{235}\text{U}_{92}$  and the uranium-239 isotope can be represented as  $^{239}\text{U}_{92}$ .

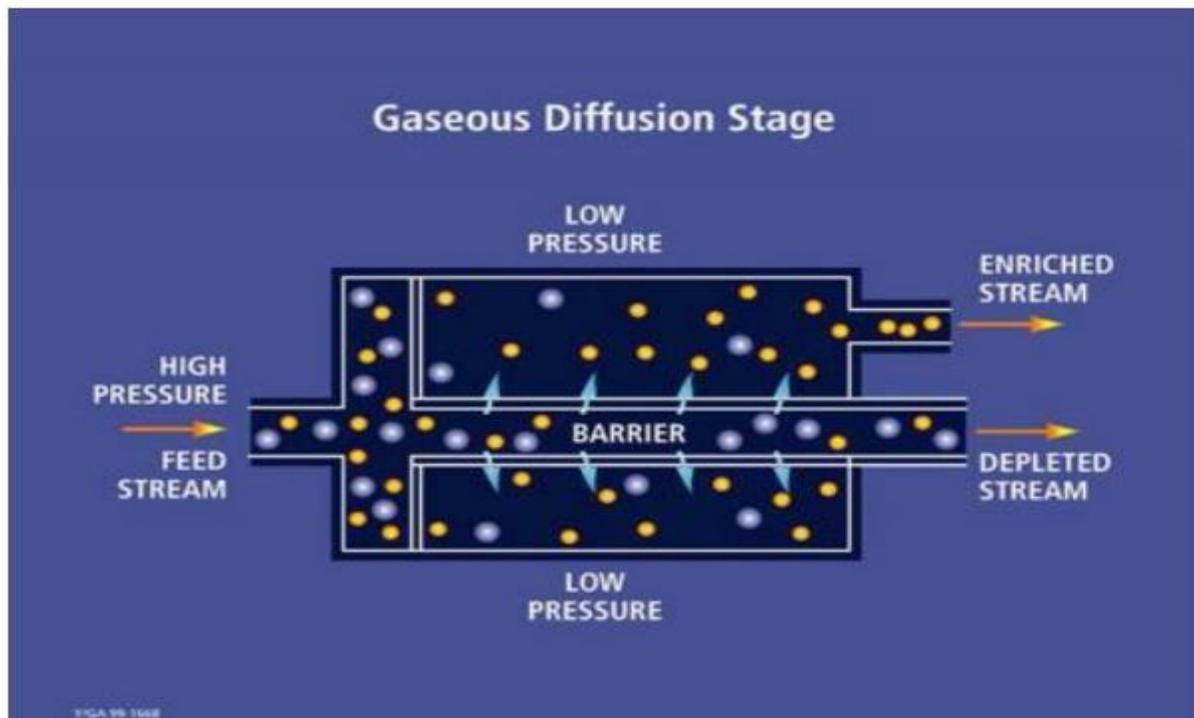
The relative abundance of each isotope can be determined using **mass spectrometry**. A mass spectrometer ionizes atoms and molecules with a high-energy electron beam and then deflects the ions through a magnetic field based on their mass-to-charge ratios.

### Isotope Separation Methods

Once the power that was hidden in uranium became evident, the emphasis shifted to methods to separate the much more potent U-235 from its abundant relative, U-238. This question consumed thousands of hours and millions of dollars.

Scientists had concluded that enriched samples of uranium-235 were necessary for further research and that the isotope might serve as an efficient fuel source for an explosive device. "Enrichment" meant increasing the proportion of U-235, relative to U-238, in a uranium sample. This required separating the two isotopes and discarding U-238. Uranium-235 occurred in a ratio of 1:139 in natural uranium ore. Since they were chemically identical, they could not be separated by chemical means. Furthermore, with their masses differing by less than 1 percent, separation by physical means would be extremely difficult and expensive.

Nevertheless, scientists pressed forward on several complicated techniques of physical separation, all based on the small difference in atomic weight between the uranium isotopes. Manhattan Project director General Leslie Groves wanted to investigate as many possibilities as possible, and had the resources to simultaneously pursue multiple speculative projects.



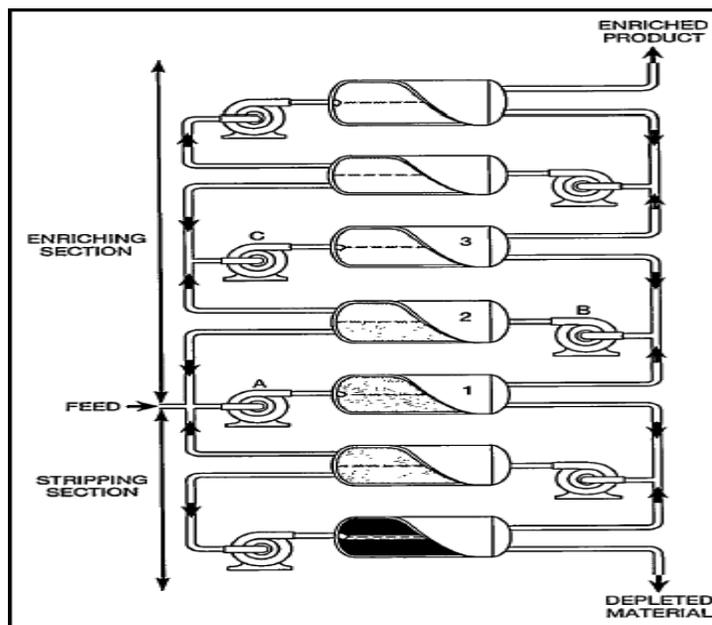
### **Electromagnetic Separation**

The electromagnetic method, pioneered by Alfred Nier of the University of Minnesota, used a mass spectrometer, or spectrograph, to send a stream of charged particles through a strong magnetic field. Atoms of the lighter isotope (U-235) would be deflected more by the magnetic field than those of the heavier isotope (U-238), resulting in two streams that could then be collected by different receivers.

The electromagnetic method as it existed in 1940, however, would have taken too long to separate quantities sufficient to be used in the current war. In fact, 27,000 years would have been required for a single spectrometer to separate 1 gram of uranium-235.

Ernest O. Lawrence of the Radiation Lab at the University of California at Berkeley favored this method and converted his giant cyclotron to accomplish this form of separation more efficiently. This model led to the eventual design and construction of the huge Y-12 Plant complex at Oak Ridge, Tennessee. Because of its exorbitant cost, electromagnetic separation was largely abandoned after the war for weapons production, but it played an important role in the development of the field of nuclear medicine.

## Gaseous Diffusion



Gaseous diffusion's principle was simple: molecules of a lighter isotope would pass through a porous barrier more readily than those of a heavier isotope. The tiny weight difference between U-235 and U-238 meant that initial separation would be negligible. Repeat the process hundreds of times in sequential "cascades," though, and the end product would be significantly enriched uranium.

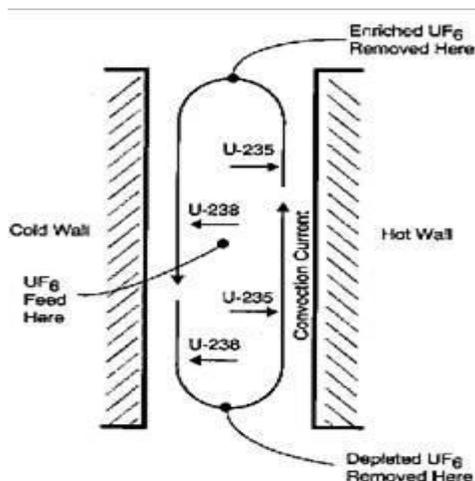
Gaseous diffusion seemed promising in theory, but would clearly be difficult to implement on an industrial scale. Besides the massive scale involved, it was completely unclear in 1940 and 1941 how to construct a satisfactory apparatus for gaseous diffusion. Because of these problems, the S-1 committee did not make this method a priority.

Significant early work on gaseous diffusion happened in Britain, primarily at chemical conglomerate Imperial Chemical Industries (ICI) and the University of Birmingham. Both succeeded in producing a prototype of gaseous diffusion. Starting in 1941, a team at Columbia University in New York also researched gaseous diffusion, and produced a slightly different model.

Centrifuge research faltered in 1942, and General Leslie Groves pushed for more research into gaseous diffusion. In mid-1943, Roosevelt and Churchill signed the Quebec Agreement, under which British nuclear research was subsumed into the Manhattan Project; this meant full exchange of information. But serious problems remained. Besides the need for a porous barrier, component design would have to accommodate uranium hexafluoride, one of the most corrosive gases in the world.

Groves soon ordered the construction of K-25, but as construction crews cleared the site and poured the foundation it was still unclear what exactly was going to go inside the plant. To protect the pipes from corrosion, contractors undertook the new process of nickel coating. Sealing the pipes was also a problem, as grease would interfere with the process and uranium hexafluoride could not be permitted to leak out. The eventual solution was a completely novel seal material: Teflon.

Kellex Corporation undertook the barrier problem: developing a thin metal membrane with millions of tiny openings. After months of research and competition with an incomplete design from the team at Columbia, Groves accepted the Kellex design and ordered it installed in K-25. K-25, the largest roofed building in the world upon construction, would eventually serve as an intermediary step between S-50 and Y-12. Gaseous diffusion was important throughout the Cold War, but uses far more energy than centrifuges, and is now nearly obsolete.



### Liquid Thermal Diffusion

The Uranium Committee briefly demonstrated an interest in a fourth enrichment process during 1940, only to conclude that it would not be worth pursuing. This process, liquid thermal diffusion, was being investigated by Philip Abelson at the Carnegie Institution in Washington. Abelson placed pressurized liquid uranium hexafluoride into the space between two concentric vertical pipes. With the outer wall cooled by a circulating water jacket and the inner wall heated by high-pressure steam, the lighter U-235 isotope tended to concentrate near the hot wall and the heavier U-238 near the cold. Over time, convection would carry the lighter isotope to the top of the column where it could be drawn off. Taller columns would produce more separation.

Like other enrichment methods, liquid thermal diffusion was at an early stage in 1940. Abelson eventually relocated his experimentation to the Naval Research

Laboratory in Washington, DC, whereupon money was obtained to construct a pilot plant at the Philadelphia Navy Yard. When Oppenheimer learned the Navy was using liquid thermal diffusion for enriched uranium in submarines, the Manhattan Project subsequently built the S-50 Plant, which enriched uranium slightly before it was sent to K-25 and Y-12 for further enrichment. The inefficiency of this method meant that, like electromagnetic separation, it was obsolete after the war.

## **WHOLE NUMBERS**

The **whole numbers** are the part of the number system which includes all the positive integers from 0 to infinity. These numbers exist in the number line. Hence, they are all real numbers. We can say, all the whole numbers are real numbers, but not all the real numbers are whole numbers. Thus, we can define whole numbers as the set of natural numbers and 0. Integers are the set of whole numbers and negative of natural numbers. Hence, integers include both positive and negative numbers including 0. Real numbers are the set of all these types of numbers, i.e., natural numbers, whole numbers, integers and fractions.

The complete set of natural numbers along with '0' are called whole numbers. The examples are: 0, 11, 25, 36, 999, 1200, etc.

What is a Neutron?

The answer to this puzzle was provided by **James Chadwick**, who boldly stated that this was a new type of fundamental particle that is neutral, and he called them **Neutrons**. From the conservation of energy and momentum, he was able to derive with considerable accuracy the mass of this new particle. He found that the mass of a neutron was very close to that of a proton.

$$M_N = 1.00866 \text{ u} = 1.6749 \times 10^{-27} \text{ kg}$$

So now the nucleus had another resident, and the proton-neutron pair was called a Nucleon. The discovery of Neutron led to a better understanding of atomic mass and atomic number also with isotopes which is what radioactivity is based on!

- Z – Atomic Number = number of protons/ electrons
- N – Neutron Number = Number of Neutron
- A – Atomic Mass Number = Z + N = Total number of protons and neutrons

So now the elements of the periodic table had a new form of representation;

For example, the nucleus of a Uranium atom is represented by a  $^{235}_{92}\text{U}$ , which means that one atom of Uranium 235 contains 235 nucleons, of which 92 are protons, and the rest 143 are neutrons.

### **What are Isotopes?**

Isotopes are variants of a particular element with different numbers of neutrons. For example, the two isotopes of Uranium are,  $^{235}_{92}\text{U}$  and  $^{239}_{92}\text{U}$ . You will see here that the number of protons is the same in both the isotopes, but they contain 143 and 147 neutrons, respectively. The presence of an extra neutron significantly changes the behaviour of that particular atom. There are two different types of isotopes, stable and radioactive. Stable isotopes can exist in their free state without breaking down spontaneously. Radioactive isotopes are too unstable to sustain themselves, and they spontaneously break down into two lighter daughter elements with the emission of particles such as alpha, beta, and gamma rays.

### **What are Isobars?**

Isobars are elements that have the same number of nucleons (sum of protons and neutrons). The series of elements with 40 Mass numbers serve as a good example;  $^{40}_{16}\text{S}$ ,  $^{40}_{17}\text{Cl}$ ,  $^{40}_{18}\text{Ar}$ ,  $^{40}_{19}\text{K}$ , and  $^{40}_{20}\text{Ca}$ . The nucleus of all the above-mentioned elements contain the same number of particles in the nucleus but contain varying numbers of protons and neutrons.

### **What are Isotones?**

Isotones are atoms that have the same neutron number but different proton number. For example,  $^{36}_{16}\text{S}$ ,  $^{37}_{17}\text{Cl}$ ,  $^{38}_{18}\text{Ar}$ ,  $^{39}_{19}\text{K}$ , and  $^{40}_{20}\text{Ca}$  are all isotones of 20 since they all contain 20 neutrons.

Nuclear energy and Radioactivity relies on the unstable isotopes of heavy elements to tap the explosive power of the nucleus. The discovery of one fundamental particle unlocked such amazing doors for humanity.

## UNIT II

### NUCLEAR CHEMISTRY II

#### RADIOACTIVITY

the emission of ionizing radiation or particles caused by the spontaneous disintegration of atomic nuclei.

**Radioactive decay** (also known as nuclear decay, radioactivity, radioactive disintegration or nuclear disintegration) is the process by which an unstable atomic nucleus loses energy by radiation. A material containing unstable nuclei is considered radioactive. Three of the most common types of decay are alpha decay, beta decay, and gamma decay, all of which involve emitting one or more particles or photons. The weak force is the mechanism that is responsible for Alpha decay occurs when the nucleus ejects an alpha particle (helium nucleus).

Beta decay occurs in two ways;

- (i) beta-minus decay, when the nucleus emits an electron and an antineutrino in a process that changes a neutron to a proton, or
- (ii) beta-plus decay, when the nucleus emits a positron and a neutrino in a process that changes a proton to a neutron.

• In gamma decay a radioactive nucleus first decays by the emission of an  $\alpha$  or  $\beta$  particle. The daughter nucleus that results is usually left in an excited state and it can decay to a lower energy state by emitting a gamma ray photon.

• In Neutron emission highly excited neutron-rich nuclei, formed due to other types of decay, occasionally lose energy by way of neutron emission, resulting in a change from one isotope to another of the same element.

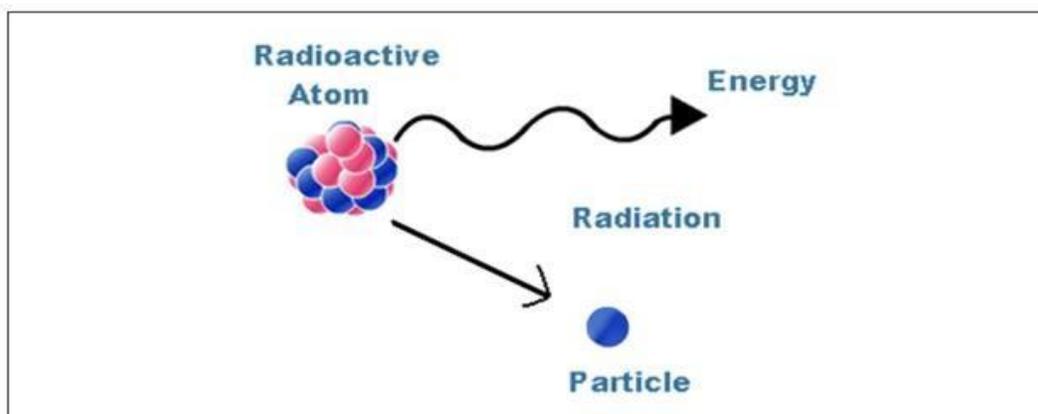
• In Electron capture The nucleus may capture an orbiting electron, causing a proton to convert into a neutron in a process called electron capture. All of these processes result in a well-defined nuclear transmutation.

beta decay.

#### **Radioactive emanation.**

A **radioactive gas** given off by certain radioactive elements; all of these gases are isotopes of the element radon. Also known as emanation.

## Properties of Alpha, Beta and Gamma Rays



During radioactivity, particles like alpha, beta & gamma rays are emitted by an atom, due to unstable atom trying to gain stability. Hence, the atoms eventually decay by emitting a particle that transforms when they are unstable and transforms the nucleus into a lower energy state. This process of decaying continues till the nucleus attains a stable stage.

There exist three major types of radiations emitted by the radioactive particles namely:

- Alpha
- Beta
- Gama

These radiations are released from the nucleus of an atom. Their behavior differs from one another, though all the three causes some ionization and carry some penetration power. Let's discuss the properties of beta, alpha and gamma one by one.

### Alpha Rays

Alpha rays are the positively charged particles. Alpha-particle is highly active and energetic helium atom that contains two neutrons and protons. These particles have the minimum penetration power and highest ionization power. They can cause serious damage if get into the body due to their high ionization power. They

are capable of ionizing numerous atoms by a short distance. It is due to the fact that the radioactive substances that release alpha particles are required to be handled after wearing rubber gloves.

### **Beta Rays**

Beta particles are extremely energetic electrons that are liberated from the inner nucleus. They bear negligible mass and carry the negative charge. A neutron in the nucleus splits into a proton and an electron on the emission of a beta particle. Hence, it is the electron that is emitted by the nucleus at a rapid pace. Beta particles have a higher penetration power when compared to alpha particles and can travel through the skin with ease. Beta particles can be dangerous and any contact with the body must be avoided, though their ionization power is low.

### **Gamma Rays**

The waves arising from the high-frequency end of the electromagnetic spectrum that has no mass are known as gamma rays. They hold the highest power of penetration. They are the most penetrating but least ionizing and very difficult to resist them from entering the body. The Gamma rays carry a large amount of energy and can also travel via thick concrete and thin lead.

The below table describes the characteristics of beta, alpha and gamma radiations and compares the masses and charges of the three rays.

Property	$\alpha$ \alpha ray	$\beta$ \beta ray	$\gamma$ \gamma ray
<b>Nature</b>	Positive charged particles, ${}^4_2\text{He}$ nucleus	Negatively charged particles (electrons).	Uncharged $\lambda \sim 0.01 \text{ \AA}$ , electromagnetic radiation
<b>Charge</b>	+2e	-e	0
<b>Mass</b>	$6.6466 \times 10^{-27} \text{ kg}$	$9.109 \times 10^{-31} \text{ kg}$	0
<b>Range</b>	$\sim 10 \text{ cm}$ in air, can be stopped by 1mm of Aluminium	Upto a few m in air, can be stopped by a thin layer of Aluminium	Several m in air, can be stopped by a thick layer of Lead
<b>Natural Sources</b>	By natural radioisotopes e.g. ${}^{92}\text{U}^{236}$	By radioisotopes e.g. ${}^{29}\text{Co}^{68}$	Excited nuclei formed as a result of Gamma decay

Stay tuned with Byju's to learn more about characteristics of alpha, beta and gamma rays along with their differentiation and common features.

### Radioactive decay rates

Constant quantities:

- The *half-life*— $t_{1/2}$ , is the time taken for the activity of a given amount of a radioactive substance to decay to half of its initial value; see List of nuclides.
- The *decay constant*— $\lambda$ , "lambda" the reciprocal of the mean lifetime (in  $\text{s}^{-1}$ ), sometimes referred to as simply *decay rate*.
- The *mean lifetime*— $\tau$ , "tau" the average lifetime ( $1/e$  life) of a radioactive particle before decay.

Although these are constants, they are associated with the statistical behavior of populations of atoms. In consequence, predictions using these constants are less accurate for minuscule samples of atoms.

In principle a half-life, a third-life, or even a  $(1/\sqrt{2})$ -life, can be used in exactly the same way as half-life; but the mean life and half-life  $t_{1/2}$  have been adopted as standard times associated with exponential decay.

Time-variable quantities:

- *Total activity*—  $A$ , is the number of decays per unit time of a radioactive sample.
- *Number of particles*— $N$ , is the total number of particles in the sample.
- *Specific activity*— $S_A$ , number of decays per unit time per amount of substance of the sample at timeset to zero ( $t = 0$ ). "Amount of substance" can be the mass, volume or moles of the initial sample.

$$t_{1/2} = \frac{\ln(2)}{\lambda} = \tau \ln(2)$$

$$A = -\frac{dN}{dt} = \lambda N$$

$$S_A a_0 = -\frac{dN}{dt} \Big|_{t=0} = \lambda N_0$$

where  $N_0$  is the initial amount of active substance — substance that has the same percentage of unstable particles as when the substance was formed.

### **Half-life**

A more commonly used parameter is the half-life. Given a sample of a particular radionuclide, the half-life is the time taken for half the radionuclide's atoms to decay. For the case of one-decay nuclear reactions:

$$N = N_0 e^{-\lambda t} = N_0 e^{-t/\tau},$$

the half-life is related to the decay constant as follows: set  $N = N_0/2$  and  $t = T_{1/2}$  to obtain

$$t_{1/2} = \frac{\ln 2}{\lambda} = \tau \ln 2.$$

This relationship between the half-life and the decay constant shows that highly radioactive substances are quickly spent, while those that radiate weakly endure longer. Half-lives of known radionuclides vary widely, from more than  $10^{24}$  years for the very nearly stable nuclide  $^{128}\text{Te}$ , to  $2.3 \times 10^{-23}$  seconds for highly unstable nuclides such as  $^7\text{H}$ .

The factor of  $\ln(2)$  in the above relations results from the fact that the concept of "half-life" is merely a way of selecting a different base other than the natural base  $e$  for the lifetime expression. The time constant  $\tau$  is the  $e^{-1}$ -life, the time until only  $1/e$  remains, about 36.8%, rather than the 50% in the half-life of a radionuclide. Thus,  $\tau$  is longer than  $t_{1/2}$ . The following equation can be shown to be valid:

$$N(t) = N_0 e^{-t/\tau} = N_0 2^{-t/t_{1/2}}.$$

Since radioactive decay is exponential with a constant probability, each process could as easily be described with a different constant time period that (for example) gave its "(1/3)-life" (how long until only 1/3 is left) or "(1/10)-life" (a time period until only 10% is left), and so on. Thus, the choice of  $\tau$  and  $t_{1/2}$  for marker-times, are only for convenience, and from convention. They reflect a fundamental principle only in so much as they show that the *same proportion* of a given radioactive substance will decay, during any time-period that one chooses.

Mathematically, the  $n^{\text{th}}$  life for the above situation would be found in the same way as above—by setting  $N = N_0/n$ ,  $t = T_{1/n}$  and substituting into the decay solution to obtain

$$t_{1/n} = \frac{\ln n}{\lambda} = \tau \ln n.$$

Example for carbon-14

Carbon-14 has a half-life of 5,730 years and a decay rate of 14 disintegrations per minute (dpm) per gram of natural carbon.

If an artifact is found to have radioactivity of 4 dpm per gram of its present C, we can find the approximate age of the object using the above equation:

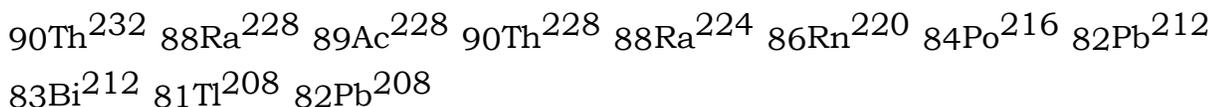
$$\begin{aligned} N &= N_0 e^{-t/\tau}, \\ \text{where: } \frac{N}{N_0} &= 4/14 \approx 0.286, \\ \tau &= \frac{T_{1/2}}{\ln 2} \approx 8267 \text{ years}, \\ t &= -\tau \ln \frac{N}{N_0} \approx 10356 \text{ years}. \end{aligned}$$

## DISINTEGRATION SERIES

“All the disintegration steps involved in the formation of a non-radioactive element from a radioactive element constitute the disintegration series.”

**Types of Disintegration Series-** There are four disintegration series.

1. **i) Thorium Series or 4n series-** The mass number of all the elements of this series are divisible by 4. The various steps of this series are given below:



2) **Neptunium Series or (4n+1) Series-** The mass number of the elements of this series are divided by 4, the remainder is always one. The elements formed in this series are not found in nature. It is called artificial series. The various steps of this series are as-



3) **Uranium Series or (4n+2) Series-** The mass number of the elements of this series are divided by 4, remainder is always 2, This series starts from  $\text{U}^{238}$  and ends at  $\text{Pb}^{206}$ .

4) **Actinurium Series or (4n+3) series-** The mass number of the elements of this series are divided by 4, remainder is always 3. This series starts from  ${}_{92}\text{U}^{235}$ . The name actinurium (ACU) was given to the isotope  ${}_{92}\text{U}^{235}$  earlier. Therefore the series is called actinium series

### Geiger-Nuttall law

The Geiger-Nuttall law or Geiger-Nuttall rule relates the decay constant of a radioactive isotope with the energy of the alpha particles emitted. Roughly speaking, it states that short-lived isotopes emit more energetic alpha particles than long-lived ones. The relationship also shows that half-lives are exponentially dependent on decay energy, so that very large changes in half-life make comparatively small differences in decay energy, and thus alpha particle energy

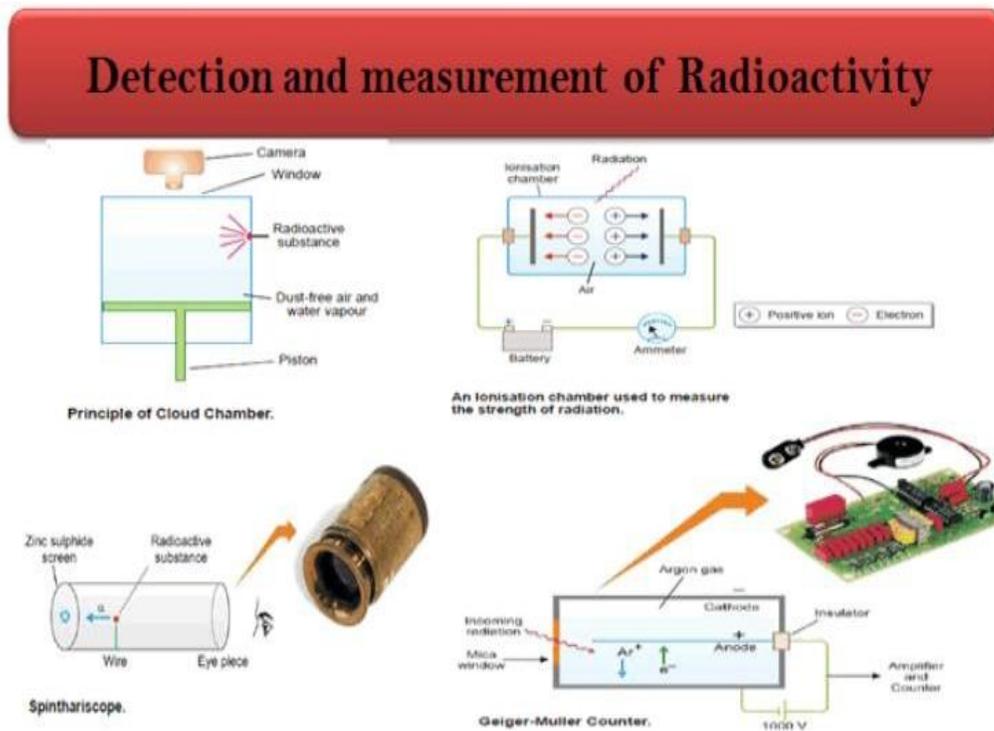
In nuclear physics, the Geiger-Nuttall law or Geiger-Nuttall rule relates the decay constant of a radioactive isotope with the energy of the alpha particles emitted. Roughly speaking, it states that short-lived isotopes emit more energetic alpha particles than long-lived ones.

The relationship also shows that half-lives are exponentially dependent on decay energy, so that very large changes in half-life make comparatively small differences in decay energy, and thus alpha particle energy. In practice, this means that alpha particles from all alpha-emitting isotopes across many orders of magnitude of difference in half-life, all nevertheless have about the same decay energy.

Formulated in 1911 by Hans Geiger and John Mitchell Nuttall as a relation between the decay constant and the range of alpha particles in air, in its modern form the Geiger–Nuttall law is

$$\log_{10} \lambda = -a_1 \frac{Z}{\sqrt{E}} + a_2$$

where  $\lambda$  is the decay constant ( $\lambda = \ln 2 / \text{half-life}$ ),  $Z$  the atomic number,  $E$  the total kinetic energy (of the alpha particle and the daughter nucleus), and  $a_1$  and  $a_2$  are constants. The law works best for nuclei with even atomic number and even atomic mass. The trend is still there for even-odd, odd-even, and odd-odd nuclei but not as pronounced.

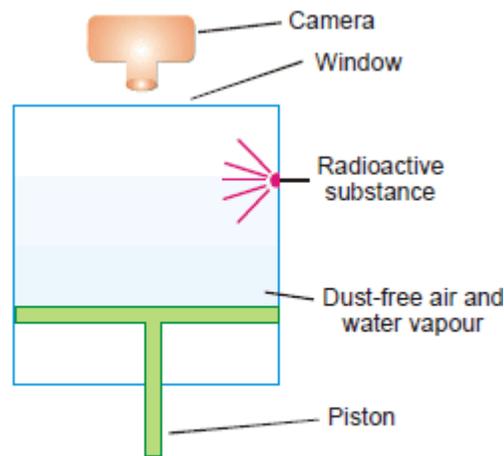


The radioactive radiation can be detected and measured by a number of methods. The important ones used in modern practice are listed below.

**(1) Cloud Chamber**

- This technique is used for detecting radioactivity.

- The chamber contains air saturated with water vapour.
- When the piston is lowered suddenly, the gas expands and is supercooled.
- As an  $\alpha$ - or  $\beta$ -particle passes through the gas, ions are created along its path. These ions provide nuclei upon which droplets of water condense.
- The trail or cloud thus produced marks the track of the particle. The track can be seen through the window above and immediately photographed.
- Similarly,  $\alpha$ - or  $\beta$ -particles form a trail of bubbles as they pass through liquid hydrogen.
- The bubble chamber method gives better photographs of the particle tracks.

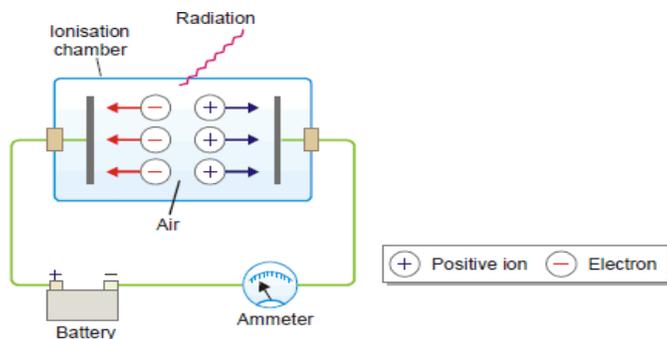


**Principle of Cloud Chamber.**

## (2) ***Ionization Chamber***

- \*\* This is the simplest device used to measure the strength of radiation.
- \*\* An ionization chamber is fitted with two metal plates separated by air.
- \*\* When radiation passes through this chamber, it knocks electrons from gas molecules and positive ions are formed.
- \*\* The electrons migrate to the anode and positive ions to the cathode. Thus a small current passes between the plates. This current can be measured with an ammeter, and gives the strength of radiation that passes through the ionization chamber.

\*\* In an ionization chamber called Dosimeter, the total amount of electric charge passing between the plates in a given time is measured. This is proportional to the total amount of radiation that has gone through the chamber.



An Ionisation chamber used to measure the strength of radiation.

### **Geiger-Muller Counter**

\*\* This device is used for detecting and measuring the rate of emission of  $\alpha$ - or  $\beta$  particles.

\*\* It consists of a cylindrical metal tube (cathode) and a central wire (anode).

\*\* The tube is filled with argon gas at reduced pressure (0.1 atm).

\*\* A potential difference of about 1000 volts is applied across the electrodes.

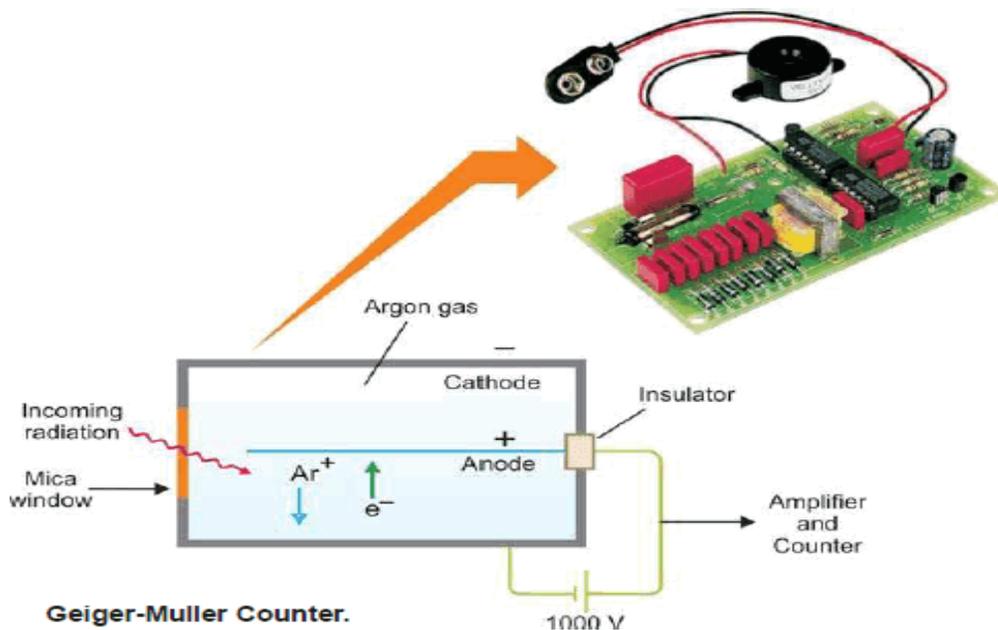
\*\* When an  $\alpha$ - or  $\beta$ -particle enters the tube through the mica window, it ionizes the argon atoms along its path.



\*\* The argon ions ( $\text{Ar}^+$ ) are drawn to the cathode and electrons to anode. Thus for a fraction of a second, a pulse of electrical current flows between the electrodes and completes the circuit around.

\*\* Each electrical pulse marks the entry of one  $\alpha$ - or  $\beta$ -particle into the tube and is recorded in an automatic counter.

\*\* The number of such pulses registered by a radioactive material per minute, gives the intensity of its radioactivity.



## PARTICLE ACCELERATOR

A particle accelerator is a machine that uses electromagnetic fields to propel charged particles to very high speeds and energies, and to contain them in well-defined beams.

There are two basic classes of accelerators: electrostatic and electrodynamic (or electromagnetic) accelerators.<sup>[3]</sup> Electrostatic accelerators use static electric fields to accelerate particles. The most common types are the Cockcroft-Walton generator and the Van de Graaff generator. A small-scale example of this class is the cathode ray tube in an ordinary old television set. The achievable kinetic energy for particles in these devices is determined by the accelerating voltage, which is limited by electrical breakdown. Electrodynamic or electromagnetic accelerators, on the other hand, use changing electromagnetic fields (either magnetic induction or oscillating radio frequency fields) to accelerate particles. Since in these types the particles can pass through the same accelerating field multiple times, the output energy is not

limited by the strength of the accelerating field. This class, which was first developed in the 1920s, is the basis for most modern large-scale accelerators.

### Linear induction accelerator

Linear induction accelerators utilize ferrite-loaded, non-resonant induction cavities. Each cavity can be thought of as two large washer-shaped disks connected by an outer cylindrical tube. Between the disks is a ferrite toroid. A voltage pulse applied between the two disks causes an increasing magnetic field which inductively couples power into the charged particle beam.

The linear induction accelerator was invented by Christofilos in the 1960s. Linear induction accelerators are capable of accelerating very high beam currents (>1000 A) in a single short pulse. They have been used to generate X-rays for flash radiography (e.g. DARHT at LANL), and have been considered as particle injectors for magnetic confinement fusion and as drivers for free electron lasers.

In a linear particle accelerator (linac), particles are accelerated in a straight line with a target of interest at one end. They are often used to provide an initial low-energy kick to particles before they are injected into circular accelerators. The longest linac in the world is the Stanford Linear Accelerator, SLAC, which is 3 km (1.9 mi) long. SLAC is an electron-positron collider.

Linear high-energy accelerators use a linear array of plates (or drift tubes) to which an alternating high-energy field is applied. As the particles approach a plate they are accelerated towards it by an opposite polarity charge applied to the plate. As they pass through a hole in the plate, the polarity is switched so that the plate now repels them and they are now accelerated by it towards the next plate. Normally a stream of "bunches" of particles are accelerated, so a carefully controlled AC voltage is applied to each plate to continuously repeat this process for each bunch.

As the particles approach the speed of light the switching rate of the electric fields becomes so high that they operate at radio frequencies, and so microwave cavities are used in higher energy machines instead of simple plates.

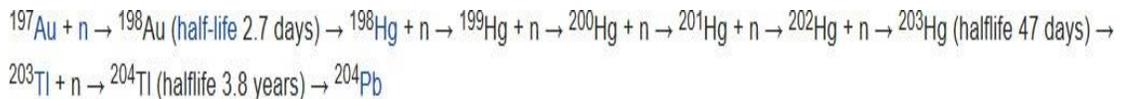
Linear accelerators are also widely used in medicine, for radiotherapy and radiosurgery. Medical grade linacs accelerate electrons using a klystron and a complex bending magnet arrangement which produces a beam of 6-30 MeV energy. The electrons can be used directly or they can be collided with a target to produce a beam of X-rays. The reliability, flexibility and accuracy of the radiation beam produced has largely supplanted the older use of cobalt-60 therapy as a treatment tool.

## Nuclear transmutation

Nuclear transmutation is the conversion of one chemical element or an isotope into another chemical element.<sup>[1]</sup> Because any element (or isotope of one) is defined by its number of protons (and neutrons) in its atoms, i.e. in the atomic nucleus, nuclear transmutation occurs in any process where the number of protons or neutrons in the nucleus is changed.

Natural transmutation by stellar nucleosynthesis in the past created most of the heavier chemical elements in the known existing universe, and continues to take place to this day, creating the vast majority of the most common elements in the universe, including helium, oxygen and carbon. Most stars carry out transmutation through fusion reactions involving hydrogen and helium, while much larger stars are also capable of fusing heavier elements up to iron late in their evolution.

Artificial transmutation may occur in machinery that has enough energy to cause changes in the nuclear structure of the elements. Such machines include particle accelerators and tokamak reactors. Conventional fission power reactors also cause artificial transmutation, not from the power of the machine, but by exposing elements to neutrons produced by fission from an artificially produced nuclear chain reaction. For instance, when a uranium atom is bombarded with slow neutrons, fission takes place. This releases, on average, 3 neutrons and a large amount of energy. The released neutrons then cause fission of other uranium atoms, until all of the available uranium is exhausted. This is called a chain reaction.



- **Elastic Scattering**

number of protons of the target nuclide.

- **Fission Reactions**

Typical and well-known neutron-induced fission reactions are:

$^{235}\text{U} (n, 3 n)$  fission products

$^{239}\text{Pu} (n, 3 n)$  fission products

These reactions release energy. The released neutrons induce further reactions, causing continuous chain reactions.

- **Fusion Reactions**

The fusion reaction of deuterium and tritium is particularly interesting because of its potential of providing energy for the future.

$\text{T} (d, n) \text{He}$

## **Nuclear Fission**

Nuclear fission is a nuclear reaction or a radioactive decay process in which the nucleus of an atom splits into two or more smaller, lighter nuclei. The fission process often produces gamma photons, and releases a very large amount of energy even by the energetic standards of radioactive decay.

The other basic type of nuclear weapon produces a large proportion of its energy in nuclear fusion reactions. Such fusion weapons are generally referred to as **thermonuclear weapons** or more colloquially as **hydrogen bombs** (abbreviated as **H-bombs**), as they rely on fusion reactions between isotopes of hydrogen (deuterium and tritium). All such weapons derive a significant portion of their energy from fission reactions used to "trigger" fusion reactions, and fusion reactions can themselves trigger additional fission reactions.<sup>[13]</sup>

Only six countries—United States, Russia, United Kingdom, China, France, and India—have conducted thermonuclear weapon tests. (Whether India has detonated a "true" multi-staged thermonuclear weapon is controversial.)<sup>[14]</sup> North Korea claims to have tested a fusion weapon as of January 2016, though this claim is disputed. Thermonuclear weapons are considered much more difficult to successfully design and execute than primitive fission weapons. Almost all of the nuclear weapons deployed today use the thermonuclear design because it is more efficient. Thermonuclear bombs work by using the energy of a fission bomb to

compress and heat fusion fuel. In the Teller-Ulam design, which accounts for all multi-megaton yield hydrogen bombs, this is accomplished by placing a fission bomb and fusion fuel (tritium, deuterium, or lithium deuteride) in proximity within a special, radiation-reflecting container. When the fission bomb is detonated, gamma rays and X-rays emitted first compress the fusion fuel, then heat it to thermonuclear temperatures. The ensuing fusion reaction creates enormous numbers of high-speed neutrons, which can then induce fission in materials not normally prone to it, such as depleted uranium. Each of these components is known as a "stage", with the fission bomb as the "primary" and the fusion capsule as the "secondary". In large, megaton-range hydrogen bombs, about half of the yield comes from the final fissioning of depleted uranium.

Virtually all thermonuclear weapons deployed today use the "two-stage" design described above, but it is possible to add additional fusion stages—each stage igniting a larger amount of fusion fuel in the next stage. This technique can be used to construct thermonuclear weapons of arbitrarily large yield, in contrast to fission bombs, which are limited in their explosive force.

Fusion reactions do not create fission products, and thus contribute far less to the creation of nuclear fallout than fission reactions, but because all thermonuclear weapons contain at least one fission stage, and many high-yield thermonuclear devices have a final fission stage, thermonuclear weapons can generate at least as much nuclear fallout as fission-only weapons.

A hydrogen bomb or H-bomb is a type of nuclear weapon that explodes from the intense energy released by nuclear fusion. Hydrogen bombs may also be called thermonuclear weapons.

## **Nuclear reactor**

A nuclear reactor, formerly known as an atomic pile, is a device used to initiate and control a self-sustained nuclear chain reaction. Nuclear reactors are used at nuclear power plants for electricity generation and in nuclear marine propulsion. Heat from nuclear fission is passed to a working fluid, which in turn runs through steam turbines. These either drive a ship's propellers or turn electrical generators' shafts. Nuclear generated steam in principle can be used for industrial process heat or for district heating. Some reactors are used to produce isotopes for medical and industrial use, or for production of weapons-grade plutonium. As of early 2019, the IAEA reports there are 454 nuclear power reactors and 226 nuclear research reactors in operation around the world.

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A nuclear reactor produces and controls the release of energy from splitting the atoms of certain elements. In a nuclear power reactor, the energy released is used as heat to make steam to generate electricity. (In a research reactor the main purpose is to utilise the actual neutrons produced in the core. In most naval reactors, steam drives a turbine directly for propulsion.)

The principles for using nuclear power to produce electricity are the same for most types of reactor. The energy released from continuous fission of the atoms of the fuel is harnessed as heat in either a gas or water, and is used to produce steam. The steam is used to drive the turbines which produce electricity (as in most fossil fuel plants).

The world's first nuclear reactors operated naturally in a uranium deposit about two billion years ago. These were in rich uranium orebodies and moderated by percolating rainwater. The 17 known at Oklo in west Africa, each less than 100 kW thermal, together consumed about six tonnes of that uranium. It is assumed that these were not unique worldwide.

Today, reactors derived from designs originally developed for propelling submarines and large naval ships generate about 85% of the world's nuclear electricity. The main design is the pressurised water reactor (PWR) which has water at over 300°C under pressure in its primary cooling/heat transfer circuit, and generates steam in a secondary circuit. The less numerous boiling water reactor (BWR) makes steam in the primary circuit above the reactor core, at similar temperatures and pressure. Both types use water as both coolant and moderator, to slow neutrons. Since water normally boils at 100°C, they have robust steel pressure vessels or tubes to enable the higher operating temperature. (Another type uses heavy water, with deuterium atoms, as moderator. Hence the term 'light water' is used to differentiate.)

### **Components of a nuclear reactor**

There are several components common to most types of reactors:

**Fuel.** Uranium is the basic fuel. Usually pellets of uranium oxide (UO<sub>2</sub>) are arranged in tubes to form fuel rods. The rods are arranged into fuel assemblies in the reactor core.\* In a 1000 MWe class PWR there might be 51,000 fuel rods with over 18 million pellets.

\* In a new reactor with new fuel a neutron source is needed to get the reaction going. Usually this is beryllium mixed with polonium, radium or other alpha-emitter. Alpha particles from the decay cause a release of neutrons from the beryllium as it turns to carbon-12. Restarting a reactor with some used fuel may not require this, as there may be enough neutrons to achieve criticality when control rods are removed.

**Moderator.** Material in the core which slows down the neutrons released from fission so that they cause more fission. It is usually water, but may be heavy water or graphite.

**Control rods.** These are made with neutron-absorbing material such as cadmium, hafnium or boron, and are inserted or withdrawn from the core to control the rate of reaction, or to halt it.\* In some PWR reactors, special control rods are used to enable the core to sustain a low level of power efficiently. (Secondary control systems involve other neutron absorbers, usually boron in the coolant – its concentration can be adjusted over time as the fuel burns up.) PWR control rods are inserted from the top, BWR cruciform blades from the bottom of the core.

\* In fission, most of the neutrons are released promptly, but some are delayed. These are crucial in enabling a chain reacting system (or reactor) to be controllable and to be able to be held precisely critical.

**Coolant.** A fluid circulating through the core so as to transfer the heat from it. In light water reactors the water moderator functions also as primary coolant. Except in BWRs, there is secondary coolant circuit where the water becomes steam. (See also later section on primary coolant characteristics.) A PWR has two to four primary coolant loops with pumps, driven either by steam or electricity – China’s Hualong One design has three, each driven by a 6.6 MW electric motor, with each pump set weighing 110 tonnes.

**Pressure vessel or pressure tubes.** Usually a robust steel vessel containing the reactor core and moderator/coolant, but it may be a series of tubes holding the fuel and conveying the coolant through the surrounding moderator.

**Steam generator.** Part of the cooling system of pressurised water reactors (PWR & PHWR) where the high-pressure primary coolant bringing heat from the reactor is used to make steam for the turbine, in a secondary circuit. Essentially a heat exchanger like a motor car radiator.\* Reactors have up to six 'loops', each with a steam generator. Since 1980 over 110 PWR reactors have had their steam generators replaced after 20-30 years service, 57 of these in USA.

\* These are large heat exchangers for transferring heat from one fluid to another – here from high- pressure primary circuit in PWR to secondary circuit where water turns to steam. Each structure weighs up to 800 tonnes and contains from 300 to 16,000 tubes about 2 cm diameter for the primary coolant, which is radioactive due to nitrogen-16 (N-16, formed by neutron bombardment of oxygen, with half- life of 7 seconds). The secondary water must flow through the support structures for the tubes. The whole thing needs to be designed so that the tubes don't vibrate and fret, operated so that deposits do not build up to impede the flow, and maintained chemically to avoid corrosion. Tubes which fail and leak are plugged, and surplus capacity is designed to allow for this. Leaks can be detected by monitoring N- 16 levels in the steam as it leaves the steam generator.

**Containment.** The structure around the reactor and associated steam generators which is designed to protect it from outside intrusion and to protect those outside from the effects of radiation in case of any serious malfunction inside. It is typically a metre-thick concrete and steel structure.

Newer Russian and some other reactors install core melt localisation devices or 'core catchers' under the pressure vessel to catch any melted core material in the event of a major accident.

There are several different types of reactors as indicated in the following table.

### Nuclear power plants in commercial operation or operable

Reactor type	Main countries	Number	GWe	Fuel	Coolant	Moderator
Pressurised water reactor (PWR)	USA, France, Japan, Russia, China, South Korea	300	284	enriched UO <sub>2</sub>	water	water
Boiling water reactor (BWR)	USA, Japan, Sweden	65	65	enriched UO <sub>2</sub>	water	water
Pressurised heavy water reactor (PHWR)	Canada, India	48	24	natural UO <sub>2</sub>	heavy water	heavy water
Gas-cooled reactor (AGR)	UK	14	8	natural U (metal), enriched UO <sub>2</sub>	CO <sub>2</sub>	graphite
Light water graphite reactor (LWGR)	Russia	13	9	enriched UO <sub>2</sub>	water	graphite
Fast neutron reactor (FBR)	Russia	2	1.4	PuO <sub>2</sub> and UO <sub>2</sub>	liquid sodium	none
	TOTAL	442	391			

For reactors under construction, see information paper on Plans for New Reactors Worldwide

### Fuelling a nuclear power reactor

Most reactors need to be shut down for refuelling, so that the reactor vessel can be opened up. In this case refuelling is at intervals of 12, 18 or 24 months, when a quarter to a third of the fuel assemblies are replaced with fresh ones. The CANDU and RBMK types have pressure tubes (rather than a pressure vessel enclosing the reactor core) and can be refuelled under load by disconnecting individual pressure tubes.

If graphite or heavy water is used as moderator, it is possible to run a power reactor on natural instead of enriched uranium. Natural uranium has the same elemental composition as when it was mined (0.7% U-235, over 99.2% U-238), enriched uranium has had the proportion of the fissile isotope (U-235) increased by a process called enrichment, commonly to 3.5 - 5.0%. In this case the moderator can be ordinary water, and such reactors are collectively called light water reactors. Because the light water absorbs neutrons as well as slowing them, it is less efficient as a moderator than heavy water or graphite.

During operation, some of the U-238 is changed to plutonium, and Pu-239 ends up providing about one-third of the energy from the fuel.

In most reactors the fuel is ceramic uranium oxide (UO<sub>2</sub> with a melting point of 2800°C) and most is enriched. The fuel pellets (usually about 1 cm diameter and 1.5 cm long) are typically arranged in a long zirconium alloy (zircaloy) tube to form a fuel rod, the zirconium being hard, corrosion-resistant and transparent to neutrons.\* Numerous rods form a fuel assembly, which is an open lattice and can be lifted into and out of the reactor core. In the most common reactors these are about 4 metres long. A BWR fuel assembly may be about 320 kg, a PWR one 655 kg, in which case they hold 183 kg uranium and 460 kgU respectively. In both, about 100 kg of zircaloy is involved.

\* Zirconium is an important mineral for nuclear power, where it finds its main use. It is therefore subject to controls on trading. It is normally contaminated with hafnium, a neutron absorber, so very pure 'nuclear grade' Zr is used to make the zircaloy, which is about 98% Zr plus about 1.5% tin, also iron, chromium and sometimes nickel to enhance its strength.

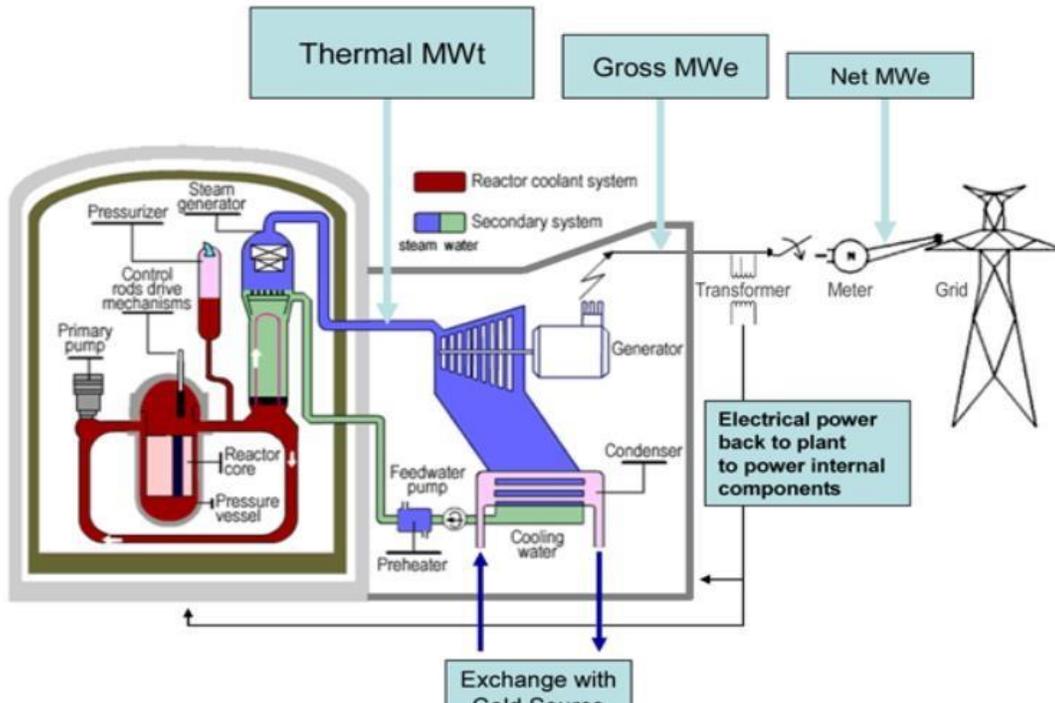
A significant industry initiative is to develop accident-tolerant fuels which are more resistant to melting under conditions such as those in the Fukushima accident, and with the cladding being more resistant to oxidation with hydrogen formation at very high temperatures under such conditions.

Burnable poisons are often used in fuel or coolant to even out the performance of the reactor over time from fresh fuel being loaded to refuelling. These are neutron absorbers which decay under neutron exposure, compensating for the progressive build up of neutron absorbers in the fuel as it is burned, and hence allowing higher fuel burn-up (in terms of GW days per tonne of U)\*. The best known is gadolinium, which is a vital ingredient of fuel in naval reactors where installing fresh fuel is very inconvenient, so reactors are designed to run more than a decade between refuellings (full power equivalent – in practice they are not run continuously). Gadolinium is incorporated in the ceramic fuel pellets. An alternative is zirconium diboride integral fuel burnable absorber (IFBA) as a thin coating on normal pellets.

\* Average burn-up of fuel discharged from US reactors has increased to nearly 50 GWd/t, from half that in the 1980s.

Gadolinium, mostly at up to 3g oxide per kilogram of fuel, requires slightly higher fuel enrichment to compensate for it, and also after burn-up of about 17 GWd/t it retains about 4% of its absorptive effect and does not decrease further. The ZrB<sub>2</sub> IFBA burns away more steadily and completely, and has

no impact on fuel pellet properties. It is now used in most US reactors and a few in Asia. China has the technology for AP1000 reactors.



## RADIOISOTOPE APPLICATION

A **synthetic radioisotope** is a radionuclide that is not found in nature: no natural process or mechanism exists which produces it, or it is so unstable that it decays away in a very short period of time. Examples include technetium-95 and promethium-146. Many of these are found in, and harvested from, spent nuclear fuel assemblies. Some must be manufactured in particle accelerators.

Most synthetic radioisotopes have a short half-life. Though a health hazard, radioactive materials have many medical and industrial uses.

### Nuclear medicine

The field of nuclear medicine covers use of radioisotopes for diagnosis or treatment.

### Diagnosis

Radioactive tracer compounds, radiopharmaceuticals, are used to observe the function of various organs and body systems. These compounds use a

chemical tracer which is attracted to or concentrated by the activity which is being studied. That chemical tracer incorporates a short lived radioactive isotope, usually one which emits a gamma ray which is energetic enough to travel through the body and be captured outside by a gamma camera to map the concentrations. Gamma cameras and other similar detectors are highly efficient, and the tracer compounds are generally very effective at concentrating at the areas of interest, so the total amounts of radioactive material needed are very small.

The metastable nuclear isomer Tc-99m is a gamma-ray emitter widely used for medical diagnostics because it has a short half-life of 6 hours, but can be easily made in the hospital using a technetium-99m generator. Weekly global demand for the parent isotope molybdenum-99 was 440 TBq (12,000 Ci) in 2010, overwhelmingly provided by fission of uranium-235

### **Treatment**

Several radioisotopes and compounds are used for medical treatment, usually by bringing the radioactive isotope to a high concentration in the body near a particular organ. For example, iodine-131 is used for treating some disorders and tumors of the thyroid gland.

### **Industrial radiation sources**

Alpha particle, beta particle, and gamma ray radioactive emissions are industrially useful. Most sources of these are synthetic radioisotopes. Areas of use include the petroleum industry, industrial radiography, homeland security, process control, food irradiation and underground

### **Detection.**

Radiolabeling is not necessary for some applications. For some purposes, soluble ionic salts can be used directly without further modification (e.g., gallium-67, gallium-68, and radioiodine isotopes). These uses rely on the chemical and biological properties of the radioisotope itself, to localize it within the organism or biological system.

Molecular imaging is the biomedical field that employs radiotracers to visualize and quantify biological processes using positron emission tomography (PET) and single-photon emission computed tomography (SPECT) imaging. Again, a key feature of using radioactivity in life science applications is that it is a quantitative technique, so PET/SPECT not only reveals where a radiolabelled molecule is but how much is there.

Radiobiology (also known as radiation biology) is a field of clinical and basic medical sciences that involves the study of the action of radioactivity on

biological systems. The controlled action of deleterious radioactivity on living systems is the basis of radiation therapy.

### **Phosphorus**

Phosphorus-33 is used to label nucleotides. It is less energetic than P-32 and does not require protection with plexi glass. A disadvantage is its higher cost compared to P-32, as most of the bombarded P-31 will have acquired only one neutron, while only some will have acquired two or more. Its maximum specific activity is 5,118 Ci/mmol (189.4 PBq/mol).

Phosphorus-32 is widely used for labeling nucleic acids and phosphoproteins. It has the highest emission energy (1.7 MeV) of all common research radioisotopes. This is a major advantage in experiments for which sensitivity is a primary consideration, such as titrations of very strong interactions (i.e., very low dissociation constant), footprinting experiments, and detection of low-abundance phosphorylated species.  $^{32}\text{P}$  is also relatively inexpensive. Because of its high energy, however, its safe use requires a number of engineering controls (e.g., acrylic glass) and administrative controls. The half-life of  $^{32}\text{P}$  is 14.2 days, and its maximum specific activity is 9131 Ci/mmol.

### **Iodine**

Iodine-125 is commonly used for labeling proteins, usually at tyrosine residues. Unbound iodine is volatile and must be handled in a fume hood. Its maximum specific activity is 2,176 Ci/mmol (80.51 PBq/mol)

## **Radioisotopes in Industry**

### **Industrial tracers**

Radioisotopes are used by manufacturers as tracers to monitor fluid flow and filtration, detect leaks, and gauge engine wear and corrosion of process equipment. Small concentrations of short-lived isotopes can be detected whilst no residues remain in the environment. By adding small amounts of radioactive substances to materials used in various processes it is possible to study the mixing and flow rates of a wide range of materials, including liquids, powders, and gases and to locate leaks.

Radiotracers are used widely in industry to investigate processes and highlight the causes of inefficiency. They are particularly useful where process optimization can bring material benefits, such as in the transport of sediments. Radiotracers are also used in the oil and gas industry to help determine the extent of oil fields.

## **Inspection**

Radioactive materials are used to inspect metal parts and the integrity of welds across a range of industries. Industrial gamma radiography exploits the ability of various types of radiation to penetrate materials to different extents. Gamma radiography works in much the same way as X-rays screen luggage at airports. Instead of the bulky machine needed to produce X-rays, all that is needed to produce effective gamma rays is a small pellet of radioactive material in a sealed titanium capsule.

The capsule is placed on one side of the object being screened, and some photographic film is placed on the other side. The gamma rays, like X-rays, pass through the object and create an image on the film. Just as X-rays show a break in a bone, gamma rays show flaws in metal castings or welded joints. The technique allows critical components to be inspected for internal defects without damage.

X-ray sets can be used when electric power is available and the object to be scanned can be taken to the X-ray source and radiographed. Radioisotopes have the supreme advantage that they can be taken to the site when an examination is required – and no power is needed. However, they cannot be simply turned off, and so must be properly shielded both when in use and at other times.

## **Carbon dating**

Analyzing the relative abundance of particular naturally-occurring radioisotopes is of vital importance in determining the age of rocks and other materials that are of interest to geologists, anthropologists, hydrologists, and archaeologists, among others.

Naturally-occurring radioisotopes

Carbon-14 (half-life: 5730 yr):

Used to measure the age of wood, other carbon-containing materials (up to 20,000 years), and subterranean water (up to 50,000 years).

Chlorine-36 (301,000 yr):

Used to measure sources of chloride and the age of water (up to 2 million years).

Lead-210 (22.3 yr):

Used to date layers of sand and soil up to 80 years.

Tritium, H-3 (12.3 yr):

Used to measure 'young' groundwater (up to 30 years).

Artificially-produced radioisotopes Americium-241 (half-life: 432 yr):  
Used in backscatter gauges, smoke detectors, fill height detectors, and in measuring ash content of coal.

Caesium-137 (30.17 yr):  
Used for radiotracer technique for identification of sources of soil erosion and deposition, as well as in density and fill height level switches. Also for low-intensity gamma sterilisation.

Chromium-51 (27.7 yr):  
Used to label sand to study coastal erosion, also a tracer in study of blood.

Cobalt-60 (5.27 yr), lanthanum-140 (1.68 d), scandium-46 (83.8 d), silver-110m (250 d), gold-198 (2.7 d):  
Used together in blast furnaces to determine resident times and to quantify yields to measure the furnace performance.

Cobalt-60 (5.27 yr):  
Widely used for gamma sterilisation, industrial radiography, density, and fill height switches.

Gold-198 (2.7 d) & technetium-99m (6 hr):  
Used to study sewage and liquid waste movements, as well as tracing factory waste causing ocean pollution, and to trace sand movement in river beds and ocean floors.

Gold-198 (2.7 d):  
Used to label sand to study coastal erosion.

Hydrogen-3 (in tritiated water) (12.3 yr):  
Used as a tracer to study sewage and liquid wastes.

Iridium-192 (73.8 d):  
Used in gamma radiography to locate flaws in metal components.

Krypton-85 (10.756 yr):  
Used for industrial gauging.

Manganese-54 (312.5 d):  
Used to predict the behaviour of heavy metal components in effluents from mining waste water.

Nickel-63 (100 yr)  
Used in light sensors in cameras and plasma display, also electronic discharge prevention and in electron capture detectors for thickness gauges. Also for long-life beta-voltaic batteries. Made from nickel-62 by neutron capture.

Selenium-75 (120 d):

Used in gamma radiography and non-destructive testing.

Strontium-90 (28.8.yr):

Used for industrial gauging.

Thallium-204 (3.78 yr):

Used for industrial gauging.

Ytterbium-169 (32 d):

Used in gamma radiography and non-destructive testing.

Zinc-65 (244 d):

Used to predict the behaviour of heavy metal components in effluents from mining wastewater

### **Radiation Hazards.**

Exposure to radiation is safe in small amounts and when it is strictly controlled during a medical exam such as an X-ray, for example. However, long-term exposure to small amounts of radiation can lead to **gene mutations** and increase the risk of **cancer** and exposure to a large amount over a brief period can lead to radiation...

S. National Library of Medicine(0.00 / 0 votes)Rate this definition: Radioactive Hazard Release. Uncontrolled release of radioactive material from its containment. This either threatens to, or does, cause exposure to a radioactive hazard. Such an incident may occur accidentally or deliberately. The effect of radiation in the environment can be dangerous and fatal to humans and animals. The damage it causes depends on the level of radiation and the resiliency of the organism. Radiation causes molecules to lose electrons thus destroying it. Killing certain enzymes in the body can simply make you sick.

Radiological hazards are chemical hazards. Radioactive chemicals emit harmful radiation that at large doses is harmful soon after exposure and at small doses is harmful years or decades later. Our food may become contaminated through the absorption of rad

For example:

- Someone who has had many CT scans starting at a young age is more likely to get cancer later in life than someone who hasn't had any or as many of these tests. CT scans generally use more radiation than other X-ray tests. The risk of an adult getting cancer from a CT scan is less than 1 in 1,000.

The risk of a child getting cancer from the same CT scan can be much higher.

- A child who was treated with radiation for cancer is more likely to get another cancer later in life.
- A person who has been exposed to large amounts of radiation from a nuclear accident is more likely to get cancer than someone who has not been exposed.

Exposure to small amounts of radiation doesn't cause any symptoms. But exposure to large amounts all at once may cause radiation sickness and death.

How do different sources of radiation compare?

Some sources of radiation give off larger amounts than others. For example, when you go through a full-body airport scanner, you're exposed to very small amounts of radiation. But if you live near the site of a nuclear accident, you're exposed to large amounts of radiation.

You may be exposed to more radiation than other people if you:

- Live at high altitude.
- Have certain medical tests (such as X-rays or CT scans) or treatments (such as radiation treatment for cancer).
- Are exposed to radon gas in your home.

To understand more about radiation exposure, you may find it helpful to compare some common sources of radiation to a standard dose from a chest X-ray. A chest X-ray gives off very small amounts of radiation.

## UNIT - III

### INDUSTRIAL CHEMISTRY

#### Fossil Fuels

Fossil fuels are buried flammable geologic deposits of organic substances such as dead plants and animals that got deposited under several thousand feet of silt. These deposits decayed with the passage of time and got converted to natural gas, coal and petroleum due to the extreme heat and pressure inside the earth's crust. They are also known as non-renewable sources of energy as it takes a very long time for it to replenish.

#### Types, Formation and Uses of Fossil Fuels

Fossil fuels are of the following types:

- Coal
- Petroleum
- Natural gas

#### Coal

- It is a hard, black coloured substance made up of carbon, hydrogen, nitrogen, oxygen and sulphur.
- The major types of coal are- anthracite, bituminous and lignite.
- Anthracite has a higher carbon concentration and is the hardest type of coal.
- Lignite has a high concentration of oxygen and hydrogen but a low concentration of carbon.
- Bituminous is a moderate form of coal.
- Coal is processed industrially to obtain derivatives like coke, coal tar and coal gas.

#### Formation of Coal

- The process of formation of coal is known as coalification.
- The dense forest present in the low-lying wetland got buried in the earth, millions of years ago.
- Soil kept depositing over them and they got compressed.
- As they went deeper and deeper, they faced high temperature and pressure.

- As a result, the substances slowly got converted into coal.

### **Uses of Coal**

- Coal was used to produce steam in the railway engines initially.
- It is used to cook food.
- It is used to generate electricity in thermal plants.
- It is used in industries as fuel.

### **Petroleum**

- It is a clear, oily liquid, usually green or black in colour.
- It has a very strange smell and is a mixture of petroleum gas, diesel, paraffin wax, petrol, lubricating oil, etc.
- It is also termed as “Black Gold” because of its wide range of uses in many industries.

### **Formation of Petroleum**

- The sea animals and plants died and their bodies settled at the bottom of the sea.
- They got compressed by the layers of sand and clay.
- Their encounter with high temperature and pressure converts them into petroleum.
- The petroleum is separated from the crude oil by a series of processes in a refinery. This is known as petroleum refining.

### **Uses of Petroleum**

- It is used to power internal combustion engines in the form of petrol.
- It is used in roofing, road pavements and as a water repellent.
- It is used in manufacturing detergents, plastics, fibres, polyethene, etc.

### **Natural gas**

- It is a clean and non-toxic fossil fuel.
- It is colourless and odourless and can be easily transferred through pipelines.
- It is stored as compressed natural gas (CNG) under high pressure.
- It is a less polluting and less expensive fossil fuel.
- Methane is the most important natural gas.

## **Formation of Natural Gas**

- The phytoplankton and zooplankton sink to the bottom of the ocean and mix with organic materials to form an organic-rich mud.
- The mud buried under more sediments and lithifies to form an organic shale. This prevents its exposure to oxygen. This is done to protect the organic materials from being decomposed by bacteria.
- The increasing pressure and temperature transform the shale into a waxy material known as the kerogen.
- At temperatures between 90-160°C kerogen is transformed into natural gas.

## **Uses of Natural gas**

- Compressed Natural Gas is used for generating power.
- It is used as fuels in automobiles.
- It can be used at homes for cooking.
- It is used as a starting material in chemicals and fertilizers.

## **Are Fossil Fuels Renewable?**

Fossil fuels are a non-renewable source of energy. Most of the energy used by us is obtained by the burning of fossil fuels. These fossil fuels are used up at a faster rate. They cannot be regrown at a scale compared to their consumption. With the increased demand for the production of various energies, fossil fuel energy is declining. It is difficult to replace them. That is why they are known as a non-renewable source of energy.

## **Advantages and Disadvantages of Fossil Fuels**

### **Advantages:**

- Fossil fuels can generate a large amount of electricity at a single location.
- They can be found very easily.
- They are cost-effective.
- Transportation of oil and gas can be done easily through pipelines.
- They have become safer over time.
- Despite being a finite resource, it is available in plenty.

## Disadvantages

- Fossil fuels emit carbon dioxide when burnt which is a major greenhouse gas and the primary source of pollution. This has contributed to global warming.
- They are a non-renewable resource, i.e., once used they cannot be replaced.
- Combustion of fossil fuels makes the environment more acidic. This has led to unpredictable and negative changes in the environment.
- Harvesting of fossil fuels also causes fatal diseases among the people. For eg., the coal miners often suffer from Black Lung Disease. The natural gas drillers are constantly exposed to chemicals and silica which is dangerous for their health.

These are the natural sources of energy and have extensive applications in industrial as well as domestic purposes.

## PETROLEUM REFINERIES IN INDIA

No.	Refinery	Oil company
	Jamnagar Refinery (for exports)	Reliance Industries Limited
	Jamnagar Refinery (for domestic market)	Reliance Industries Limited
	Vadinar Refinery	Nayara Energy Limited
	Kochi Refinery	Bharat Petroleum Corporation Limited

## Refineries in India Important Facts

1. The Reliance Jamnagar Refinery in Gujarat stands out as one of the world's largest.
2. These refineries play a crucial role in processing crude oil into products like petrol, diesel, and kerosene.
3. Major refinery clusters are located in states such as Gujarat, Maharashtra, Uttar Pradesh, and Tamil Nadu.
4. India has been actively working on expanding its refining capacity to meet the rising demand for petroleum products.
5. Indian refineries have been incorporating advanced technologies to enhance efficiency and minimize environmental impact.

6. Both public sector companies like Indian Oil Corporation (IOCL), Bharat Petroleum (BPCL), and Hindustan Petroleum (HPCL), as well as private players like Reliance Industries, are significant contributors to the Indian refining sector.
7. Oil refineries serve as significant employment generators, providing job opportunities for a large number of people and contributing to overall employment in the country.
8. India has attracted substantial foreign investments in its refining sector, highlighting its appeal to international players.
9. The oil refining sector holds paramount importance in India's economic growth, as it provides essential fuels for transportation and energy for various industries.
10. There is a concerted effort to adopt eco-friendly practices in the refining process to address environmental concerns.
11. The Indian government has implemented various initiatives aimed at fostering the development of the refining sector, including policy reforms and incentives.
12. India also engages in the export of refined petroleum products, contributing significantly to its foreign exchange earnings.

### **Gaseous Fuels**

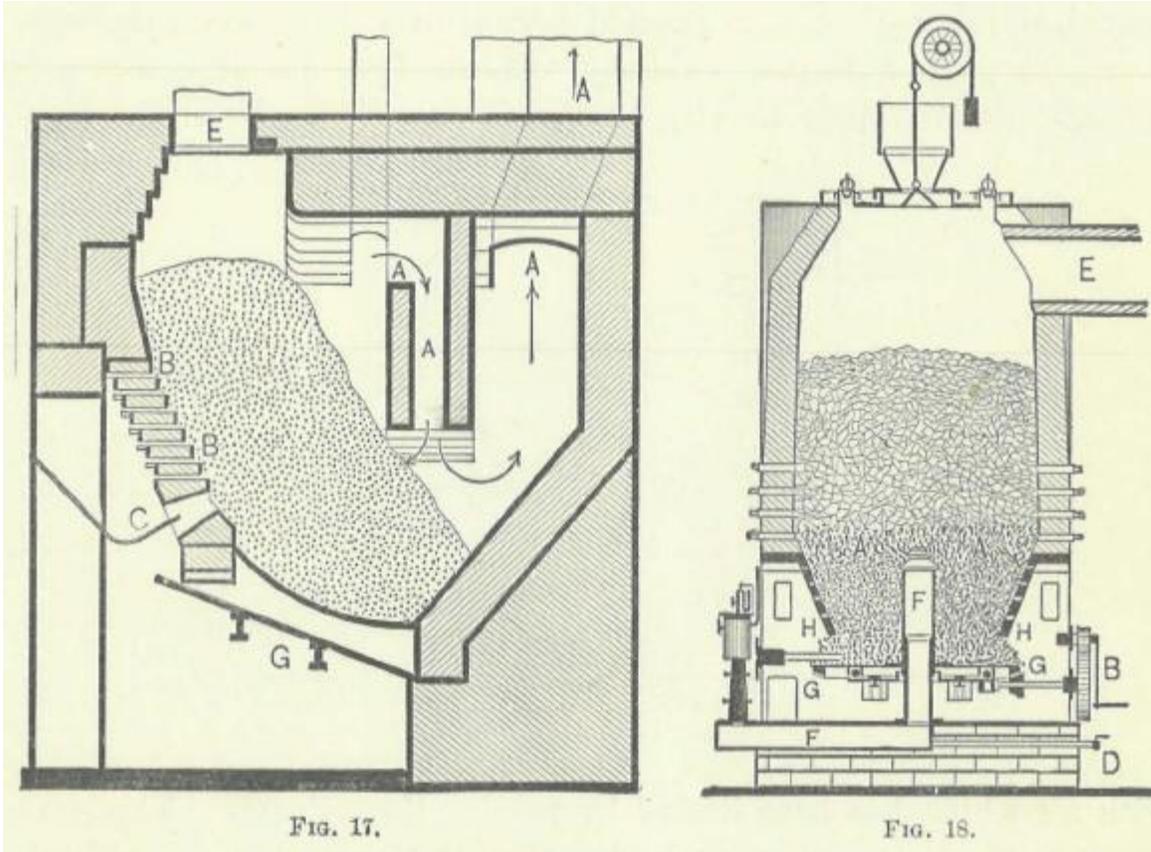
Gaseous fuels may be divided into four classes: natural gas, producer gas, water gas and coal gas.

**Natural gas** exists already formed in the earth, and is obtained by boring tube wells, similar to petroleum wells. Its essential heat producing constituents are methane (CH<sub>4</sub>) and hydrogen. It is the cheapest and most efficient of all fuels, when properly burned; but it requires a large amount of air for its combustion, and special burners must be used.

**Producer gas** is made by forcing air through a bed of incandescent coal or coke, in specially constructed furnaces. Its essential heat constituent is carbon monoxide (CO), of which it contains about 28 to 30 per cent. But it also contains about 63 per cent of nitrogen from the air, and some carbon dioxide, which dilute the gas very much, and reduce its calorific intensity greatly. It is extensively used for fuel, because of its cheapness, cleanliness, and the regularity of the temperature obtained.

In converting carbon to carbon monoxide, about one-third of the heat value of the carbon is set free, thus heating the gas very hot. If it is at once led, through short flues, into the combustion chamber and burned with air, a much higher temperature is obtained, than if it is permitted to cool before burning. In modern gas producers, this waste of heat is largely avoided by introducing steam into

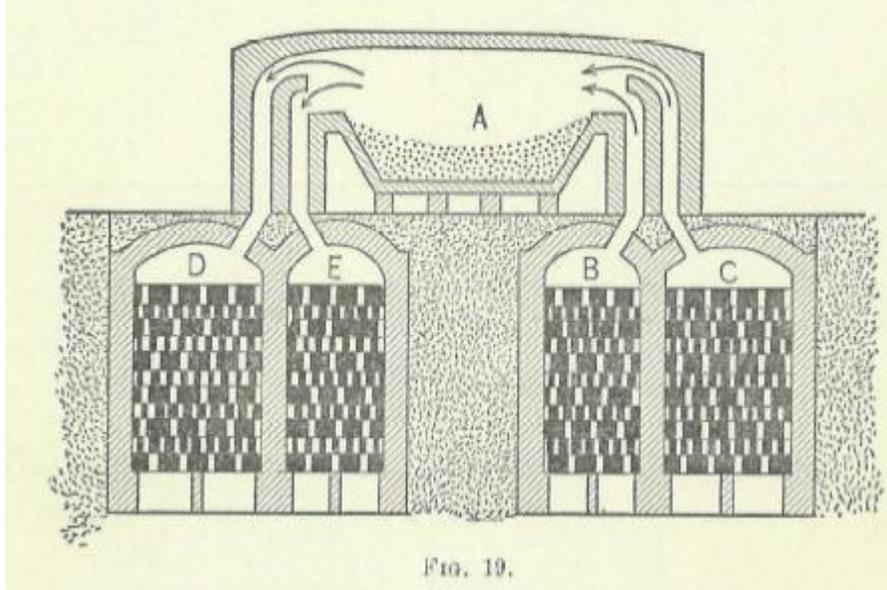
the incandescent coal, together with the air; the steam dissociates into hydrogen and oxygen, and the latter gas combines with the carbon, forming more carbon monoxide. These gases, mixing with the producer gas, increase its calorific intensity.



In the **Siemens gas producer** \* (Fig. 17), the coal is introduced at (E), falls upon the step grate (B, B), and is brought to incandescence by air entering through the openings while steam is injected from the pipe (C), and the gas formed escapes through (A, A). The ashes fall through the grate (G) into the pit, which is kept closed except when cleaning. A more modern producer (Taylor's) is shown in Fig. 18. The coal rests on a bed of ashes (A, A), and air is forced through the blast pipe (F), raising the fuel to incandescence. The gas formed passes out by the pipe (E). The grate (G) is made to revolve by the crank at (B), and the ashes fall over the edge of the grate at (H). The bed of ashes is kept about 3 feet deep on the revolving bottom at all times. Steam from the pipe (D) is introduced with the air through the blast pipe, which is provided with a hood to disseminate them through the fuel. In all producer gas plants, the regenerative heating system is used.

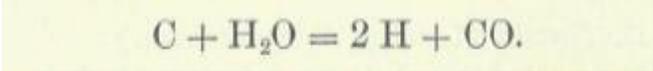
The Siemens regenerative furnace is a type of this style of heating. This furnace is represented in its simplest form in :Fig. 19. The material to be heated is placed

on the hearth of the furnace (A). There are four passages, B, C, D, and E, filled with loosely piled fire-brick called the "checker work." On their way to the chimney, the hot gases from the furnace pass through and heat two checker works, e.g. (B) and (C). When they are sufficiently heated, the flow of furnace gases is turned into (D) and (E), through which they pass to the chimney. Then fuel gas is conducted through the hot passage (B), to the furnace (A), where it mixes

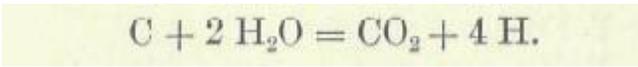


with air which has been heated by passing through (C). The temperature of (A) is thus much higher than if the air and gas arrived at (A) cold. While (B) and (C) are being thus cooled, (D) and (E), are being heated by the furnace gases, and after a time, the dampers are turned, and the gas made to pass through (E), and the air through (D), while the combustion products pass through (B) and (C) to the chimney. Hence the process is an alternating one, the checker works on one side being heated, while those on the other are giving up their heat to the gas and air respectively. Since the interstices between the bricks of the checker work frequently become clogged with ashes and soot, the combustion gases are sometimes passed through flues containing narrow tubes, through which the gas and air are passing to the furnace, in a direction opposite to that taken by the fire gases. The waste gases from blast furnaces contain over 30 per cent of carbon monoxide and about 63 per cent of nitrogen. These gases are largely employed near the furnaces for heating purposes. Water gas is sometimes used as a fuel, but oftener as a constituent of illuminating gas. It is made by blowing steam over

incandescent anthracite coal or coke, and is a mixture of about 45 per cent each of carbon monoxide and hydrogen, with small amounts of nitrogen, oxygen, and carbon dioxide. For the best results, the temperature must not fall below 1000° C.; above this point, the reaction is:



But at lower temperatures, the following takes place:



smoke or soot. Its calorific value is about 3000 C. per cubic meter. One kilo of coke produces about 1.13 cubic meters of water gas, but anthracite gives a better yield ..

The fuel is brought to incandescence by a blast of air, and during this part of the process the heat generally goes to waste. When it is white hot, the air is cut off, and the steam is turned on; decomposition occurs, according to the first reaction above. As soon as the temperature falls below 1000° C., the steam is cut off and the air blast turned on till the coal is again white hot. Thus alternate blowings of air and steam are carried on. The generator gas produced by the air blast is sometimes saved and used, but in making illuminating gas it goes to waste. For illuminating gas, this water gas is "enriched" with naphtha.

Coal gas is made by distilling bituminous coal in retorts. It contains hydrogen and marsh gas in large quantities, - about 40 per cent of each, - besides small amounts of carbon monoxide, carbon dioxide, nitrogen, oxygen, and hydrocarbons of the C<sub>n</sub>H<sub>2n</sub> and C<sub>n</sub>H<sub>2n-2</sub> series, which impart illuminating properties. It has a limited use in domestic stoves and as a source of power in gas engines.

The average composition of the various fuel gases is shown in the following table \* :-

	H	CH <sub>4</sub>	CO	C <sub>2</sub> H <sub>4</sub>	CO <sub>2</sub>	N	O	H <sub>2</sub> S
Natural gas (Ohio) . . . . .	2.2	92.6	0.5	0.3	0.3	3.6	0.3	0.2
Coal gas . . . . .	47.0	40.5	6.0	4.0	0.5	1.5	0.5	—
Water gas . . . . .	45.7	2.0	45.8	—	4.0	2.0	0.5	—
Producer gas . . . . .	6.0	3.0	23.5	—	1.5	65.0	—	—

When burned. with 20 per cent excess of air, and assuming that the escaping gases have a temperature of 500°F., 1000 cubic feet of gas will evaporate the

following number of pounds of water, at from 60° F. to 212° F. :-

Natural gas . . . . .	893 pounds *
Coal gas . . . . .	591 “
Water gas . . . . .	262 “
Producer gas . . . . .	115 “

**Liquefied petroleum gas (fuel):** This is the most common meaning of LPG. It is a flammable gas mixture composed primarily of propane, butane, and other hydrocarbons. LPG is a versatile fuel source used in various applications, including:

- **Domestic:** cooking fuel in homes and restaurants, heating appliances, hot water heaters
- **Industrial:** fuel for boilers, furnaces, kilns, and other equipment
- **Transportation:** fuel for cars, trucks, buses, and other vehicles
- **Agriculture:** drying crops, pest control, irrigation pumps

### **What are Safety Matches?**

A safety match is a type of match that can be lit even if it is wet. The head of a safety match is protected by a coating of red phosphorus, whereas the head of a regular match is not. When you strike a safety match, the friction between the head and the striking surface causes some of the red phosphorus to rub off. This ignites and starts the flame.

### **The Composition of Safety Matches**

The composition of safety matches is a closely guarded secret. However, there are a few things that we know about them. First and foremost, safety matches are composed of two main elements: the match head and the stick.

The match head is made up of a combustible material that, when lit, causes the stick to ignite. The stick is made of a non-combustible material that will not ignite on its own but will light when in contact with the flame from the match head. This is why you can blow out a safety match and use it again.

### **The History of Safety Matches**

The history of safety matches is a long one. According to one legend, an American named Joshua P. White invented them in 1828 after he was inspired by a Hindu monk who had shown him how to create light by striking

two pieces of sandpaper together. However, it wasn't until 1892 that Joseph Swan and John Walker succeeded in creating a workable and safe match.

Their version used white phosphorus, which was later discontinued due to its toxicity. These days, most safety matches are composed of strike-on-box matches (made of phosphoric acid) and strike-anywhere matches (made of potassium chlorate, potassium nitrate, and red phosphorus).

### **Safety Match Manufacturing: Lighting the Way with Precision**

Ah, safety matches! Those tiny sticks that bring light and warmth with a simple strike. But have you ever wondered how these seemingly simple objects are made?

Here's a glimpse into the fascinating world of safety match manufacturing:

#### **The Process:**

1. **Raw Materials:** It all starts with the selection of high-quality wood, like aspen or poplar, for the matchsticks. Phosphorus, sulfur, and other chemicals are also crucial ingredients for the striking surface and the igniting tip.
2. **Splint Making:** The wood is cut into thin strips, called splints, which are then dried and polished to ensure smooth striking.
3. **Dip and Dry:** The splints are dipped into a chemical bath containing paraffin wax, phosphorus, and other ingredients. This forms the striking surface and the head of the match. After dipping, they are dried thoroughly.
4. **Tipping:** The tip of the match gets a special coating, usually containing red phosphorus and antimony sulfide. This is the part that ignites when struck.
5. **Box Packaging:** The finished matchsticks are then carefully counted and assembled into boxes lined with striking surfaces. Labels and designs are added, and voila! Your handy box of safety matches is ready.

#### **Safety First:**

Safety is paramount in every step of the process. Strict regulations and quality control measures ensure that the chemicals used are handled safely and the final product is reliable and ignites only on the designated striking surface.

## **Modernization and Beyond:**

While the basic principles of safety match manufacturing remain the same, modern technology plays a significant role in automation, quality control, and environmental sustainability. Many factories are implementing automated dipping, packing, and inspection systems to improve efficiency and accuracy.

## **The Global Matchstick Industry:**

India is a leading producer of safety matches, with Sivakasi in Tamil Nadu being a global hub for the industry. Other major players include China, Brazil, and Indonesia.

## **Interesting Facts:**

- The first practical safety match was invented in 1827 by John Walker, a chemist from England.
- The average matchstick burns for about 8 seconds.
- The striking surface on a matchbox typically contains red phosphorus and glass powder.

So, the next time you strike a match, remember the intricate manufacturing process and the dedication behind that tiny flame. It's a testament to human ingenuity and our ability to harness simple materials to light up our lives.

## **Why are Safety Matches Called “Safety” Matches?**

The strike pad on a safety match is composed of two different materials: red phosphorus and potassium chlorate. When the match is struck, the two substances mix and ignite, creating a flame. However, this reaction is a little temperamental—if it's not done just right, it can create a potentially dangerous spark.

To prevent accidents, the phosphorus and chlorate are separated by a strip of glass that's coated with a material that won't ignite (usually China clay). This strip keeps the two substances from touching and causing an accident until the match is lit.

## **How Do You Make A Safety Match?**

When talking about the composition of safety matches, match heads are typically made of a composition of potassium chlorate, phosphorus, and sulphur. The head of the match is dipped in this mixture and then dried. When you light a match, the heat ignites the head and starts a chemical reaction that burns through the sulphur core. This sets off the striker on the side of the matchbox, which then sparks and lights the fuse.

## **Advantages of Safety Matches**

- They are easy to light and give off a long-lasting flame.
- The flame is not affected by wind and is thus stable.
- They are available in different lengths, so you can choose the one that is comfortable for you.
- They are easier to handle than lighters, and thus, are ideal for use in windy conditions.
- Disadvantages Of Safety Matches
- Matches can start fires if they are not used properly.
- They are not as reliable as lighters when it comes to starting a fire.
- Matches can also be dangerous if they are left unattended.

## **Conclusion**

Safety matches are easy to use – simply light the match and hold it to the tinder until it ignites. They have a long burning time, which means that you will not have to keep relighting them.

There are a few features of Safety Matches that make them a desirable choice for those looking for a safe and convenient solution for lighting fires. Safety Matches are flame-resistant, meaning that they will not catch fire in the presence of a fire.

A safety match is a small and simple object that is used to light fires. It is made of a wooden handle and a phosphorus button. The phosphorus button is struck against a hard surface to create a spark that ignites the tinder. The safety match is then used to light the kindling and the fire can be started.

## **PAINT**

Paint is a pigmented liquid that is applied to a surface to provide protection, decoration, or both. It is a mixture of a pigment, a binder, and a solvent. The pigment gives the paint its color, the binder holds the pigment to the surface, and the solvent thins the paint and helps it to dry.

There are many different types of paint, each with its own properties and uses. Some of the most common types of paint include:

- **Water-based paints:** These paints are easy to clean up and have low odor. They are a good choice for interior walls and ceilings.



Water based paints

- **Oil-based paints:** These paints are more durable than water-based paints and provide a harder finish. They are a good choice for trim, doors, and cabinets.



Oil based paints

- **Latex paints:** These paints are a type of water-based paint that is known for its durability and easy cleanup. They are a good choice for most interior painting projects.



Latex paints

- **Acrylic paints:** These paints are a type of water-based paint that is popular for use in arts and crafts. They dry quickly and have a wide range of colors available.



Acrylic paints

- **Enamel paints:** These paints are a type of oil-based paint that is known for its glossy finish and durability. They are a good choice for trim, doors, and cabinets.



## Enamel paints

- **Specialty paints:** These paints are designed for specific purposes, such as fire retardant paint or anti-slip paint.

When choosing a paint, it is important to consider the surface you will be painting, the desired finish, and the amount of wear and tear the paint will need to withstand. It is also important to read the label carefully to make sure that the paint is safe for use in your home.

## VARNISHES

Varnish is a resin-based solution used on wooden surfaces to provide a transparent, hard, and protective film. Most varnishes are a blend of resin, driers, and solvents. The process of applying varnish on surfaces is known as varnishing.

Varnishing is done only on wooden surfaces. Varnish plays a vital role in finishing wooden surfaces of doors, windows, floors, furniture, etc. In this article, we will discuss different types of varnish used on wood.

### Purpose And Advantages Of Varnish

- i) It gives brilliance to the painted surface.
- ii) It protects the surface against harmful atmospheric effects.
- iii) It increases the durability of the paint coating.
- iv) It makes the wooden surface beautiful without hiding the natural grains of the wood.

### **Requirements Of A Good Varnish**

- i) The varnish should not shrink or develop cracks after drying.
- ii) The thin film of varnish should be hard and durable.
- iii) The varnish should dry rapidly.
- iv) It should make the surface glossy.
- v) It should give the finished surface a uniform color and pleasing appearance.
- vi) It should not hide the natural grains of the wood.
- vii) The natural color of the varnish should not fade away when the finished surface is exposed to the atmosphere.

### Types Of Varnish

Depending upon the solvent used, varnish can be of the following types:

1. Oil varnish
2. Spirit varnish
3. Turpentine varnish
4. Asphalt varnish
5. Water varnish
6. Flat varnish
7. Spar varnish
8. Oil varnish

#### **1. Oil Varnish**

These types of varnish are produced by dissolving hard resins such as amber and copal in linseed oil. Turpentine may also be used in small quantities to make the varnish thin and to render it workable. Oil varnishes dry slowly, forming a hard and durable film over the surface.

#### **2. Spirit Varnish**

This type of varnish is manufactured by dissolving resins such as shellac or lac in methylated spirit. Suitable pigment may be added to give the required shade to the varnished surface.

Spirit varnish dries very quickly and gets easily affected by the weathering action. It is mostly used for wooden furniture.

### **3. Turpentine Varnish**

This type of varnish is prepared by dissolving gum dammer, mastic, and rosin-like resins in turpentine. These varnishes are light in color and also dry quickly. But turpentine varnishes are not as tough and hard as oil varnishes.

### **4. Asphalt Varnish**

In this type of varnish, melted asphalt is dissolved in linseed oil. Sometimes a suitable amount of turpentine or petroleum spirit is added to make this varnish thin. Asphalt varnish is normally used for varnishing fabricated iron and steel products.

### **5. Water Varnish**

This type of varnish is prepared by dissolving shellac in hot water. Shellac does not dissolve easily in water. To make it dissolve quickly ammonia or potash, soda, or borax are added to the water. These varnishes are used for painting pictures, posters, and maps.

### **6. Flat Varnish**

It is an ordinary type of varnish. Materials like wax, finely divided silica, and metallic soaps are used in this varnish to reduce the glossy finish of the varnished surface. Usually, it gives the surface a dull appearance.

### **7. Spar Varnish**

This type of varnish is mostly used on spars and other exposed parts of the ships. Flat varnish is very good weather resistant but not suitable for indoor use.

## **Process Of Varnishing**

The process of varnishing wooden surfaces is as follows:

### **1. Preparation Of Surface**

The surface is to be thoroughly rubbed smooth using sandpaper and cleaned of dust and dirt.

## **2. Knotting**

All the knots should be covered with a hot preparation of red lead and glue size.

## **3. Stopping**

After knotting, the wooded surface is stopped. This is done using hot weak glue size. This coat fills all the pores of the surface. 1 kg of glue normally forms about 10 liters of glue size.

If glue is not available, two coats of boiled linseed oil can be used as an alternative. After stopping when the surface becomes dry, it is rubbed again with sandpaper.

## **4. Applying Varnish**

When the stopping process is done, it's time to apply varnish to the surface in very thin coats. Fine haired varnishing brush should be used to apply varnish. When the first coat becomes dry, the second coat is to be applied.

## UNIT IV

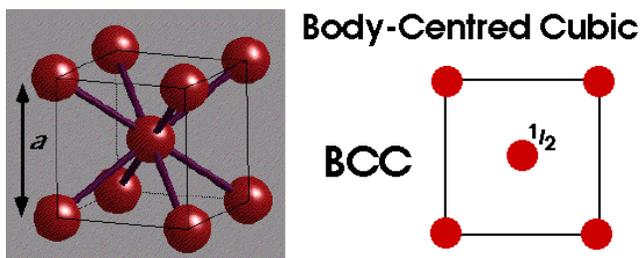
### METALLIC STATE

#### Metallic bond

Metallic bonds are the force of attraction between valence electrons and the metal atoms. It is the sharing of many detached electrons between many positive ions, where the electrons act as "glue" giving the substance a definite structure. Metallic bonds causes many of the traits of metals, such as strength, malleability, ductility, luster, conduction of heat and electricity.

#### PACKING OF ATOMS IN METAL (BCC,CCP,HCP)

##### Body Centred Cubic (BCC) Structure



At room temperatures, elements Li, Na, K, Rb, Ba, V, Cr and Fe have structures that can be described as body centre cubic (bcc) packing of spheres. The other two common ones are face centred cubic (fcc) and hexagonal closest (hcp) packing. This type of structure is shown by the diagram below. In a crystal structure, the arrangement extends over millions and millions of atoms, and the above diagram shows the unit cell, the smallest unit that, when repeatedly stacked together, will generate the entire structure.

Actually, the unit we draw is more than a unit cell. We use the centre of the atoms (or spheres) to represent the corners of the unit cell, and each of these atoms are shared by 8 unit cells. There is a whole atom located in the centre of the unit cell. Usually, the length of the cell edge is represented by  $a$ . The direction from a corner of a cube to the farthest corner is called body diagonal ( $bd$ ). The face diagonal ( $fd$ ) is a line drawn from one vertex to the opposite corner of the same face. If the edge is  $a$ , then we have:

$$\begin{aligned}fd^2 &= a^2 + a^2 = 2a^2 \\bd^2 &= fd^2 + a^2 \\&= a^2 + a^2 + a^2\end{aligned}$$

$$= 3 a^2$$

Atoms along the body diagonal ( $bd$ ) touch each other. Thus, the body diagonal has a length that is four times the radius of the atom,  $R$ .

$$bd = 4 R$$

The relationship between  $a$  and  $R$  can be worked out by the Pythagorean theorem:

$$(4 R)^2 = 3 a^2$$

Thus,

$$4 R = \sqrt{3} a$$

or

$$a = 4R/\sqrt{3}$$

Recognizing these relationships enable you to calculate parameters for this type of crystal. For example, one of the parameter is the packing fraction, the fraction of volume occupied by the spheres in the structure.

### **Cubic Close Packed (CCP) or Face Centred Cubic**

These are two different names for the same lattice.

We can think of this cell as being made by inserting another atom into each face of the simple cubic lattice - hence the "face centred cubic" name. The reason for the various colors is to help point out how the cells stack in the solid. Remember that the atoms are all the same.

The unit cell is again shown expanded for visibility. Actually, the corner atoms touch the one in the center of the face. The name "close packed" refers to the packing efficiency of 74.05%. No other packing can exceed this efficiency (although there are others with the same packing efficiency). If we stack the cells into a lattice we notice that the atoms form diagonal layers - the reason for the colors is to make these stand out. Note that diagonal layers also form along our line of sight. Since these cut across the other layers, each layer will contain all three colors. A different and better way of looking at this structure focuses on those layers. We start with a hexagonal array of spheres (the blue "A" layer). Notice that this is a close-packed arrangement - there is no way to pack more spheres into a given area.

We then place a second close-packed layer (the gold "B" layer) atop the first, so they nestle into the left-pointing holes in the first. *All spheres are actually the same atom, the colors are to help you keep track of the layers.* Notice that there are 2 separate choices for the second layer; in the animation below,

we have arbitrarily chosen to cover the left-pointing holes. We *can* put them over either all the "left-pointing" interstices or all the "right-pointing" interstices.

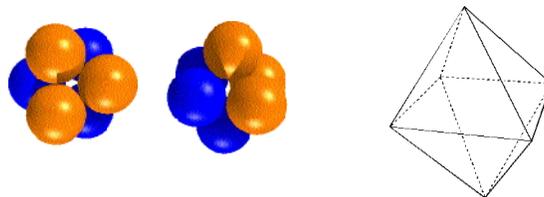
If we put them over the right-pointing interstices we generate a different layer, labeled the green or "C" layer. *Remember there are twice as many interstitial sites as spheres. (One left-pointing and one right-pointing).* We can continue to stack these layers in any order, providing that no 2 identical layers are adjacent. The cubic close packed structure can be constructed from the

A - B - C - A - B - C sequence.

An alternate sequence might be B - A - C - B - A - C ...

The resulting structure is a 3-D analog of the hexagonal packing in a plane - it is the most efficient way to pack spheres. There are two types of interstitial sites in an fcc lattice. Let us consider a pair of layers - blue and gold. Remember, the gold atoms cover all the left-pointing interstices in the blue layer, and none of the right-pointing ones.

Under each gold atom is a small space surrounded by 4 atoms in a tetrahedral arrangement. This is a *4 - coordinate tetrahedral interstitial site*. If we look at the right-pointing holes in the blue layer, we see that the gold layer does not nestle into them as it does the left-pointing ones. These cavities are surrounded by 6 atoms in octahedral geometry. This is a *6 - coordinate octahedral interstitial site*.



Go back and look at the lattice again and locate the tetrahedral and octahedral interstitial sites.

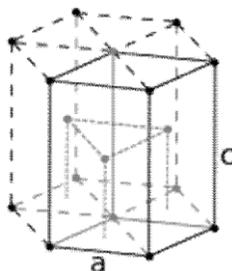
Examples of fcc / ccp metals include nickel, silver, gold, copper, and aluminum.

Another way of stacking these layers is to omit the "C" layers altogether - simply alternate "A" and "B". This is also a close-packed array, but the symmetry is different. It is called:

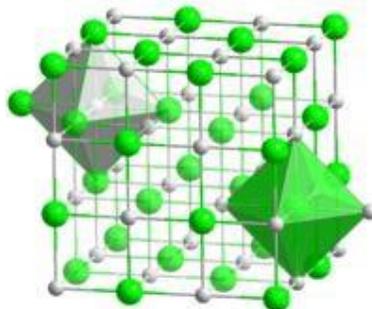
## Hexagonal Close Packed (HCP)

The hexagonal close packed structure can be made by piling layers in the A - B - A - B - A - B ..... sequence.

An alternative sequence would be A - C - A - C - A ...



Rock-salt structure

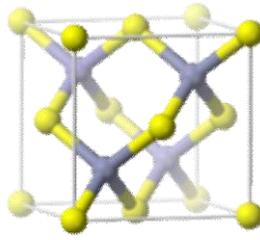


The space group of the rock-salt (NaCl) structure is called  $Fm\bar{3}m$ , or "225". The Strukturbericht designation is "B1". In the rock-salt or sodium chloride structure, each of the two atom types forms a separate face-centered cubic lattice, with the two lattices interpenetrating so as to form a 3D checkerboard pattern. Alternately, one could view this structure as a face-centered cubic structure with secondary atoms in its octahedral holes.

Examples of compounds with this structure include sodium chloride itself, along with almost all other alkali halides, and "many divalent metal oxides, sulfides, selenides, and tellurides". More generally, this structure is more likely to be formed if the cation is somewhat smaller than the anion. The coordination number of each atom in this structure is 6: each cation is coordinated to 6 anions at the vertices of an octahedron, and similarly, each anion is coordinated to 6 cations at the vertices of an octahedron.

The interatomic distance (distance between cation and anion, or half the unit cell length  $a$ ) in some rock-salt-structure crystals are: 2.3 Å ( $2.3 \times 10^{-10}$  m) for NaF, 2.8 Å for NaCl, and 3.2 Å for SnTe. Other compounds showing rock salt like structure are LiF, LiCl, LiBr, LiI, NaF, NaBr, NaI, KF, KCl, KBr, KI, RbF, RbCl, RbBr, RbI, CsF, MgO, PbS, AgF, AgCl, AgBr and ScN.

## Zincblende structure



The space group of the Zincblende structure is called  $F43m$ , or 216. The Strukturbericht designation is "B3". The Zincblende structure (also written "zinc blende") is named after the mineral zincblende (sphalerite), one form of zinc sulfide ( $\beta$ -ZnS). As in the rock-salt structure, the two atom types form two interpenetrating face-centered cubic lattices. However, it differs from rock-salt structure in how the two lattices are positioned relative to one another. The zincblende structure has tetrahedral coordination: Each atom's nearest neighbors consist of four atoms of the opposite type, positioned like the four vertices of a regular tetrahedron. Altogether, the arrangement of atoms in zincblende structure is the same as diamond cubic structure, but with alternating types of atoms at the different lattice sites.

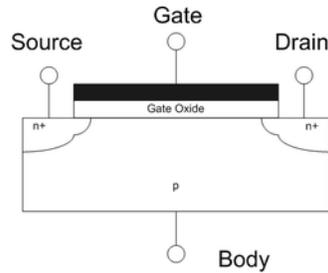
Examples of compounds with this structure include zincblende itself, lead(II) nitrate, many compound semiconductors (such as gallium arsenide and cadmium telluride), and a wide array of other binary compounds. Other compounds showing zinc blende-like structure are  $\alpha$ -AgI,  $\beta$ -BN, diamond, CuBr,  $\beta$ -CdS, BP and BAs.

### **Example: Quartz**

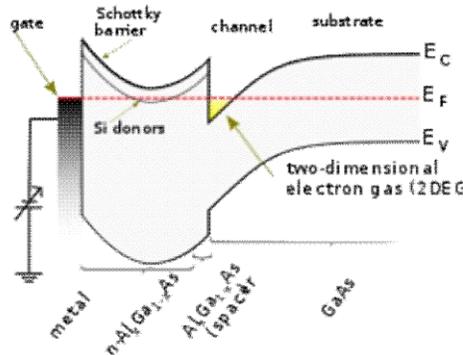
Quartz is a crystal that belongs to the hexagonal lattice system but exists in two polymorphs that are in two different crystal systems. The crystal structures of  $\alpha$ -quartz are described by two of the 18 space groups (152 and 154) associated with the trigonal crystal system, while the crystal structures of  $\beta$ -quartz are described by two of the 27 space groups (180 and 181) associated with the hexagonal crystal system.

### **Electron gas**

Electron gas is a scientific model in solid-state physics. It is an electron gas that is free to move in two dimensions, but tightly confined in the third. This tight confinement leads to quantized energy levels for motion in the third direction, which can then be ignored for most problems. Thus the electrons appear to be a 2D sheet embedded in a 3D world. The analogous construct of holes is called a two-dimensional hole gas (2DHG), and such systems have many useful and interesting properties



In MOSFETs, the 2DEG is only present when the transistor is in inversion mode, and is found directly beneath the gate oxide.



Band edge diagram of a basic HEMT. Conduction band edge  $E_C$  and Fermi level  $E_F$  determine the electron density in the 2DEG. Quantized levels form in the triangular well (yellow region) and optimally only one of them lies below  $E_F$ .

Most 2DEG are found in transistor-like structures made from semiconductors. The most commonly encountered 2DEG is the layer of electrons found in MOSFETs. When the transistor is in inversion mode, the electrons underneath the gate oxide are confined to the semiconductor-oxide interface, and thus occupy well defined energy levels. For thin-enough potential wells and temperatures not too high, only the lowest level is occupied (see the figure caption), and so the motion of the electrons perpendicular to the interface can be ignored. However, the electron is free to move parallel to the interface, and so is quasi-two-dimensional.

Other methods for engineering 2DEGs are high-electron-mobility-transistors (HEMTs) and rectangular quantum wells. HEMTs are field-effect transistors that utilize the heterojunction between two semiconducting materials to confine electrons to a triangular quantum well. Electrons confined to the heterojunction of HEMTs exhibit higher mobilities than those in MOSFETs, since the former device utilizes an intentionally undoped channel thereby mitigating the deleterious effect of ionized impurity scattering. Two closely spaced heterojunction interfaces may be used to confine electrons to a rectangular quantum well. Careful choice of the

materials and alloy compositions allow control of the carrier densities within the 2DEG.

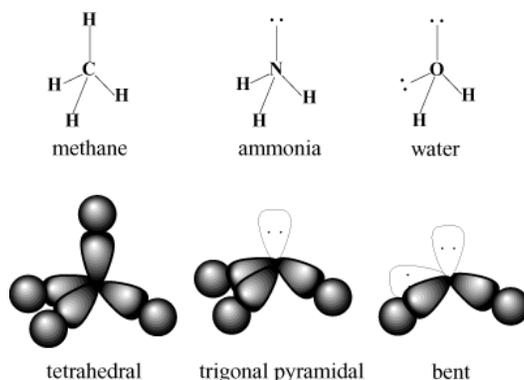
Electrons may also be confined to the surface of a material. For example, free electrons will float on the surface of liquid helium, and are free to move along the surface, but stick to the helium; some of the earliest work in 2DEGs was done using this system.<sup>[1]</sup> Besides liquid helium, there are also solid insulators (such as topological insulators) that support conductive surface electronic states.

Recently, atomically thin solid materials have been developed (graphene, as well as metal dichalcogenide such as molybdenum disulfide) where the electrons are confined to an extreme degree. The two-dimensional electron system in graphene can be tuned to either a 2DEG or 2DHG (2-D hole gas) by gating or chemical doping. This has been a topic of current research due to the versatile (some existing but mostly envisaged) applications of graphene.

A separate class of heterostructures that can host 2DEGs are oxides. Although both sides of the heterostructure are insulators, the 2DEG at the interface may arise even without doping (which is the usual approach in semiconductors). Typical example is a ZnO/ZnMgO heterostructure.<sup>[3]</sup> More examples can be found in a recent review<sup>[4]</sup> including a notable discovery of 2004, a 2DEG at the LaAlO<sub>3</sub>/SrTiO<sub>3</sub> interface<sup>[5]</sup> which becomes superconducting at low temperatures. The origin of this 2DEG is still unknown, but it may be similar to modulation doping in semiconductors, with electric-field-induced oxygen vacancies acting as the dopants.

## Pauling and Valence Bond Theory

Pauling's big contribution to chemistry was valence bond theory, which combined his knowledge of quantum mechanical theory with his knowledge of basic chemical facts, like bond lengths and bond strengths and shapes of molecules. Valence bond theory, like Lewis's bonding theory, provides a



simple model that is useful for predicting and understanding the structures of molecules, especially for organic chemistry. Later Pauling applied his understanding of molecular shapes and bonding to a pretty good explanation of protein structures. Later still, he became famous for peace activism and promoting ascorbic acid (vitamin C) as a cure for colds and cancer.

*Examples of using valence bond theory to predict the structures of molecules.*

Valence bond theory is good for explaining the "ground state" properties of molecules, or the properties of molecules that only involve the lowest energy states. However, just like a hydrogen atom can be "excited" by light, moving the electron from  $n = 1$  to  $n = 2, 3, 4...$  states, molecules have excited states that can be very important for reactions, colors, etc. Valence bond theory is not good for anything involving excited states, so we will talk about Molecular Orbital Theory as our next big topic.

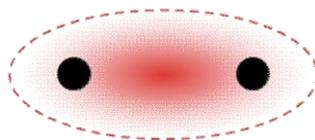
## **Valence bond theory**

In chemistry, valence bond (VB) theory is one of two basic theories, along with molecular orbital (MO) theory, that were developed to use the methods of quantum mechanics to explain chemical bonding. It focuses on how the atomic orbitals of the dissociated atoms combine to give individual chemical bonds when a molecule is formed. In contrast, molecular orbital theory has orbitals that cover the whole molecule.

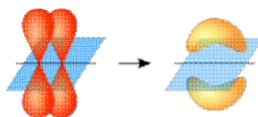
## **Theory**

According to this theory a covalent bond is formed between the two atoms by the overlap of half filled valence atomic orbitals of each atom containing one unpaired electron. A valence bond structure is similar to a Lewis structure, but where a single Lewis structure cannot be written, several valence bond structures are used. Each of these VB structures represents a specific Lewis structure. This combination of valence bond structures is the main point of resonance theory. Valence bond theory considers that the overlapping atomic orbitals of the participating atoms form a chemical bond. Because of the overlapping, it is most probable that electrons should be in the bond region. Valence bond theory views bonds as weakly coupled orbitals (small overlap). Valence bond theory is typically easier to employ in ground state

molecules. The inner-shell orbitals and electrons remain essentially unchanged during the formation of bonds.



$\sigma$  bond between two atoms: localization of electron density



Two p-orbitals forming a  $\pi$ -bond.

The overlapping atomic orbitals can differ. The two types of overlapping orbitals are sigma and pi. Sigma bonds occur when the orbitals of two shared electrons overlap head-to-head. Pi bonds occur when two orbitals overlap when they are parallel. For example, a bond between two s-orbital electrons is a sigma bond, because two spheres are always coaxial. In terms of bond order, single bonds have one sigma bond, double bonds consist of one sigma bond and one pi bond, and triple bonds contain one sigma bond and two pi bonds. However, the atomic orbitals for bonding may be hybrids. Often, the bonding atomic orbitals have a character of several possible types of orbitals. The methods to get an atomic orbital with the proper character for the bonding is called hybridization.

### **Applications of valence bond theory**

An important aspect of the Valence Bond theory is the condition of maximum overlap, which leads to the formation of the strongest possible bonds. This theory is used to explain the covalent bond formation in many molecules.

For example, in the case of the  $F_2$  molecule, the F-F bond is formed by the overlap of  $p_z$  orbitals of the two F atoms, each containing an unpaired electron. Since the nature of the overlapping orbitals are different in  $H_2$  and  $F_2$  molecules, the bond strength and bond lengths differ between  $H_2$  and  $F_2$  molecules.

In an HF molecule the covalent bond is formed by the overlap of the 1s orbital of H and the  $2p_z$  orbital of F, each containing an unpaired electron. Mutual sharing of electrons between H and F results in a covalent bond in HF.

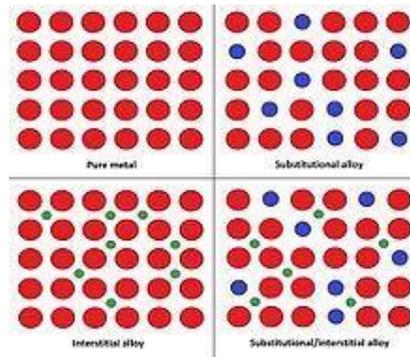
## Structure of Alloys

An alloy is a combination of metals or of a metal and another element. Alloys are defined by a metallic bonding character. An alloy may be a solid solution of metal elements or a mixture of metallic phases. Intermetallic compounds are alloys with a defined stoichiometry and crystal structure. Zintl phases are also sometimes considered alloys depending on bond types.

Alloys are used in a wide variety of applications. In some cases, a combination of metals may reduce the overall cost of the material while preserving important properties. In other cases, the combination of metals imparts synergistic properties to the constituent metal elements such as corrosion resistance or mechanical strength. Examples of alloys are steel, solder, brass, pewter, duralumin, bronze and amalgams. The alloy constituents are usually measured by mass percentage for practical applications, and in atomic fraction for basic science studies. Alloys are usually classified as substitutional or interstitial alloys, depending on the atomic arrangement that forms the alloy. They can be further classified as homogeneous or heterogeneous or intermetallic.

Bronze, an alloy of copper and tin, was the first alloy discovered, during the prehistoric period now known as the Bronze Age. It was harder than pure copper and originally used to make tools and weapons, but was later superseded by metals and alloys with better properties. In later times bronze has been used for ornaments, bells, statues, and bearings. Brass is an alloy made from copper and zinc. Unlike pure metals, most alloys do not have a single melting point, but a melting range during which the material is a mixture of solid and liquid phases. The temperature at which melting begins is called the solidus, and the temperature when melting is just complete is called the liquidus. For many alloys there is a particular alloy proportion (in some cases more than one), called either a eutectic mixture or a peritectic composition, which gives the alloy a unique and low melting point, and no liquid/solid slush transition.

## Substitutional and interstitial alloys



Different atomic mechanisms of alloy formation, showing pure metal, substitutional, interstitial, and a combination of the two.

When a molten metal is mixed with another substance, there are two mechanisms that can cause an alloy to form, called *atom exchange* and the *interstitial mechanism*. The relative size of each element in the mix plays a primary role in determining which mechanism will occur. When the atoms are relatively similar in size, the atom exchange method usually happens, where some of the atoms composing the metallic crystals are substituted with atoms of the other constituent. This is called a *substitutional alloy*. Examples of substitutional alloys include bronze and brass, in which some of the copper atoms are substituted with either tin or zinc atoms respectively. In the case of the interstitial mechanism, one atom is usually much smaller than the other and cannot successfully substitute for the other type of atom in the crystals of the base metal. Instead, the smaller atoms become trapped in the spaces between the atoms of the crystal matrix, called the *interstices*. This is referred to as an *interstitial alloy*. Steel is an example of an interstitial alloy, because the very small carbon atoms fit into interstices of the iron matrix. Stainless steel is an example of a combination of interstitial and substitutional alloys, because the carbon atoms fit into the interstices, but some of the iron atoms are substituted by nickel and chromium atoms.

Iron is usually found as iron ore on Earth, except for one deposit of native

iron in Greenland, which was used by the Inuit people. Native copper, however, was found worldwide, along with silver, gold, and platinum, which were also used to make tools, jewelry, and other objects since Neolithic times. Copper was the hardest of these metals, and the most widely distributed. It became one of the most important metals to the ancients. Eventually, humans learned to smelt metals such as copper and tin from ore, and, around 2500 BC, began alloying the two metals to form bronze, which was much harder than

its ingredients. Tin was rare, however, being found mostly in Great Britain. In the Middle East, people began alloying copper with zinc to form brass. Ancient civilizations took into account

the mixture and the various properties it produced, such as hardness, toughness and melting point, under various conditions of temperature and work hardening, developing much of the information contained in modern alloy phase diagrams.<sup>[13]</sup> For example, arrowheads from the Chinese Qin dynasty (around 200 BC) were often constructed with a hard bronze-head, but a softer bronze-tang, combining the alloys to prevent both dulling and breaking during use.<sup>[14]</sup>

## **HUME-ROTHERY RATIOS**

The Hume-Rothery rules, named after William Hume-Rothery, are a set of basic rules that describe the conditions under which an element could dissolve in a metal, forming a solid solution. There are two sets of rules; one refers to substitutional solid solutions, and the other refers to interstitial solid solutions.

### **Substitutional solid solution rules**

For substitutional solid solutions, the Hume-Rothery rules are as follows:

- The atomic radius of the solute and solvent atoms must differ by no more than 15%:
- The crystal structures of solute and solvent must be similar.
- Complete solubility occurs when the solvent and solute have the same valency.<sup>[1]</sup> A metal of higher valency is more likely to dissolve in a metal with lower valency.
- The solute and solvent should have similar electronegativity. If the electronegativity difference is too great, the metals tend to form intermetallic compounds instead of solid solutions.

### **Interstitial solid solution rules**

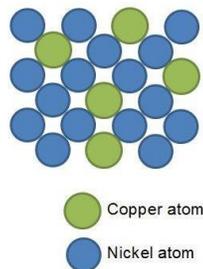
For interstitial solid solutions, the Hume-Rothery rules are:

- Solute atoms should have radius no larger than 59% of the radius of solvent atoms.
- The solute and solvent should have similar electronegativity.
- They should show a wide range of composition.

Solid solution strengthening is a type of alloying that can be used to improve the strength of a pure metal. The technique works by adding atoms of one element (the alloying element) to the crystalline lattice of another element (the base metal), forming a solid solution. The local nonuniformity in the lattice due to the alloying element makes plastic deformation more difficult by impeding dislocation motion. In contrast, alloying beyond the solubility limit can form a second phase, leading to strengthening via other mechanisms (e.g. the precipitation of intermetallic compounds).

### **Solid Solutions**

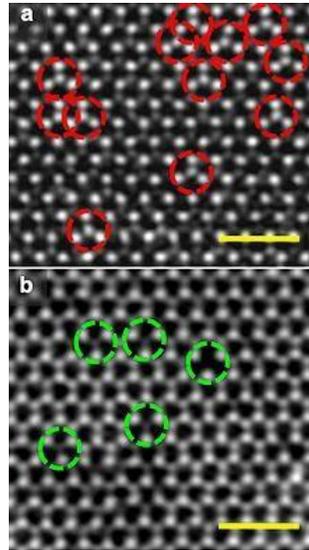
Just as two liquids can mix to form a liquid solution, two solids can mix to form a solid solution. For example, copper and nickel mix to form a solid solution. This means that the copper and nickel atoms completely mix with each other no matter how much copper or nickel there is. The image shows copper and nickel atoms in a solid solution.



*A plane of atoms in a solid solution of copper and nickel*

### **Crystallographic defect**

Crystalline solids exhibit a periodic crystal structure. The positions of atoms or molecules occur on repeating fixed distances, determined by the unit cell parameters. However, the arrangement of atoms or molecules in most crystalline materials is not perfect. The regular patterns are interrupted by crystallographic defects.



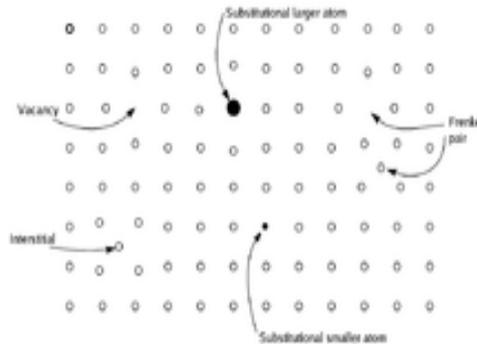
Electron microscopy of antisites (a, Mo substitutes for S) and vacancies (b, missing S atoms) in a monolayer of molybdenum disulfide. Scale bar: 1 nm.<sup>[1]</sup>

### Point defects

Point defects are defects that occur only at or around a single lattice point. They are not extended in space in any dimension. Strict limits for how small a point defect is are generally not defined explicitly. However, these defects typically involve at most a few extra or missing atoms. Larger defects in an ordered structure are usually considered dislocation loops. For historical reasons, many point defects, especially in ionic crystals, are called *centers*: for example a vacancy in many ionic solids is called a luminescence center, a color center, or F-center. These dislocations permit ionic transport through crystals leading to electrochemical reactions. These are frequently specified using Kröger–Vink Notation.

- Vacancy defects are lattice sites which would be occupied in a perfect crystal, but are vacant. If a neighboring atom moves to occupy the vacant site, the vacancy moves in the opposite direction to the site which used to be occupied by the moving atom. The stability of the surrounding crystal structure guarantees that the neighboring atoms will not simply collapse around the vacancy. In some materials, neighboring atoms actually move away from a vacancy, because they experience attraction from atoms in the surroundings. A vacancy (or pair of vacancies in an ionic solid) is sometimes called a Schottky defect.

- Interstitial defects are atoms that occupy a site in the crystal structure at which there is usually not an atom. They are generally high energy configurations. Small atoms in some crystals can occupy interstices without high energy, such as hydrogen in palladium.

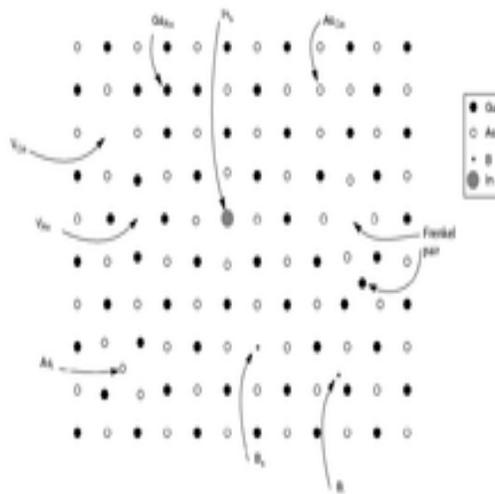


Schematic illustration of some simple point defect types in a monatomic solid

- A nearby pair of a vacancy and an interstitial is often called a Frenkel defect or Frenkel pair. This is caused when an ion moves into an interstitial site and creates a vacancy.
- Due to fundamental limitations of material purification methods, materials are never 100% pure, which by definition induces defects in crystal structure. In the case of an impurity, the atom is often incorporated at a regular atomic site in the crystal structure. This is neither a vacant site nor is the atom on an interstitial site and it is called a *substitutional* defect. The atom is not supposed to be anywhere in the crystal, and is thus an impurity. In some cases where the radius of the substitutional atom (ion) is substantially smaller than that of the atom (ion) it is replacing, its equilibrium position can be shifted away from the lattice site. These types of substitutional defects are often referred to as off-center ions. There are two different types of substitutional defects: Isovalent substitution and aliovalent substitution. Isovalent substitution is where the ion that is substituting the original ion is of the same oxidation state as the ion it is replacing. Aliovalent substitution is where the ion that is substituting the original ion is of a different oxidation state than the ion it is replacing. Aliovalent substitutions change the overall charge within the ionic compound, but the ionic compound must be neutral. Therefore, a charge compensation mechanism is required. Hence either one of the metals is partially or fully oxidised or reduced, or ion vacancies are created.
- Antisite defects occur in an ordered alloy or compound when atoms of different type exchange positions. For example, some alloys have a regular

structure in which every other atom is a different species; for illustration assume that type A atoms sit on the corners of a cubic lattice, and type B atoms sit in the center of the cubes. If one cube has an A atom at its center, the atom is on a site usually occupied by a B atom, and is thus an antisite defect. This is neither a vacancy nor an interstitial, nor an impurity.

➤ Topological defects are regions in a crystal where the normal chemical bonding environment is topologically different from the surroundings. For instance, in a perfect sheet of graphite (graphene) all atoms are in rings containing six atoms. If the sheet contains regions where the number of atoms in a ring is different from six, while the total number of atoms remains the same, a topological defect has formed. An example is the Stone Wales defect in nanotubes, which consists of two adjacent 5-membered and two 7-membered atom rings.



Schematic illustration of defects in a compound solid, using GaAs as an example.

- Also amorphous solids may contain defects. These are naturally somewhat hard to define, but sometimes their nature can be quite easily understood. For instance, in ideally bonded amorphous silica all Si atoms have 4 bonds to O atoms and all O atoms have 2 bonds to Si atom. Thus e.g. an O atom with only one Si bond (a dangling bond) can be considered a defect in silica. Moreover, defects can also be defined in amorphous solids based on empty or densely packed local atomic neighbourhoods, and the properties of such 'defects' can be shown to be similar to normal vacancies and interstitials in crystals.
- Complexes can form between different kinds of point defects. For example, if a vacancy encounters an impurity, the two may bind

together if the impurity is too large for the lattice. Interstitials can form 'split interstitial' or 'dumbbell' structures where two atoms effectively share an atomic site, resulting in neither atom actually occupying the site.

### **Line defects**

Dislocations are linear defects, around which the atoms of the crystal lattice are misaligned. There are two basic types of dislocations, the *edge* dislocation and the *screw* dislocation. "Mixed" dislocations, combining aspects of both types, are also common.

### **Planar defects**

Grain boundaries occur where the crystallographic direction of the lattice abruptly changes. This usually occurs when two crystals begin growing separately and then meet.

- Antiphase boundaries occur in ordered alloys: in this case, the crystallographic direction remains the same, but each side of the boundary has an opposite phase: For example, if the ordering is usually ABABABAB (hexagonal close-packed crystal), an antiphase boundary takes the form of ABABBABA.
- Stacking faults occur in a number of crystal structures, but the common example is in close-packed structures. They are formed by a local deviation of the stacking sequence of layers in a crystal. An example would be the ABABCABAB stacking sequence.
- A twin boundary is a defect that introduces a plane of mirror symmetry in the ordering of a crystal. For example, in cubic close-packed crystals, the stacking sequence of a twin boundary would be ABCABCACBA.
- On planar surfaces of single crystals, steps between atomically flat terraces can also be regarded as planar defects. It has been shown that such defects and their geometry have significant influence on the adsorption of organic molecules

### **Bulk defects**

- Three-dimensional macroscopic or bulk defects, such as pores, cracks, or inclusions
- Voids — small regions where there are no atoms, and which can

be thought of as clusters of vacancies

- Impurities can cluster together to form small regions of a different phase. These are often called precipitates.

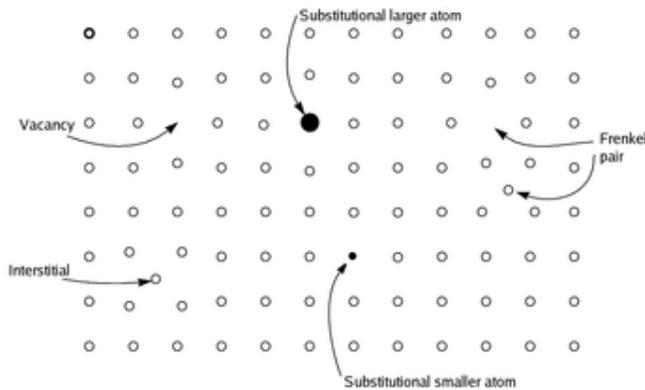
### Extrinsic defects

Various elemental analyses of diamond reveal a wide range of impurities. They mostly originate, however, from inclusions of foreign materials in diamond, which could be nanometer-small and invisible in an optical microscope. Also, virtually any element can be

hammered into diamond by ion implantation. More essential are elements which can be introduced into the diamond lattice as isolated atoms (or small atomic clusters) during the diamond growth.

### Non-stoichiometric compound

Non-stoichiometric compounds are chemical compounds, almost always solid inorganic compounds, having elemental composition whose proportions cannot be represented by integers; most often, in such materials,



some small percentage of atoms are missing or too many atoms are packed into an otherwise perfect lattice work.

Origin of title phenomena in crystallographic defects. Shown is a two-dimensional slice through a primitive cubic crystal system showing the regular square array of atoms on one face (open circles, o), and with these, places where atoms are missing from a regular site to create *vacancies*, displaced to an adjacent acceptable space to create a *Frenkel pair*, or substituted by a smaller or larger atom not usually seen (closed circles, •), in each case resulting in a material that is moved toward being measurably non-stoichiometric.

Contrary to earlier definitions, modern understanding of non-stoichiometric compounds view them as homogenous, and not mixtures of stoichiometric chemical compounds. Since the solids are overall electrically neutral, the defect is compensated by a change in the charge of other atoms in the solid, either by changing their oxidation state, or by replacing them with atoms of different elements with a different charge. Many metal oxides and sulfides have non-stoichiometric examples; for example, stoichiometric iron(II) oxide, which is rare, has the formula FeO, whereas the more common material is nonstoichiometric, with the formula Fe<sub>0.95</sub>O. The type of equilibrium defects in non-stoichiometric compounds can vary with attendant variation in bulk properties of the material. Non-stoichiometric compounds also exhibit special electrical or chemical properties because of the defects; for example, when atoms are missing, electrons can move through the solid more rapidly. Non-stoichiometric compounds have applications in ceramic and superconductive material and in electrochemical system designs.

Nonstoichiometry is pervasive for metal oxides, especially when the metal is not in its

highest oxidation state. For example, although wüstite (ferrous oxide) has an ideal (stoichiometric) formula FeO, the actual stoichiometry is closer to Fe<sub>0.95</sub>O. The non-stoichiometry reflect the ease of oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> effectively replacing a small portion of Fe<sup>2+</sup> with two thirds their number of Fe<sup>3+</sup>. Thus for every three "missing" Fe<sup>2+</sup> ions, the crystal contains two Fe<sup>3+</sup> ions to balance the charge. The composition of a non-stoichiometric compound usually varies in a continuous manner over a narrow range. Thus, the formula for wüstite is written as Fe<sub>1-x</sub>O, where  $x$  is a small number (0.05 in the previous example) representing the deviation from the "ideal" formula. Nonstoichiometry is especially important in solid, three-dimensional polymers that can tolerate mistakes. To some extent, entropy drives all solids to be non-stoichiometric. But for practical purposes, the term

describes materials where the non-stoichiometry is measurable, usually at least 1% of the ideal composition.

The monosulfides of the transition metals are often nonstoichiometric. Best known perhaps is nominally iron(II) sulfide (the mineral pyrrhotite) with a composition Fe<sub>1-x</sub>S ( $x = 0$  to 0.2). The rare stoichiometric FeS endmember is known as the mineral *troilite*. Pyrrhotite is remarkable in that it has numerous polytypes, i.e. crystalline forms differing in symmetry (monoclinic or hexagonal) and composition (Fe<sub>7</sub>S<sub>8</sub>, Fe<sub>9</sub>S<sub>10</sub>, Fe<sub>11</sub>S<sub>12</sub> and others). These materials are always iron-deficient owing to the presence of lattice defects, namely iron vacancies. Despite those defects, the composition is usually expressed as a ratio of large numbers and the crystals symmetry is relatively

high. This means the iron vacancies are not randomly scattered over the crystal, but form certain regular configurations. Those vacancies strongly affect the magnetic properties of pyrrhotite: the magnetism increases with the concentration of vacancies and is absent for the stoichiometric FeS.

Palladium hydride is a nonstoichiometric material of the approximate composition

$\text{PdH}_x$  ( $0.02 < x < 0.58$ ). This solid conducts hydrogen by virtue of the mobility of the hydrogen atoms within the solid.

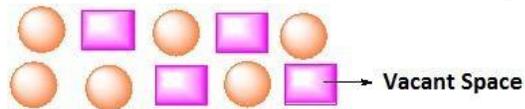
Tungsten oxides are sometimes difficult to determine if a material is non-stoichiometric or if the formula is best represented by large numbers. The oxides of tungsten illustrate this situation. Starting from the idealized material tungsten trioxide, one can generate a series of related materials that are slightly deficient in oxygen. These oxygen-deficient species can be described as  $\text{WO}_{3-x}$ , but in fact they are stoichiometric species with large unit cells with the formulas  $\text{W}_n\text{O}_{3n-2}$ , where  $n = 20, 24, 25, 40$ . Thus, the last species can be described with the stoichiometric formula  $\text{W}_{40}\text{O}_{118}$ , whereas the non-stoichiometric description  $\text{WO}_{2.95}$  implies a more random distribution of oxide vacancies.

### Stoichiometric Defects

- These ranges of point defects do not disturb the stoichiometry of the solid.
- They are also called *intrinsic* or thermodynamic defects.
- Non-ionic solids exhibit their defects as vacancy defects and interstitial defects.

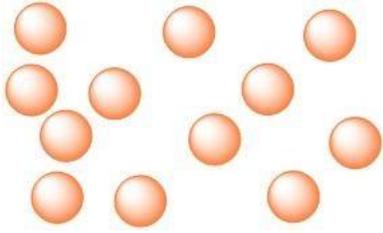
#### Vacancy Defect:

A crystal containing vacant lattice sites is said to have vacancy defect. This defect can also develop due to heating up of a substance.



#### Interstitial Defect:

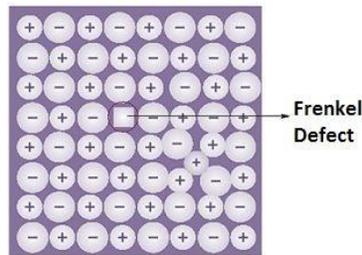
A crystal in which some constituent particles occupy an interstitial site, are said to have interstitial defect which increases the density of the substance.



Ionic solids exhibit their defects as Frenkel and Schottky defects.

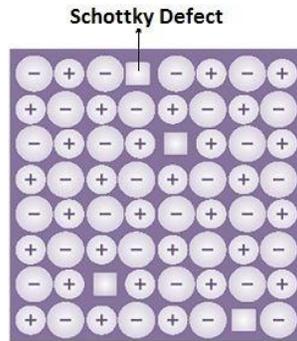
### **Frenkel Defect:**

- This defect is exhibited by the ionic substances due to the large difference in size of ions.
- The smaller ion (cation) is displaced from its normal site to an interstitial site which creates a vacancy defect at its original site and an interstitial defect at the new location.
- It is also called dislocation defect.
- It does not alter the density of the solid.
- For example, ZnS, AgCl, AgBr and AgI due to small size of  $Zn^{2+}$  and  $Ag^+$  ions.



### **Schottky Defect:**

- This defect in ionic solids is equivalent to the vacancy defect in non-ionic solids.
- In order to maintain electrical neutrality, the number of missing cations and anions are equal.
- Schottky defect also decreases the density of the substance.
- This defect is shown by ionic substances in which the cation and anion are of almost similar sizes.
- In NaCl there are approximately  $10^6$  Schottky pairs per  $cm^3$  at room temperature. In  $1 cm^3$  there are about  $10^{22}$ . Thus, there is one Schottky defect per  $10^{16}$  ions.
- For example, NaCl, KCl, CsCl and AgBr.
- Out of these AgBr shows both, Frenkel as well as Schottky defects.



## SEMI CONDUCTORS

A semiconductor material has an electrical conductivity value falling between that of a metal, like copper, gold, etc. and an insulator, such as glass. Their resistance decreases as their temperature increases, which is behaviour opposite to that of a metal. Their conducting properties may be altered in useful ways by the deliberate, controlled introduction of impurities ("doping") into the crystal structure. Where two differently-doped regions exist in the same crystal, a semiconductor junction is created. The behavior of charge carriers which include electrons, ions and electron holes at these junctions is the basis of diodes, transistors and all modern electronics. Some examples of semiconductors are silicon, germanium, and gallium arsenide. After silicon, gallium arsenide is the second most common semiconductor used in laser diodes, solar cells, microwave frequency integrated circuits, and others. Silicon is a critical element for fabricating most electronic circuits.

Semiconductor devices can display a range of useful properties such as passing current more easily in one direction than the other, showing variable resistance, and sensitivity to light or heat. Because the electrical properties of a semiconductor material can be modified by doping, or by the application of electrical fields or light, devices made from semiconductors can be used for amplification, switching, and energy conversion.

The conductivity of silicon is increased by adding a small amount of pentavalent (antimony, phosphorus, or arsenic) or trivalent (boron, gallium, indium) atoms (part in  $10^8$ ). This process is known as doping and resulting semiconductors are known as doped or extrinsic semiconductors. Apart from doping, the conductivity of a semiconductor can equally be improved by increasing its temperature. This is contrary to the behaviour of a metal in which conductivity decreases with increase in temperature.

The modern understanding of the properties of a semiconductor relies on quantum physics to explain the movement of charge carriers in a crystal lattice.<sup>[1]</sup> Doping greatly increases the number of charge carriers within the crystal. When a doped semiconductor contains mostly free holes it is called "p-type", and when it contains mostly free electrons it is known as "n-type". The semiconductor materials used in electronic devices are doped under precise conditions to control the concentration and regions of p- and n-type dopants. A single semiconductor crystal can have many p- and n-type regions; the p-n junctions between these regions are responsible for the useful electronic behavior.

Although some pure elements and many compounds display semiconductor properties, silicon, germanium, and compounds of gallium are the most widely used in electronic devices. Elements near the so-called "metalloid staircase", where the metalloids are located on the periodic table, are usually used as semiconductors.

### **Amorphous semiconductors**

Some materials, when rapidly cooled to a glassy amorphous state, have semiconducting properties. These include B, Si, Ge, Se, Te and there are multiple theories to explain them.

### **Intrinsic semiconductor**

An intrinsic (pure) semiconductor, also called an undoped semiconductor or i-type semiconductor, is a pure semiconductor without any significant dopant species present. The number of charge carriers is therefore determined by the properties of the material itself instead of the amount of impurities. In intrinsic semiconductors the number of excited electrons and the number of holes are equal:  $n = p$ . This may even be the case after doping the semiconductor, though only if it is doped with both donors and acceptors equally. In this case,  $n = p$  still holds, and the semiconductor remains intrinsic, though doped.

The electrical conductivity of intrinsic semiconductors can be due to crystallographic defects or electron excitation. In an intrinsic semiconductor the number of electrons in the conduction band is equal to the number of holes in the valence band. An example is  $\text{Hg}_{0.8}\text{Cd}_{0.2}\text{Te}$  at room temperature.

An indirect band gap intrinsic semiconductor is one in which the maximum energy of the valence band occurs at a different  $k$  ( $k$ -space wave vector) than the minimum energy of the conduction band. Examples include silicon and germanium. A direct band gap intrinsic semiconductor is one where the

maximum energy of the valence band occurs at the same  $k$  as the minimum energy of the conduction band. Examples include gallium arsenide. A silicon crystal is different from an insulator because at any temperature above absolute zero, there is a non-zero probability that an electron in the lattice will be knocked loose from its position,

leaving behind an electron deficiency called a "hole". If a voltage is applied, then both the electron and the hole can contribute to a small current flow.

The conductivity of a semiconductor can be modeled in terms of the band theory of solids. The band model of a semiconductor suggests that at ordinary temperatures there is a finite possibility that electrons can reach the conduction band and contribute to electrical conduction. The term intrinsic here distinguishes between the properties of pure "intrinsic" silicon and the dramatically different properties of doped n-type or p-type semiconductors.

### **Extrinsic semiconductor**

An extrinsic semiconductor is one that has been *doped*; during manufacture of the semiconductor crystal a trace element or chemical called a doping agent has been incorporated chemically into the crystal, for the purpose of giving it different electrical properties than the pure semiconductor crystal, which is called an *intrinsic semiconductor*. In an extrinsic semiconductor it is these foreign dopant atoms in the crystal lattice that mainly provide the charge carriers which carry electric current through the crystal. The doping agents used are of two types, resulting in two types of extrinsic semiconductor. An *electron donor* dopant is an atom which, when incorporated in the crystal, releases a mobile conduction electron into the crystal lattice. An extrinsic semiconductor which has been doped with electron donor atoms is called an n-type semiconductor, because the majority of charge carriers in the crystal are negative electrons. An *electron acceptor* dopant is an atom which accepts an electron from the lattice, creating a vacancy where an electron should be called a *hole* which can move through the crystal like a positively charged particle. An extrinsic semiconductor which has been doped with electron acceptor atoms is called a p-type semiconductor, because the majority of charge carriers in the crystal are positive holes.

Doping is the key to the extraordinarily wide range of electrical behavior that semiconductors can exhibit, and extrinsic semiconductors are used to make semiconductor electronic devices such as diodes, transistors, integrated circuits, semiconductor lasers, LEDs, and photovoltaic cells. Sophisticated semiconductor fabrication processes like implant different dopant elements in different regions of the same semiconductor crystal wafer, creating

semiconductor devices on the wafer's surface. For example a common type of transistor, the n-p-n bipolar transistor, consists of an extrinsic semiconductor crystal with two regions of n-type semiconductor, separated by a region of p-type semiconductor, with metal contacts attached to each part.

### **N-type semiconductor**

An N-Type semiconductor is created by adding pentavalent impurities like phosphorus (P), arsenic (As), antimony (Sb), or bismuth (Bi). A pentavalent impurity is called a donor atom because it is ready to give a free electron to a semiconductor. The impurities are called dopants. The purpose of doing this is to make more charge carriers, or electron wires available in the material for conduction. In n-type semiconductors the number of electrons is more than the holes, so electrons are measured as majority charge carriers and holes are referred to as minority charge carriers.

Semiconductor materials like silicon and germanium have four electrons in their outer shell (valence shell). All the four electrons are used by the semiconductor atom in forming bonds with its neighbouring atoms, leaving a low number of electrons available for conduction. Pentavalent elements are those elements which have five electrons in their outer shell. When pentavalent impurities like phosphorus or arsenic are added into semiconductor, four electrons form bonds with the surrounding silicon atoms leaving one electron free. The resulting material has a large number of free electrons. Since electrons are negative charge carriers, the resultant material is called n-type (or negative type) semiconductor. The

pentavalent impurity that is added is called a 'dopant' and the process of addition is called 'doping' in simple the 8 electron is required to make a covalent bond and 1 electron remain in outer most shell which start acting as a free electron.

N-Type semiconductors are manufactured by doping 'intrinsic' or pure semiconductor material. The amount of impurity added is very small compared to the amount of semiconductor. The characteristics and nature of the resultant semiconductor can be controlled by controlling the quantity of the dopant.

### **P-type semiconductor**

A p-type semiconductor is a type of semiconductor. Ordinary semiconductors are made of materials that do not conduct (or carry) an electric current very well but are not highly resistant to doing so. They fall half way between conductors and insulators. An electric current occurs when electrons move

through a material. In order to move, there must be an electron 'hole' in the material for the electron to move into. A p-type semiconductor has more holes than electrons. This allows the current to flow along the material from hole to hole but only in one direction.

Semiconductors are most often made from silicon. Silicon is an element with four electrons in its outer shell. To make a p-type semiconductor extra materials like boron or aluminium are added to the silicon. These materials have only three electrons in their outer shell. When the extra material replaces some of the silicon it leaves a 'hole' where the fourth electron would have been if the semiconductor was pure silicon.

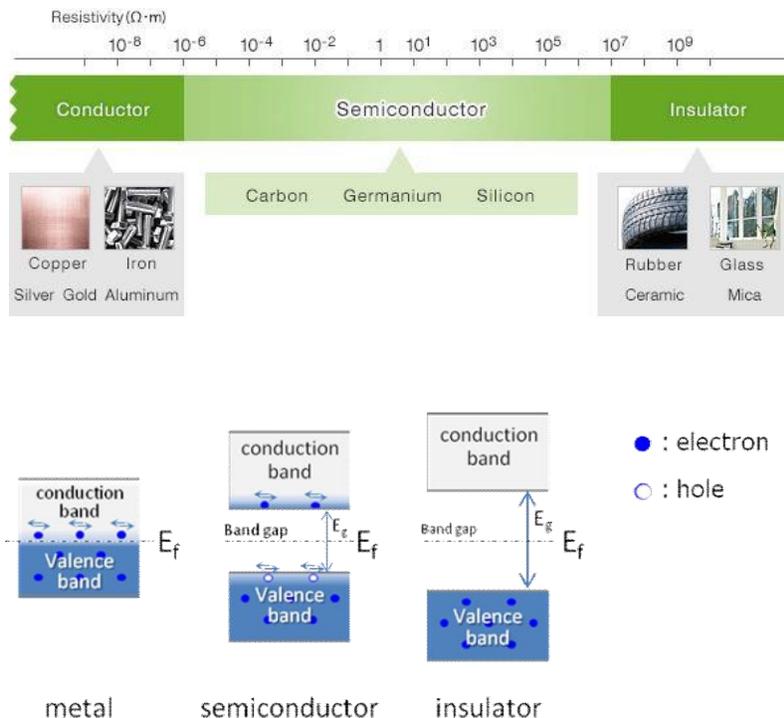
P-type semiconductors are made by doping the pure semiconductor material. The amount of impurity added is very small compared to the amount of semiconductor. The exact character of the semiconductor can be changed by varying the amount of 'dopant' that is added.

### **Properties of semiconductors**

The name "semiconductor" is widely known, but what are semiconductors? Semiconductors possess specific electrical properties. A substance that conducts electricity is called a conductor, and a substance that does not conduct electricity is called an insulator. Semiconductors are substances with properties somewhere between them. Electrical properties can be indicated by resistivity. Conductors such as gold, silver and copper have low resistance and conduct electricity easily.

Insulators such as rubber, glass and ceramics have high resistance and are difficult for electricity to pass through. Semiconductors have properties somewhere between these two. Their resistivity might change according to the temperature for example. At a low temperature, almost no electricity passes through them. But when the temperature rises, electricity passes through them easily.

Semiconductors containing almost no impurities conduct almost no electricity. But when some elements are added to the semiconductors, electricity passes through them easily. Semiconductors comprising a single element are called elemental semiconductors, including the famous semiconductor material Silicon. On the other hand, semiconductors made up of two or more compounds are called compound semiconductors, and are used in semiconductor lasers, light-emitting diodes, etc.

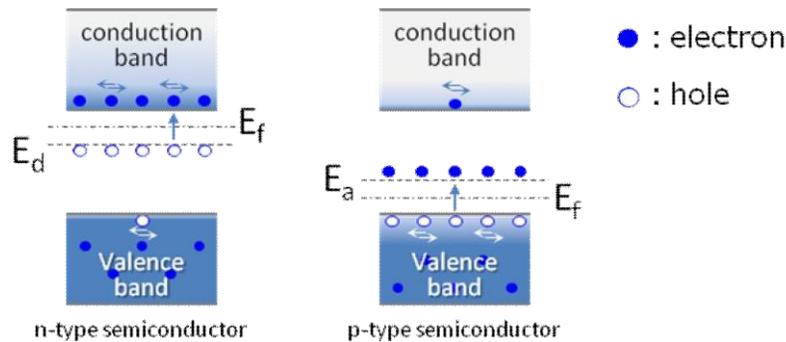


In metals, the conduction band and the valence band come very close to each other and may even overlap, with the Fermi energy ( $E_f$ ) somewhere inside. This means that the metal always has electrons that can move freely and so can always carry current. Such electrons are known as free electrons. These free electrons are responsible for current that flows through a metal. In semiconductors and insulators, the valence band and conduction band are separated by a forbidden energy gap ( $E_g$ ) of sufficient width, and the Fermi energy ( $E_f$ ) is between the valence and conduction band. To get to the conduction band, the electron has to gain enough energy to jump the band gap. Once this is done, it can conduct.

In semiconductors at room temperature, the band gap is smaller, there is enough thermal energy to allow electrons to jump the gap fairly easily and make the transitions in conduction band, given the semiconductor limited conductivity. At low temperature, no electron possesses sufficient energy to occupy the conduction band and thus no movement of charge is possible. At absolute zero, semiconductors are perfect insulators. The density of electrons in conduction band at room temperature is not as high as in metals, thus cannot conduct current as good as metal. The electrical conductivity of semiconductor is not as high as metal but also not as poor as electrical insulator. That is why, this type of material is called semiconductor - means half conductor.

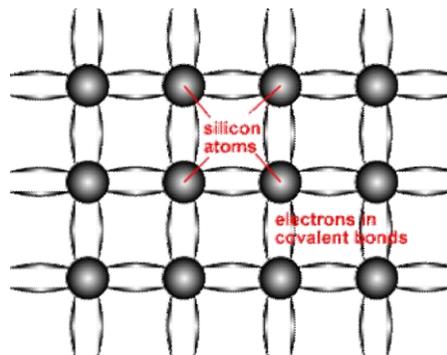
The band gap for insulators is large so very few electrons can jump the gap. Therefore, current does not flow easily in insulators. The difference between insulators and semiconductors is the size of the band gap energy. In insulator

where forbidden gap is very large and as a result the energy required by the electron to cross over to the conduction band is practically large enough. Insulators do not conduct electricity easily. That means the electrical conductivity of insulator is very poor. Semiconductor crystal used for IC etc. is high purity single crystal silicon of 99.9%, but when actually making a circuit, impurities are added to control the electrical properties. Depending on the added impurities, they become n- type and p-type semiconductors.



Pentavalent phosphorus (P) or arsenic (As) are added to high purity silicon for n-type semiconductors. These impurities are called donors. The energy level of the donor is located close to the conduction band, that is, the energy gap is small. Then, electrons at this energy level are easily excited to the conduction band and contribute to the conductivity. On the other hand, trivalent boron (B) etc. is added to p type semiconductor. This is called an acceptor. The energy level of the acceptor is close to the valence band. Since there are no electrons here, electrons in the valence band are excited here. As a result, holes are formed in the valence band, which contributes to the conductivity.

## Semiconductor Structure

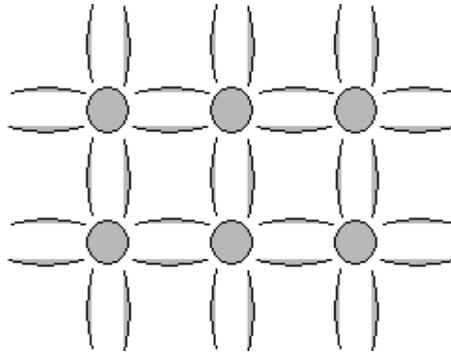


Schematic representation of covalent bonds in a silicon crystal lattice. Each line connecting the atoms represents an electron being shared between the two. Two electrons being shared are what form the covalent bond.

The atoms in a semiconductor are materials from either group IV of the periodic table, or from a combination of group III and group V (called III-V semiconductors), or of combinations from group II and group VI (called II-VI semiconductors). Silicon is the most commonly used semiconductor material as it forms the basis for integrated circuit (IC) chips and is the most mature technology and most solar cells are also silicon based. A full periodic table is given in the page Periodic Table. Several of the material properties of silicon are given in the page Silicon Material Parameters.

The bond structure of a semiconductor determines the material properties of a semiconductor. One key effect is limit the energy levels which the electrons can occupy and how they move about the crystal lattice. The electrons surrounding each atom in a semiconductor are part of a covalent bond. A covalent bond consists of two atoms "sharing" a single electron, such that each atom is surrounded by 8 electrons. The electrons in the covalent bond are held in place by this bond and hence they are localised to region surrounding the atom. Since they cannot move or change their energy, electrons in a bond are not considered "free" and cannot participate in current flow, absorption or other physical processes of interest in solar cells. However, only at absolute zero are all electrons in a bonded arrangement. At elevated temperatures, the electron can gain enough energy to escape from its bond, and if this happens, the electron is free to move about the crystal lattice and participate in conduction. At room temperature, a semiconductor has enough free electrons to allow it to conduct current, while at, or close to absolute temperatures, a semiconductor behaves like an insulator.

The presence of the bond introduces two distinct energy states for the electrons. The lowest energy position for the electron is to be in its bound state. However, if the electron has enough thermal energy to break free of its bond, then it becomes free. The electron cannot attain energy values intermediate to these two levels; it is either at a low energy position in the bond, or it has gained enough energy to break free and therefore has a certain minimum energy. This minimum energy is called the "band gap" of a semiconductor. The number and energy of the free electrons is basic to the operation of electronic devices. The space left behind by the electrons allows a covalent bond to move from one electron to another, thus appearing to be a positive charge moving through the crystal lattice. This empty space is commonly called a "hole", and is similar to an electron, but with a positive charge.



Animation showing formation of "free" electrons and holes when an electron can escape its bond.

The most important parameters of a semiconductor material for solar cell operation are:

- the band gap;
- the number of free carriers available for conduction; and
- the "generation" and recombination of free carriers in response to light shining on the material.

### **Semiconductors & Electronics**

The movement towards environmentally friendly products, including 'green' cars and more efficient energy use, coupled with the growing use of mobile phones and personal communications, is driving demand for semiconductors and sophisticated electronics worldwide. Semiconductor manufacturers today need to be constantly developing new materials and technologies to meet these needs.

With their extremely high quality requirements, the semiconductor and electronics industries have used multivariate analysis for many years to develop models and monitor processes in real-time to improve product development, minimize waste and optimize output. This holds true within all aspects of the sector. For example, improved manufacturing process control can be achieved through first increasing process observability by using a combination of new instruments and cluster analysis. These techniques use acoustic waves to relay information about several physical parameters from within an injection mold. As these variables cannot be controlled individually, CAMO software is used to calculate their relationship to one another, and how that relates to the product.

## **Electronics and semiconductor manufacturing industry in India**

The Indian electronics industry is seeing growth encouraged both by government policies and incentives and by international investment. Its key and most resource-intensive segment, the semiconductor industry has substantial potential for growth since domestic demand is growing briskly. Semiconductors are required by a large number of industries, including telecommunications, information technology, industrial machinery and automation, medical electronics, automobile, engineering, power and solar photovoltaic, defense and aerospace, consumer electronics, and appliances. According to a NOVONOUS report, a steady and significant spurt in the semiconductor industry will increase the domestic market size fivefold during 2013-2020. As of 2015, however, the skill gap in Indian industry threatened progress, with 65 to 70 per cent of the market relying on imports.

### **Semiconductor industry**

With the newly heralded era of Internet of Things (IoT) dictating that the new generation of interconnected devices be capable of smart-computing, Indian semiconductor industry is set for a stable upsurge with bright prospects provided India's generic obstacles like redtape-ism, fund crunch and infrastructural deficits are adequately addressed. The fast growing electronics system design manufacturing (ESDM) industry in India has vibrant design capabilities with the number of units exceeding 120. As stated by the Department of Electronics and Information Technology (DeitY), approximately 2,000 chips are being designed in India every year with more than 200,000 engineers currently employed to work on various aspects of IC design and verification.

## UNIT V

### INORGANIC POLYMERS & SILICATES

#### **Inorganic Polymer**

Inorganic polymers are polymers with a skeletal structure that does not include carbon atoms in the backbone. Polymers containing inorganic and organic components are sometimes called hybrid polymers, and most so-called inorganic polymers are hybrid polymers. One of the best known examples is polydimethylsiloxane, otherwise known commonly as silicone rubber. Inorganic polymers offer some properties not found in organic materials including low temperature flexibility, electrical conductivity, and nonflammability. The term inorganic polymer refers generally to one-dimensional polymers, rather than to heavily crosslinked materials such as silicate minerals. Inorganic polymers with tunable or responsive properties are sometimes called smart inorganic polymers. A special class of inorganic polymers are geopolymers, which may be anthropogenic or naturally occurring.

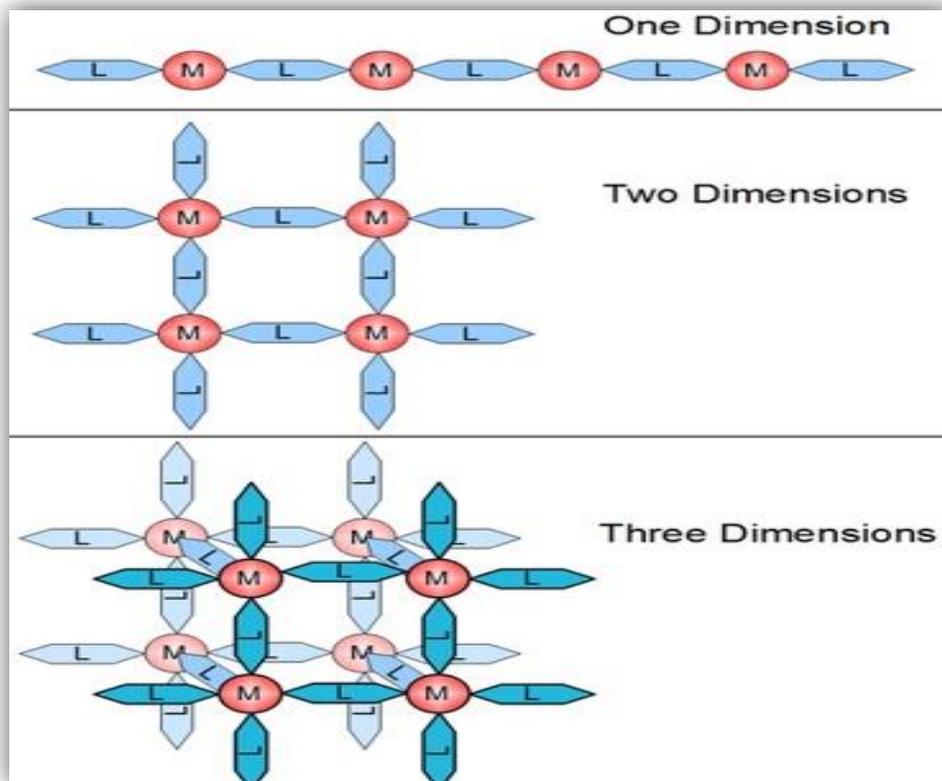
The difference between organic and inorganic polymers is that the organic polymers essentially contain carbon atoms in the backbone whereas the inorganic polymers do not contain carbon atoms. Inorganic polymers are polymers with a skeletal structure that does not include carbon atoms. Polymers containing inorganic and organic components are named hybrid polymers. One of the best known examples is polydimethylsiloxane, otherwise known commonly as silicone rubber, the backbone. Examples of inorganic substances include all metals, ammonia, hydrogen sulfide, chlorine, salt, minerals such as gypsum and generally all compounds that do not contain carbon-hydrogen bonds. By definition, an inorganic substance is a substance that does not contain carbon.

#### **Coordination polymer**

A coordination polymer is an inorganic or organometallic polymer structure containing metal cation centers linked by ligands. More formally a coordination polymer is a coordination compound with repeating coordination entities extending in 1, 2, or 3 dimensions.

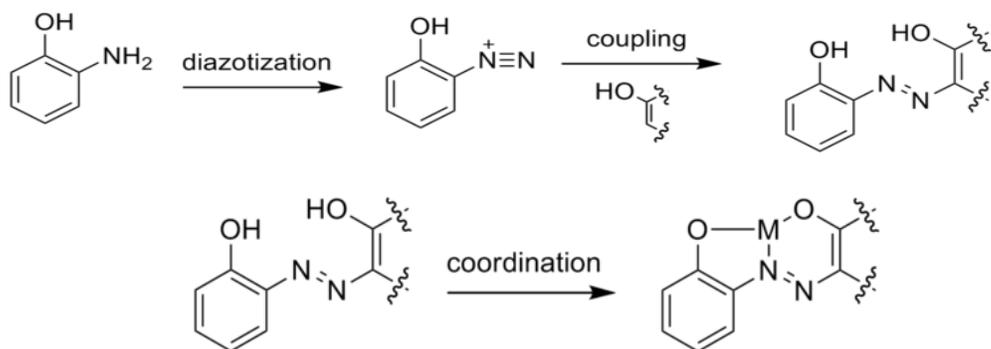
Coordination polymers can be classified in a number of different ways according to their structure and composition. One important classification is referred to as dimensionality. A structure can be determined to be one-, two-

or three-dimensional, depending on the number of directions in space the array extends in. A one-dimensional structure extends in a straight line (along the x axis); a two-dimensional structure extends in a plane (two directions, x and y axes); and a three-dimensional structure extends in all three directions.



The crystal structure and dimensionality of the coordination polymer is determined by the functionality of the linker and the coordination geometry of the metal center. Dimensionality is generally driven by the metal center which can have the ability to bond to as many as 16 functional sites on linkers; however this is not always the case as dimensionality can be driven by the linker when the linker bonds to more metal centres than the metal centre does linkers. The highest known coordination number of a coordination polymer is 14, though coordination numbers are most often between 2 and 10. Examples of various coordination numbers are shown in planar geometry in Figure 2. In Figure 1 the 1D structure is 2-coordinated, the planar is 4-coordinated, and the 3D is 6-coordinated.

**Applications** Coordination polymers are commercialized as dyes. Particularly useful are derivatives of aminophenol. Metal complex dyes using copper or chromium are commonly used for producing dull colors. Tridentate ligand dyes are useful because they are more stable than their bi- or mono-dentate counterparts.



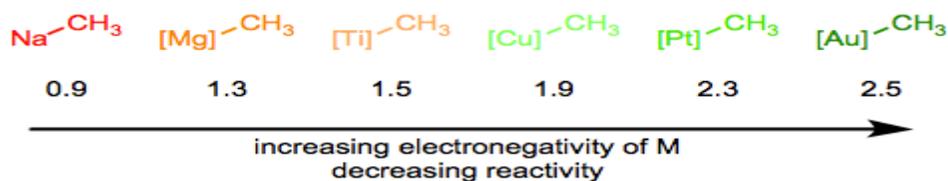
## Metal Alkyls

Metal alkyls feature a metal-carbon  $\sigma$  bond and are usually actor ligands, although some alkyl ligands behave as spectators. Our aim will be to understand the general dependence of the behavior of alkyl ligands on the metal center and the ligand's substituents. Using this knowledge, we can make meaningful comparisons between related metal alkyl complexes and educated predictions about their likely behavior. Because alkyl ligands are central to organometallic chemistry, I've decided to spread this discussion across multiple posts. We'll deal first with the general properties of metal alkyls.



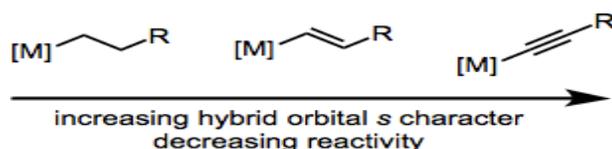
## General Properties

In the Simplifying the Organometallic Complex series, we decomposed the M-C bond into a positively charged metal and negatively charged carbon. This deconstruction procedure is consistent with the relative electronegativities of carbon and the transition metals. It can be very useful for us to imagine metal alkyls essentially as stabilized carbanions—but it's also important to understand that M-C bonds run the gamut from extremely ionic and salt-like ( $NaCH_3$ ) to essentially covalent ( $[HgCH_3]^+$ ). The reactivity of the alkyl ligand is inversely related to the electronegativity of the metal center.



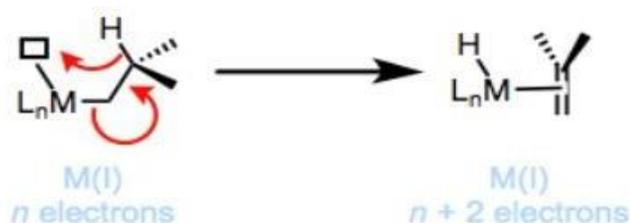
Reactivity decreases as the metal's electronegativity increases. Values given are Pauling electronegativities.

The hybridization of the carbon atom is also important, and the trend here follows the trend in nucleophilicity as a function of hybridization in organic chemistry.  $sp$ -Hybridized ligands are the least nucleophilic, followed by  $sp^2$  and  $sp^3$  ligands respectively.



Note that this trend is similar to the nucleophilicity of carbanions as a function of hybridization.

### Synthesis of Alkyl Complexes



1. The  $\beta$ -carbon must bear a hydrogen.
2.  $M-C$  and  $C-H$  must be *syn coplanar*.
- 3a. The metal must possess a vacant coordination site and an accessible empty orbital.
- 3b. The metal must possess 16 or fewer total electrons.
4. For rapid elimination, the metal must be at least  $d^2$ .

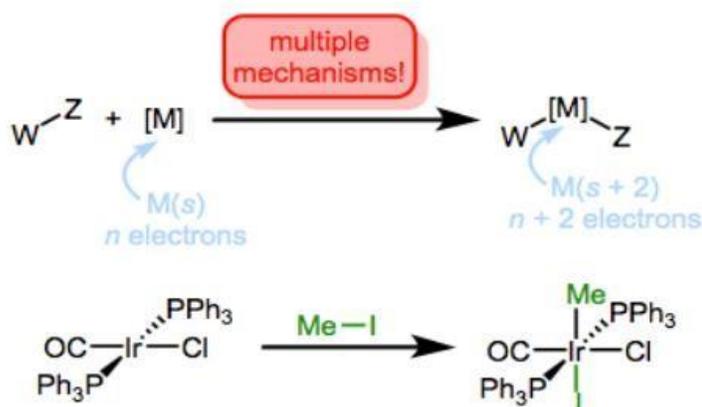
## Synthesis of Alkyl Complexes

Metals bearing good leaving groups are analogous to organic electrophiles, and are susceptible to nucleophilic attack by organolithiums, Grignard reagents, and other polarized organometallics. These reactions can be viewed as a kind of transmetalation, as the alkyl ligand moves from one metal to another. Electron-withdrawing X-type ligands like  $-\text{Cl}$  and  $-\text{Br}$  should jump out as good leaving groups. On the other hand, clean substitution of L-type ligands by anionic nucleophiles is much more rare (anionic complexes would result).

### Oxidative

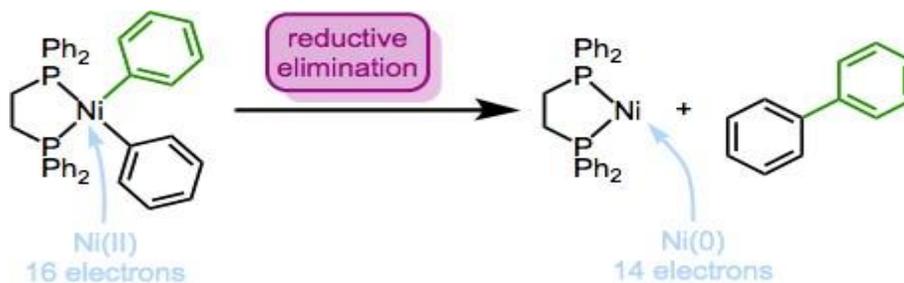


Simple and straightforward: nucleophile attacks electrophilic metal.

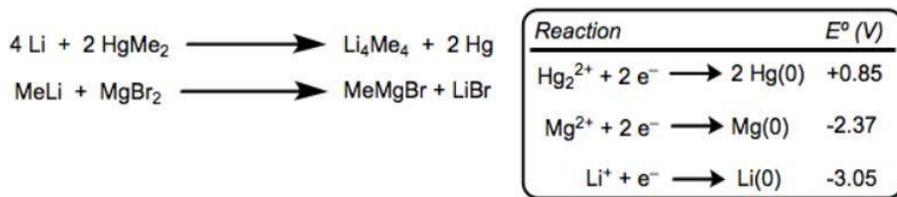


### Reductive Elimination

The microscopic reverse of oxidative addition. The metal loses two covalent ligands, its formal oxidation state decreases by two units, total electron count decreases by two units, and an  $\text{R-X}$  bond forms. Reductive elimination is favorable when the  $\text{R-X}$  bond in the organic product is more stable than the  $\text{M-R}$  and  $\text{M-X}$  bonds in the starting complex (a thermodynamic issue). It should be noted, however, that the kinetics of reductive elimination depend substantially on the steric bulk of the eliminating ligands. Concerted reductive elimination of  $\text{R-H}$  usually possesses a lower activation energy than  $\text{R-R}$  elimination.



## Silicate



## SILICATE

A salt in which the anion contains both silicon and oxygen, especially one of the anion  $\text{SiO}_4^{2-}$ . any of the many minerals consisting primarily of  $\text{SiO}_4^{2-}$  combined with metal ions, forming a major component of the rocks of the earth's crust.

Silicates are also used to make glass and ceramics. To do so, hard, formless material like sand or ceramic clay is heated to high temperatures, turning it into malleable material that can be formed to make drinking glasses, for example, or when lead is added to the molten liquid--crystal glass.

The most common silicate minerals fall into four types of structures, described in more detail below: isolated tetrahedra, chains of silica tetrahedra, sheets of tetrahedra, and a framework of interconnected tetrahedra. The link below opens a page in a new window, which contains 3-dimensional versions of these different structures.

### 1) ORTHO SILICATES

Ortho silicates (or Neso or Island silicates) are the simplest silicates which contain discrete  $\text{SiO}_4^{4-}$  tetrahedral units. Structural unit of ortho silicate unit is shown below.



The ortho silicate ion is the strong conjugate base of weak orthosilicic acid as well as it will not persist in aqueous solutions. Hence in nature, ortho silicate minerals are rare and only found with cations which form highly insoluble salts.

Examples of Ortho silicates:

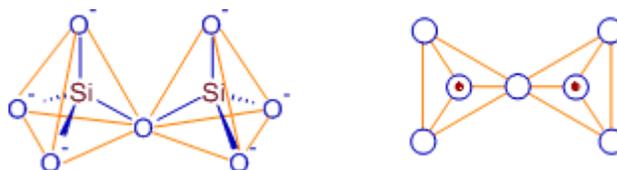
- 1) Phenacite (also known as phenakite) -  $\text{Be}_2\text{SiO}_4$
- 2) Willemite -  $\text{Zn}_2\text{SiO}_4$  - A minor silicate ore of zinc. Highly fluorescent (green) under shortwave UV.

Note: The  $\text{Be}^{2+}$  and  $\text{Zn}^{2+}$  ions are tetrahedrally surrounded by the oxygen atoms of silicate.

- 3) Olivine -  $(\text{Fe}/\text{Mg})_2\text{SiO}_4$  : Typically green in color. The cations are octahedrally coordinated to the oxygen atoms of the silicate.
- 4) Zircon -  $\text{ZrSiO}_4$  : The oldest mineral on Earth. The coordination number of  $\text{Zr}^{4+}$  is 8.

## 2) PYRO SILICATES

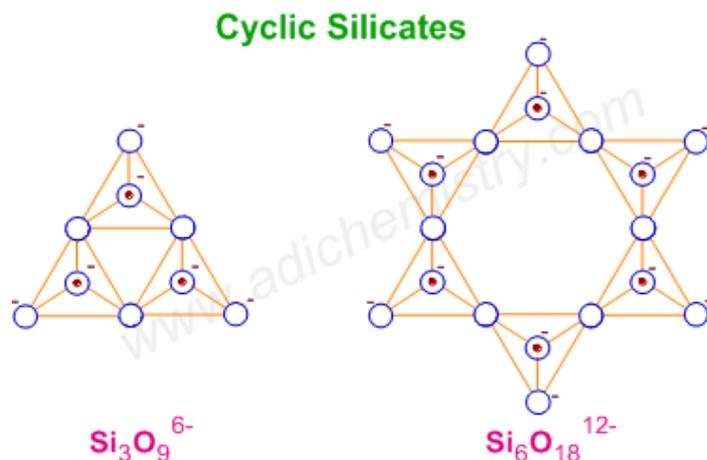
**Pyro silicate (or Soro silicate or disilicate)** contain  $\text{Si}_2\text{O}_7^{6-}$  ions which are formed by joining two tetrahedral  $\text{SiO}_4^{4-}$  which share one oxygen atom at one corner (one oxygen is removed while joining). Structure of pyrosilicate is shown below.



The pyrosilicate ion is less basic than orthosilicate ion. There only one mineral in nature containing pyrosilicate ion.

- E.g.                      1) Thortveitite -  $\text{Sc}_2\text{Si}_2\text{O}_7$

**Cyclic silicates** contain  $(\text{SiO})^{2n-}$  ions which are formed by linking three or more tetrahedral  $\text{SiO}_4^{4-}$  units cyclically. Each unit shares two oxygen atoms with other units.

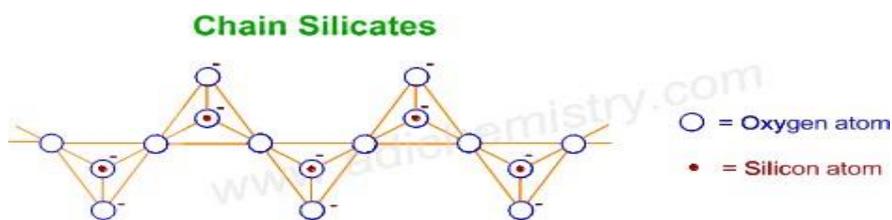


E.g.

- 1) Benitoite -  $\text{BaTi}(\text{SiO}_3)_3$  : containing three tetrahedra arranged cyclically  $[\text{Si}_3\text{O}_9]^{6-}$ .
- 2) Beryl -  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$  : containing six-silicate rings  $[\text{Si}_6\text{O}_{18}]^{12-}$ . It is an aluminosilicate. Each aluminium is surrounded by 6 oxygen atoms octahedrally. Well-known varieties of beryl include emerald and aquamarine.

## 4) CHAIN SILICATES (PYROXENES)

**Chain silicates** or pyroxenes contain  $(\text{SiO})^{2n-}$  ions which are formed by linking 'n' number of tetrahedral  $\text{SiO}_4^{4-}$  units linearly. Each unit shares two oxygen atoms with other units.



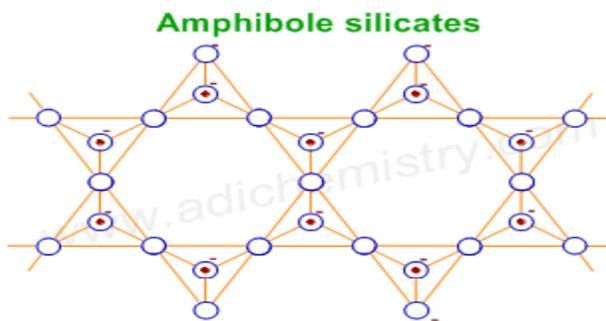
Examples of chain silicates:

- 1) Spodumene -  $\text{LiAl}(\text{SiO}_3)_2$  - a pyroxene mineral consisting of lithium aluminium inosilicate
- 2) Diopside -  $\text{CaMg}(\text{SiO}_3)_2$
- 3) Wollastonite -  $\text{Ca}_3(\text{SiO}_3)_3$

Note: The formula of cyclic silicates as well as chain silicates is  $(\text{SiO})^{2n-}$ . Hence these are considered as an oligomers of the unknown  $\text{SiO}_3^{2-}$  ion.

#### 5) DOUBLE CHAIN SILICATES (AMPHIBOLES)

The general formula of **double chain silicates (or Amphiboles)** is  $(\text{Si}_4\text{O})^{6n-}$ . There are two types of tetrahedra: those sharing 3 vertices and those sharing only 2 vertices.



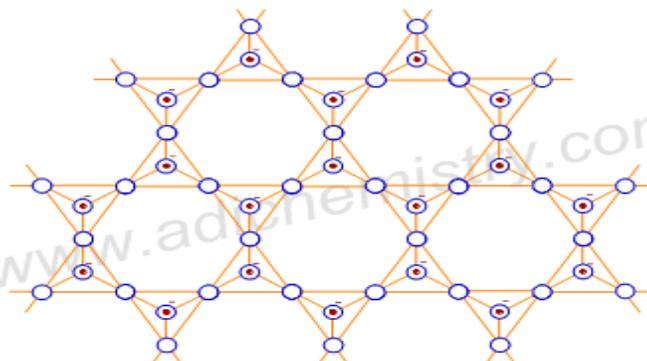
E.g.

- 1) Asbestos - These are noncombustible fibrous silicates. They have been used for thermal insulation material, brake linings, construction material and filters. These are carcinogenic amphiboles affecting the lungs. Hence their applications are restricted nowadays.
- 2) Tremolite -  $\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2(\text{OH})_2$

Note: The single and double chain silicates are collectively known as Inosilicates.

The general formula of Sheet or Phyllo or two dimensional (2-D) silicates is  $(\text{SiO})^{2n-}$ . tetrahedron shares three oxygen atoms with others and thus by forming two-dimensional sheets. These silicates can be cleaved easily just like graphite. The layers are held together by weak van der Waal's forces.

### Sheet (phyllo) Silicates



E.g.

1) Talc -  $\text{Mg}_3\text{Si}_4\text{O}_{10}(\text{OH})_2$  : It is the main ingredient of soap stone. It is the softest material with a smooth and greasy touch.

2) Micas : General formula is  $\text{X}_2\text{Y}_4\text{Z}_8\text{O}_{20}(\text{OH},\text{F})_4$  Where X = K, Na, or Ca

Y = Al, Mg, or Fe Z = Si or Al

E.g. Muscovite mica -  $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{F},\text{OH})_2$  - split into thin layers extremely easily and Lepidolite -  $\text{KLi}_2\text{Al}(\text{Al},\text{Si})_3\text{O}_{10}(\text{F},\text{OH})_2$

3) Clay : It is an aluminosilicate with sheet structure.

4) Kaolinite -  $\text{AlSiO}_5(\text{OH})_5$

### 7) THREE DIMENSIONAL SILICATES (TECTO SILICATES)

The general formula of three dimensional (3-D) or tecto or Framework silicates is  $(\text{SiO}_2)_n$ . All the oxygen atoms of  $\text{SiO}_4$  are shared with other tetrahedra and thus by forming three-dimensional network.

E.g.  $\text{SiO}_2$  - Quartz, Tridymite and Cristobalite - These are the crystalline forms of silica. When  $\text{SiO}_4^{4-}$  units are replaced by  $\text{AlO}_4^{5-}$  units, three dimensional aluminosilicates are formed.

E.g. Feldspar, Zeolites, Ult etc.,

- \* Silicate minerals are very common in the Earth crust since Oxygen and Silicon are the most abundant elements.
- \* The degree of polymerization is denoted by Oxygen to Silicon ratio (O/Si). Greater the degree of polymerization, lower will be the O/Si ratio. The values of O/Si for ortho silicates (least polymerized) = 4:1 while for tecto silicates (most polymerized silicate) = 2:1.
- \* With increase in the degree of polymerization, there is decrease in the charge per silicon atom as well as the basicity of silicate mineral. Indeed, silica (SiO<sub>2</sub>) is an acidic oxide.
- \* The basic silicate minerals readily react with weak acids and undergo weathering.

### **Beryl**

Beryl is a mineral composed of beryllium aluminium cyclosilicate with the chemical formula  $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ . Well-known varieties of beryl include emerald and aquamarine. Naturally occurring, hexagonal crystals of beryl can be up to several meters in size, but terminated crystals are relatively rare. Pure beryl is colorless, but it is frequently tinted by impurities; possible colors are green, blue, yellow, red (the rarest), and white. Beryl is also an ore source of beryllium.

Beryl belongs to the hexagonal crystal system. Normally Beryl forms hexagonal columns but can also occur in massive habits. As a cyclosilicate beryl incorporates rings of silicate tetrahedra that are arranged in columns along the C axis and as parallel layers perpendicular to the C axis, forming channels along the C axis. These channels permit a variety of ions, neutral atoms, and molecules to be incorporated into the crystal thus disrupting the overall charge of the crystal permitting further substitutions in Aluminium, Silicon, and Beryllium sites in the crystal structure. These impurities give rise to the variety of colors of beryl that can be found. Increasing alkali content within the silicate ring channels causes increases to the refractive indices and birefringence.

Beryl is a beryllium compound that is a known carcinogen with acute toxic effects leading to pneumonitis when inhaled. Care must thus be used when mining, handling, and refining these gems.

Beryl is a highly sedative stone. If taken as an elixir and gargled, Beryl crystal water can help heal throat problems and asthma. This stone is also used to treat problems with kidney stones and the bladder. It can strengthen your intestinal tract and boost your cardiovascular system.

1. Emerald Emerald gemstone is a variety of mineral beryl in green color. It is a precious gemstone. Beryl has a hardness of 7.5 to 8 on Mohs scale. The emerald is the sacred stone of the goddess Venus.
2. Green Beryl Beryl is a most and popular mineral. It has a great variety of colors, and has several important gemstone. It is a semi-precious gemstone. Its hardness on 7.5-8 Mohs Scale.
3. Emerald Category= Beryl variety Formula=  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$  Specific gravity= Average 2.76 Color= Green shades to colorless
4. Green Beryl Category= Cyclosilicate Formula=  $\text{Be}_3\text{Al}_2(\text{SiO}_3)_6$  Specific gravity= Average 2.76 Color= Green, blue, yellow, colorless, pink and others
5. between Emerald & Green Beryl Color Variations: The color of Emerald can be green to greenish-blue. While, the color of Green Beryl is pale green or very light green. They are belonging to the same mineral species Beryl.  
Inclusions : • Emeralds are generally heavily included which makes them less resistance to breakage or stretch. • In comparison, Green Beryl's are very less included.
6. Rarity: • Emeralds are very rare to be found as compared to Green Beryl. • As it is a rare event when Beryl is formed in a location where it is directly exposed to either chromium or vanadium.  
Crystal Structure: • The Crystal Structure of both of these gemstone are hexagonal in nature. • Green Beryl is colored by traces of iron are frequently heated to remove the green component and marketed as Aquamarine. • Thus, Aquamarine is sold at much higher prices than Green Beryl.  
Refractive Index: • It is an indication of the amount light rays are bent by the mineral. • The refractive index of Emerald is 1.565- 1.602 • Green Beryl has refractive index of 1.58- 1.59.
7. Origin Sources: • Emeralds are mined from the countries like Colombia, Brazil, Zambia and Zimbabwe. Green Beryl's are mined from the countries like Afghanistan, Pakistan, South Africa, South America and many more.

## **Asbestos**

Asbestos is a term used to refer to six naturally occurring silicate minerals. All are composed of long and thin fibrous crystals, each fiber being composed of many microscopic 'fibrils' that can be released into the atmosphere by abrasion and other processes. Asbestos is an excellent electrical insulator and is highly heat-resistant, so for many years it was used as a building material. However, it is now a well-known health and safety hazard and the use of asbestos as a building material is illegal in many countries. Inhalation of asbestos fibres can lead to various serious lung conditions, including asbestosis and cancer.

## Serpentine group



In London Hospital, England, 1941, nurse arranges an asbestos blanket over an electrically heated frame to create a hood over this patient to help warm them quickly



Example of asbestos cement siding and lining on a post-war temporary house in Yardley, Birmingham. Nearly 40,000 of these structures were built between 1946 and 1949 to house families.

Serpentine minerals have a sheet or layered structure. Chrysotile (commonly known as white asbestos) is the only asbestos mineral in the serpentine group. In the United States, chrysotile has been the most commonly-used type of asbestos. According to the U.S. Environmental Protection Agency (EPA) Asbestos Building Inspectors Manual, chrysotile accounts for approximately 95% of asbestos found in buildings in the United States.<sup>[49]</sup> Chrysotile is often present in a wide variety of products and materials, including:

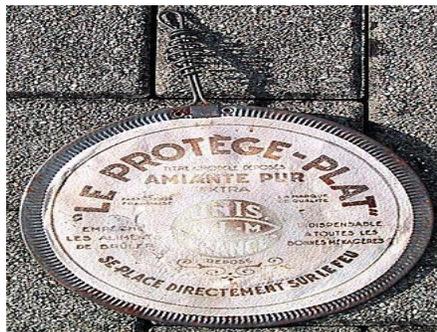
- Chlor Alkali diaphragm membranes used to make chlorine (currently in the US)<sup>[50]</sup>
- Drywall and joint compound (including texture coats)
- Plaster

- Gas mask filters pre-1960s and gas mask filters from the USSR
- Vinyl floor tiles, sheeting, adhesives
- Roofing tars, felts, siding, and shingles<sup>[51]</sup>
- "Transite" panels, siding, countertops, and pipes
- Popcorn ceilings, also known as acoustic ceilings
- Industrial and marine gaskets
- Brake pads and shoes
- Stage curtains
- Fire blankets
- Interior fire doors



- Fireproof clothing for firefighters
- Thermal pipe insulation
- Filters for removing fine particulates from chemicals, liquids and wine
- Dental cast linings
- HVAC flexible duct connectors

- Drilling fluid additives



A household heat spreader for cooking on gas stoves, made of asbestos (probably 1950s; "Amiante pur" is French)



Gasket, containing nearly unbound

### **Amphibole group**

Amphiboles including amosite (brown asbestos) and crocidolite (blue asbestos) were formerly used in many products until the early 1980s Tremolite asbestos constituted a contaminant of many if not all naturally occurring chrysotile deposits. Some products that included amphibole types of asbestos included the following:

- Low density insulating board (often referred to as AIB or asbestos insulating board) and ceilingtiles;
- Asbestos cement sheets and pipes for construction, casing for water and electrical/telecommunication services;
- Thermal and chemical insulation (e.g., fire rated doors, limpet spray, lagging and gaskets).

Cigarette manufacturer Lorillard (Kent's filtered cigarette) used crocidolite asbestos in its "Micronite" filter from 1952 to 1956. While mostly chrysotile asbestos fibers were once used in automobile brake pads, shoes, and clutch discs, contaminants of amphiboles were present. Since approximately the mid-1990s, brake pads, new or replacement, have been manufactured instead with linings made of ceramic, carbon, metallic and aramid fiber (Twaron or Kevlar—the same material used in bulletproof vests).

Artificial Christmas snow, known as flocking, was previously made with asbestos. It was used as an effect in films including *The Wizard of Oz* and department store window displays and it was marketed for use in private homes under brand names that included "Pure White", "Snow Drift" and "White Magic".

The use of asbestos in new construction projects has been banned for health and safety reasons in many developed countries or regions,

Removal of asbestos building components can also remove the fire protection they provide, therefore fire protection substitutes are required for proper fire protection that the asbestos originally provided.

## **TALC**

Talc is a clay mineral composed of hydrated magnesium silicate with the chemical formula  $Mg_3Si_4O_{10}(OH)_2$ . Talc in powdered form, often in combination with corn starch, is widely used as baby powder. This mineral is used as a thickening agent and lubricant, is an ingredient in ceramics, paint and roofing material, and is also one of the main ingredients in many cosmetic products.<sup>[5]</sup> It occurs as foliated to fibrous masses, and in an exceptionally rare crystal form. It has a perfect basal cleavage, uneven flat fracture and it is foliated with a two dimensional platy form.

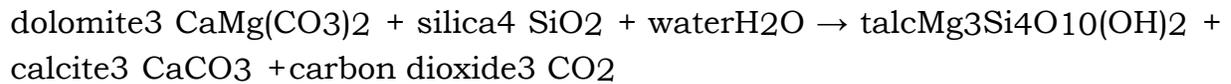
## **Formation**

Talc is a mineral that results from the metamorphism of magnesian minerals such as serpentine, pyroxene, amphibole, and olivine, in the presence of carbon dioxide and water. This is known as "talc carbonation" or "steatization" and produces a suite of rocks known as talc carbonates.

Talc is primarily formed by hydration and carbonation by this reaction:

serpentine  $2 Mg_3Si_2O_5(OH)_4$  + carbon dioxide  $3CO_2$  → talc  $Mg_3Si_4O_{10}(OH)_2$  + magnesite  $3 MgCO_3$  + water  $3 H_2O$

Talc can also be formed via a reaction between dolomite and silica, which is typical of skarnification of dolomites by silica-flooding in contact metamorphic aureoles:



Talc can also be formed from magnesian chlorite and quartz in blueschist and eclogite metamorphism by the following metamorphic reaction:



In this reaction, the ratio of talc and kyanite depends on aluminium content, with more aluminous rocks favoring production of kyanite. This is typically associated with high-pressure, low-temperature minerals such as phengite, garnet, and glaucophane within the lower blueschist facies. Such rocks are typically white, friable, and fibrous, and are known as whiteschist.

Talc is a trioctahedral layered mineral; its structure is similar to pyrophyllite, but with magnesium in the octahedral sites of the composite layers.

## Uses

Talc is used in many industries, including paper making, plastic, paint and coatings, rubber, food, electric cable, pharmaceuticals, cosmetics, and ceramics. A coarse grayish-green high-talc rock is soapstone or steatite, used for stoves, sinks, electrical switchboards, etc. It is often used for surfaces of laboratory table tops and electrical switchboards because of its resistance to heat, electricity and acids. In finely ground form, talc finds use as a cosmetic (talcum powder), as a lubricant, and as a filler in paper manufacture. It is used to coat the insides of inner tubes and rubber gloves during manufacture to keep the surfaces from sticking. Talcum powder, with heavy refinement, has been used in baby powder, an astringent powder used to prevent diaper rash. The American Academy of Pediatrics recommends that parents not use baby powder because it poses a risk of respiratory problems, including breathing trouble and serious lung damage if the baby inhales it. The small size of the particles makes it difficult to keep them out of the air while applying the powder. Zinc oxide-based ointments are a much safer alternative.

It is also often used in basketball to keep a player's hands dry. Most tailor's chalk, or French chalk, is talc, as is the chalk often used for welding or metalworking.

Talc is also used as food additive or in pharmaceutical products as a glidant. In medicine, talc is used as a pleurodesis agent to prevent recurrent pleural effusion or pneumothorax. In the European Union, the additive number is E553b.

Talc may be used in the processing of white rice as a buffing agent in the polishing stage.

Due to its low shear strength, talc is one of the oldest known solid lubricants. Also a limited use of talc as friction-reducing additive in lubricating oils is made.

The United States Food and Drug Administration considers talc (magnesium silicate) generally recognized as safe (GRAS) to use as an anticaking agent in table salt in concentrations smaller than 2%

## **MICA**

The **mica** group of sheet silicate (phyllosilicate) minerals includes several closely related materials having nearly perfect basal cleavage. All are monoclinic, with a tendency towards pseudohexagonal crystals, and are similar in chemical composition. The nearly perfect cleavage, which is the most prominent characteristic of mica, is explained by the hexagonal sheet-like arrangement of its atoms.

## **Classification**

Chemically, micas can be given the general formula



in which

X is K, Na, or Ca or less commonly Ba, Rb, or Cs;

Y is Al, Mg, or Fe or less commonly Mn, Cr, Ti, Li, etc.;

Z is chiefly Si or Al, but also may include Fe<sup>3+</sup> or Ti.

Structurally, micas can be classed as dioctahedral (Y = 4) and trioctahedral (Y = 6). If the X ion is K or Na, the mica is a common mica, whereas if the X ion is Ca, the mica is classed as a brittle mica.

Mica is widely distributed and occurs in igneous, metamorphic and sedimentary regimes. Large crystals of mica used for various applications are typically mined from granitic pegmatites

Ground mica is used in the well-drilling industry as an additive to drilling fluids. The coarsely ground mica flakes help prevent the loss of circulation by sealing porous sections of the drill hole.

Dry-ground mica is used in the production of rolled roofing and asphalt shingles, where it serves as a surface coating to prevent sticking of adjacent surfaces. The coating is not absorbed by freshly manufactured roofing because mica's platy structure is unaffected by the acid in asphalt or by weather conditions. Mica is used in decorative coatings on wallpaper, concrete, stucco, and tile surfaces. It also is used as an ingredient in flux coatings on welding rods, in some special greases, and as coatings for core and mold release compounds, facing agents, and mold washes in foundry applications. Dry-ground phlogopite mica is used in automotive brake linings and clutch plates to reduce noise and vibration (asbestos substitute); as sound-absorbing insulation for coatings and polymer systems; in reinforcing additives for polymers to increase strength and stiffness and to improve stability to heat, chemicals, and ultraviolet (UV) radiation; in heat shields and temperature insulation; in industrial coating additive to decrease the permeability of moisture and hydrocarbons; and in polar polymer

Flexible plate is used in electric motor and generator armatures, field coil insulation, and magnet and commutator core insulation. Mica consumption in flexible plate

Sheet mica is used principally in the electronic and electrical industries. Its usefulness in these applications is derived from its unique electrical and thermal properties and its mechanical properties, which allow it to be cut, punched, stamped, and machined to close tolerance

## **ZEOLITE**

Zeolite, any member of a family of hydrated aluminosilicate minerals that contain alkali and alkaline-earth metals. The zeolites are noted for their lability toward ion-exchange and reversible dehydration. They have a framework

structure that encloses interconnected cavities occupied by large metal cations (positively charged ions) and water molecules.

structural properties

The essential structural feature of a zeolite is a three-dimensional tetrahedral framework in which each oxygen atom is shared by two tetrahedra. If all tetrahedra contained silicon the framework would be neutral; substitution of aluminum for silicon creates a charge imbalance and requires other metal ions to be present in relatively large cavities of the framework. In naturally occurring zeolites these metal ions are typically mono- or di-valent ions such as sodium, potassium, magnesium, calcium, and barium. Zeolites are similar to feldspar minerals except that cavities are larger in zeolites and water is generally present. Structurally, zeolites are classified by the types of structural units that compose the framework, such as rings or polyhedra types. The cavities formed by the framework units have diameters ranging from about 2 to 8 angstroms, which permits relatively easy movement of ions between cavities.

This ease of movement of ions and water within the framework allows reversible dehydration and cation exchange, properties which vary considerably with chemical and structural differences. Dehydration character varies with the way water is bound in the structure. For those zeolites in which water is tightly bound, dehydration occurs at relatively high temperatures; by contrast, in certain zeolites with large cavities, some of the water can be released at low temperatures. The rate of ion exchange depends on the size and connections between cavities. Some ions are excluded because of specific structural properties.

#### **uses**

Some commercial uses include separation of hydrocarbons, such as in petroleum refining; drying of gases and liquids; and pollution control by selective molecular adsorption.

#### **FELDSPAR**

Feldspar, any of a group of aluminosilicate minerals that contain calcium, sodium, or potassium. Feldspars make up more than half of Earth's crust, and professional literature about them constitutes a large percentage of the literature of mineralogy.

Two important rock-forming materials that are not minerals are major components of a few rocks. These are glass and macerals. Glass forms when magma (molten rock material) is quenched—i.e., cooled so rapidly that the constituent atoms do not have time to arrange themselves into the regular arrays characteristic of minerals. Natural glass is the major constituent of a few volcanic rocks—e.g., obsidian. Macerals are macerated bits of organic matter, primarily plant materials; one or more of the macerals are the chief original constituents of all the diverse coals and several other organic-rich rocks such as oil shales.

### **Classification**

In the classification of igneous rocks of the International Union of Geological Sciences (IUGS), the feldspars are treated as two groups: the alkali feldspars and the plagioclase feldspars. The alkali feldspars include orthoclase, microcline, sanidine, anorthoclase, and the two-phase intermixtures called perthite. The plagioclase feldspars include members of the albite-anorthite solid-solution series. Strictly speaking, however, albite is an alkali feldspar as well as a plagioclase feldspar.

#### Chemical composition

All the rock-forming feldspars are aluminosilicate minerals with the general formula  $AT_4O_8$  in which  $A$  = potassium, sodium, or calcium (Ca); and  $T$  = silicon (Si) and aluminum (Al), with a Si:Al ratio ranging from 3:1 to 1:1. Microcline and orthoclase are potassium feldspars ( $KAlSi_3O_8$ ), usually designated Or in discussions involving their end-member composition. Albite ( $NaAlSi_3O_8$ —usually designated Ab) and anorthite ( $CaAl_2Si_2O_8$ —An) are end-members of the plagioclase series. Sanidine, anorthoclase, and the perthites are alkali feldspars whose chemical compositions lie between Or and Ab. As is apparent from the preceding statements, solid solution plays an important role in the rock-making feldspars. (Members of solid-solution series are single crystalline phases whose chemical compositions are intermediate to those of two or more end-members.) The alkali (Or-Ab) series exhibits complete solid solution at high temperatures but only incomplete solid solution at low temperatures; substitution of potassium for sodium is involved. The plagioclase (Ab-An) series exhibits essentially complete solid solution at both high and low temperatures; coupled substitution of sodium and silicon by calcium and aluminum occurs. The An-Or system has only limited solid-solution tendencies.

### **Production and uses**

Feldspar is a common raw material used in glassmaking, ceramics, and to some extent as a filler and extender in paint, plastics, and rubber. In glassmaking, alumina from feldspar improves product hardness, durability,

and resistance to chemical corrosion. In ceramics, the alkalis in feldspar (calcium oxide, potassium oxide, and sodium oxide) act as a flux, lowering the melting temperature of a mixture. Fluxes melt at an early stage in the firing process, forming a glassy matrix that bonds the other components of the system together. In the US, about 66% of feldspar is consumed in glassmaking, including glass containers and glass fiber. Ceramics (including electrical insulators, sanitaryware, pottery, tableware, and tile) and other uses, such as fillers, accounted for the remainder. Sciences and archaeology, feldspars are used for potassium-argon dating, argon-argon dating, and luminescence dating.

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