

CHAPTER – 1

Introduction

SOLID STATE MATERIALS – WHY AND WHAT?

In the last two decades, the three distinct technologies have evolved namely biotechnology, information technology and nanotechnology. All these three technologies are revolutionizing more than the conventional revolutions that we know of like the green revolution or the industrial revolution. This situation is especially relevant since now the solid state material technology has improved so much that a million or over functions can be incorporated in a single chip. This will see a rapid growth in our day to day activity like how we communicate with each other, how we travel. As we all know, this evolution is not characteristic of the last two decades. Solid state materials technology has been evolving for many centuries as we passed from one age to another starting from Stone Age to metals (copper and iron) age and now reached the age of nano materials.

Solid state materials and engineering is poised to provide critical inputs to both areas of biotechnology and information technology as well as creating trends of its own. For example, the cross-disciplinary fields of biomaterials and nanomaterials are making promising developments. Moreover, interdisciplinary materials research will likely to continue to yield materials with improved properties for applications that are both common place (such as building construction) and specialized (such as surveillance, aircraft and space systems). Materials of the 21st century will likely to be smarter, multi-functional, and compatible with a broad range of environments.

The importance of nano and materials technology has been already felt by many. For example, the U.S. President's proposed National Nanotechnology Initiative projected that "the emerging fields of nanoscience and nanoengineering are leading to unprecedented understanding and control over the fundamental building blocks of all physical things. These developments are likely to change the way almost everything - from vaccines to computers to automobile tires to objects not yet imagined - is designed and made." New materials can often be critical enabling drivers for new systems and applications with significant effects.

DEVELOPMENTS IN MATERIAL SCIENCE

The developments in materials science and engineering have always depended on interdisciplinary materials research. This development can be conveniently represented by the schematic description of the materials engineering process from concept to product/application (fig. 1.). This process view is a common approach in materials research circles and similar representations may be found in the literature.

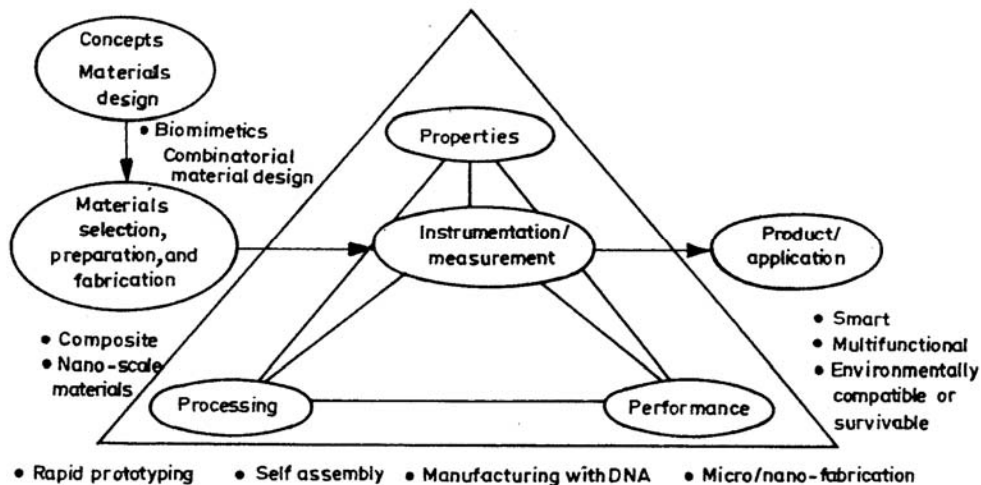


Fig. 1. Schematic representation of the General Materials Engineering Process

There are various methodologies and procedures that are adopted to generate these new generation materials. For example, biomimetics is the design of systems, materials, and their functionality to mimic nature. Current examples include layering of materials to achieve the hardness of an abalone shell or trying to understand why spider silk is stronger than steel.

Combinatorial materials design uses computing power (sometimes together with massive parallel experimentation) to screen many different materials possibilities to optimize properties for specific applications (e.g., catalysts, drugs, optical materials).

Composites are combinations of metals, ceramics, polymers, and biological materials that allow multi-functional behaviour. One common practice is reinforcing polymers or ceramics with ceramic fibers to increase strength while retaining light weight and avoiding the brittleness of the monolithic ceramic.

Nanoscale materials, i.e., materials with properties that can be controlled at submicrometer (<10-6) or nanometer (10-9) level, are an increasingly active area of research because properties in these size regimes are often fundamentally different from those of ordinary materials. Examples include carbon nanotubes, quantum dots, and biological molecules. These materials can be prepared either by purification methods or by tailored fabrication methods.

MATERIALS – APPLICATIONS

There are various areas in which these materials can be effectively employed. A few typical examples are given.

- Materials that exhibit sensing and actuation capabilities from ink-jet printers to magnetic disk drives to anti-coagulant devices.
- Smart composite materials with increased sensitivity, multiple frequency response, and variable frequency.
- Smart polymers (e.g., ionic gels that deform in response to electric fields) for use as “artificial muscles”.
- Smart materials like : clothes that respond to weather, interface with information systems, monitor vital signs, deliver medicines, and automatically protect wounds; airfoils that respond to airflow; buildings that adjust to the weather; bridges and roads that sense and repair cracks; kitchens that cook with wireless instructions; virtual reality telephones and entertainment centers; and personal medical diagnostics.
- Self-assembling materials including colloidal crystal arrays with mesoscale (50-500 nm) lattice constants that form optical diffraction gratings, and thus change color as the array swells in response to heat or chemical changes.
- New lightweight materials for automobiles that increase energy efficiency while reducing emissions.
- Materials for power sources and energy conversion devices – namely battery technology and fuel cells.
- Materials that will enable the energy systems to be more distributed with a greater capability for energy storage, as well as energy system command, control, and communication.
- Cheap, lightweight, recyclable materials (and perhaps the genetic engineering of biomass fuels) to provide cost-effective energy.
- SiC, GaN, and other wide band gap semiconductors as materials for high-power electronics.
- Functionally graded materials (i.e., materials whose properties change gradually from one end to the other) can form useful interlayers between mechanically, thermally, or electrically diverse components.
- Nonlinear optical materials for ultraviolet lasers (e.g., to enable finer lithography) with a view to increase damage threshold and conversion efficiency, minimize divergence, and tailor the absorption edge.
- Hard materials such as nanocrystalline coatings and diamonds for applications such as computer disk drives and drill bits.
- High-temperature materials such as ductile intermetallics and ceramic matrix composites for aerospace applications.

- One important research area is the formation of semiconductor “quantum dots” (i.e., several nanometer-size, faceted crystals) which can photoluminescence at different frequencies (colours) depending upon their size, allowing optical multiplexing in biological labeling.
- Another important class of nanomaterials is nanotubes. Possible applications are field-emission displays, nanoscale wires for batteries, storage of Li or H₂, and thermal management (heat pipes or insulation – the latter taking advantage of the anisotropy of thermal conductivity along and perpendicular to the tube axis). Another possibility is to use nanotubes (or fibers built from them) as reinforcement for composite materials.

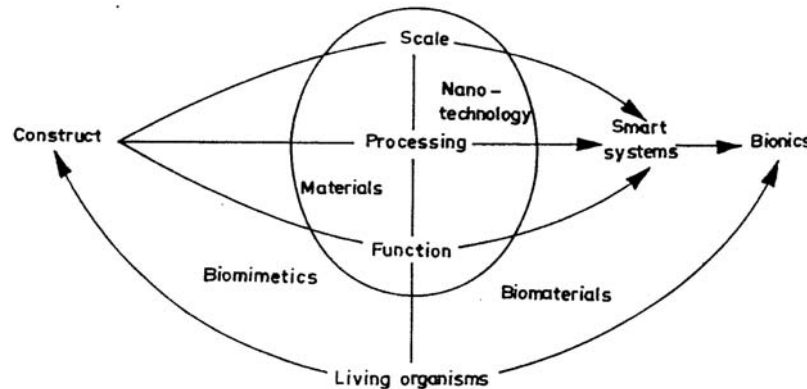


Fig. 2. The possible Synergistic Interplay of Technologies in future

MATERIALS SCIENCE – THE TRENDS

Much has been made of the trend toward producing devices with ever-decreasing scale. Many people have projected that nanometer-scale devices will continue this trend, bringing it to unprecedented levels. This includes scale reduction not only in microelectronics but also in fields such as Micro-Electro-Mechanical Systems (MEMS).

MEMS and quantum-switch-based computing

These advances have the potential to change the way we engineer our environment, construct and control systems, and interact in society.

There will be interplay of technologies in the future so as to generate new technological options. The possible emerging scene can be pictorially shown as given in fig. 2.

MEMS combines mechanical and electrical functions in chip architecture. It is possible that chemical and biological functions can also be integrated in the same chip.

Technology Revolution and Effects

The situation is very critical now since the pace of changes will be very much accelerated. This will in effect affect social and ethical concerns more and more. Not only this, the need for increased educational breadth and depth will be imposed such that our educational and learning processes have to undergo considerable change. The life spans will increase and the privacy will be considerably reduced leading to other emotional concerns. Technology’s promise is already felt and will march forward. Yet, the effects of the technology revolution will not be uniform, playing out differently on the global stage depending on acceptance, investment, and a variety of other decisions. There will be no turning back, however, since some societies will avail themselves of the revolution, and globalization will thus change the environment in which each society lives. The world is in for significant change as these advances play out on the global stage. This technology revolution is centered on materials and materials processing technologies. In view of this changing scene, it was considered worthwhile to formulate a first level text book concerning various essential properties of solid state materials and the exploitation of these properties in appropriate devices.

CHAPTER - 2

Structures of Solids

INTRODUCTION

Solids are the state of the matter that are usually highly ordered. All the substances, except helium, if cooled sufficiently, form a solid phase. Solids can be classified into two broad categories as **Crystalline** and **Amorphous**.

Crystalline solids are three dimensional analogues of a brick wall. They have a regular structure, in which the particles pack in a repeating pattern from one edge of the solid to the other.

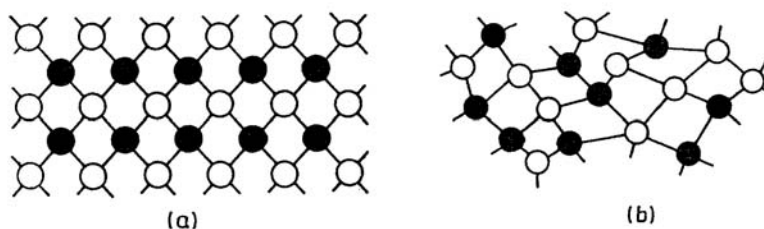


Fig. 1 (a) Schematic of Crystalline solid, (b) Schematic of Amorphous solid

Amorphous solids (literally “solids without form”) have a random structure, with little if any long-range order. Polycrystalline solids are an aggregate of a large number of small crystals or grains in which the structure is regular, but the crystals or grains are arranged in a random fashion.

The extent to which a solid is crystalline has important effect on its physical properties. For example, the polyethylene used to prepare garbage bags is amorphous solid that consists of more or less randomly oriented chains of $(-\text{CH}_2-\text{CH}_2-)$ linkages. The Crystalline form of polyethylene, which is more rigid, is used to make milk bottles.

Solids can be classified on the basis of the bond that holds the atoms or molecules together. This approach categorizes solids as either atomic, molecular, covalent, ionic or metallic.

Crystalline solids

The following paragraphs are restricted to only Crystalline solids. Crystalline solids have atoms or groups of atoms arranged in a regular array of points or lattice in three dimensions.

Lattice

Lattice is defined as an array of equivalent points in one, two or three dimensions. The simplest illustration of this is, a one dimensional lattice consisting of an infinite series of equally spaced points along a line.



Fig. 2. One dimensional lattice

In two dimension with the restrictions on their repeat distance ($'a'$ in fig. 2.) and angle, there are five types of two dimensional lattices. Starting from the highly unsymmetrical oblique (or general), to increasing levels of symmetry the two dimensional lattice types are Oblique, Rectangular, Square, Centred rectangular and Hexagonal.

In three dimension there are four possible lattice types. The simplest lattice type is known as **primitive**, given the symbol **P**, contains a single lattice point, located at the corners of the unit cell parallelepiped. This has only the translational symmetry. For the remaining lattice types, along with translational symmetry there is also presence of other symmetries. A second lattice type is **body centred**, which is given the symbol **I**. This shows lattice points at all the cell corners and at body centre with fractional coordinates $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$. This means that if an atom is placed on a general position within a body centered unit cell with fractional coordinates (x, y, z) the lattice will generate a second, identical atom at the position with fractional coordinates $(x+1/2, y+1/2, z+1/2)$.

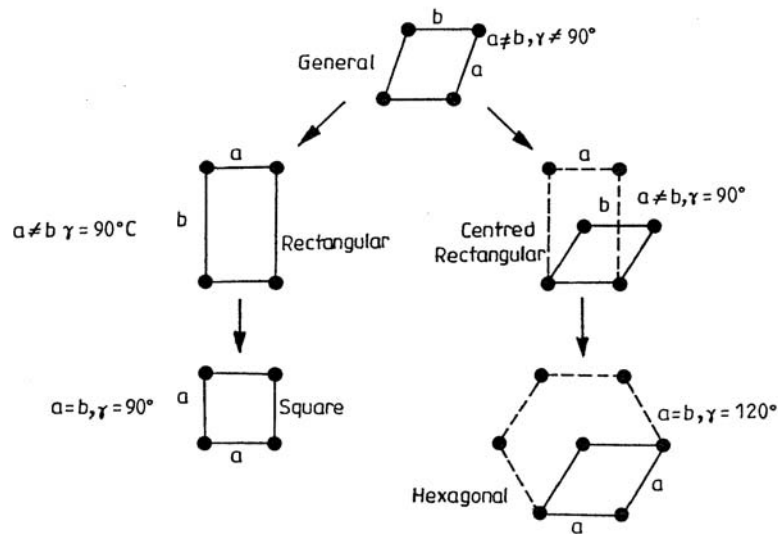


Fig. 3. Types of two dimensional lattice

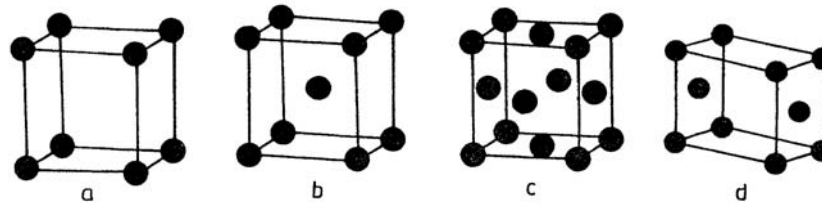


Fig. 4. Three dimensional Lattices, (a) Primitive (P), (b) Body centered (I), (c) Face centered (F), (d) C-centered (C)

A three dimensional lattice which has lattice points at all the corners and at the center of all the unit cell faces, is known as **Face centered** and given the symbol **F**. The additional translational symmetry in this case consists of the three elements at $(\frac{1}{2}, \frac{1}{2}, 0)$, $(0, \frac{1}{2}, \frac{1}{2})$, $(\frac{1}{2}, 0, \frac{1}{2})$. Hence for an atom on a general site (x, y, z) three additional identical atoms will be generated within the unit cell with the coordinates $(x+1/2, y+1/2, z+1/2)$.

Finally a lattice which has points in all the corners and at one pair of opposite face centers is known as face centered but given the symbol A, B or C. A C-type lattice refers to the case where the additional translational symmetry places lattice points at the centers of the faces delineated by the a and b directions as well as at the origin. In fractional coordinate terms, for a **C centered lattice**, in addition to the general site (x,y,z) , a second site is generated at $(x+1/2, y+1/2, z)$. The A and B face centered lattices are obtained in an identical manner but the additional lattice points occur in the bc or ac planes respectively. However, the A and B descriptions are not normally used, as the redefinition of the a, b and c directions would produce again the C centered description.

Counting the number of atoms in a three dimensional lattice

In a three dimensional unit cell each atom is shared with neighboring unit cell. The atoms in different positions are shared in a different way.

- Vertex (corner) atom is shared by 8 cells, and so contributes $\frac{1}{8}$ atom per cell
- Edge atom is shared by 4 cells, and so contributes $\frac{1}{4}$ atom per cell
- Face atom is shared by 2 cells and so contributes $\frac{1}{2}$ atom per cell
- Body centre atom is unique to 1 cell and so contribute fully to the cell

Unit Cell

Unit cell is defined as the simplest portion of the structure repeated by translation and shows the full symmetry of the crystal system.

The unit cell for the one dimensional lattice lies between two vertical lines in fig. 5. If we take this unit cell and repeated it over and over again we would reproduce the original array.

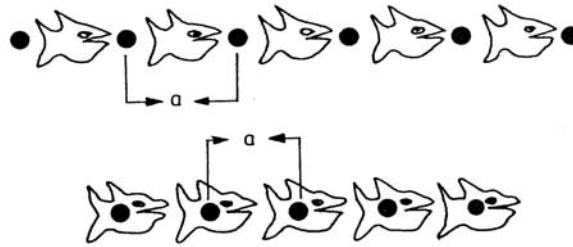


Fig. 5. One dimensional unit cell

It does not matter where in the structure we place the lattice points either on the unit cell or between the unit cells, as long as each of them have the identical surroundings.

In a two dimensional array of ions, such as shown in fig. 6, the unit cell consists of parallelogram. Any parallelogram may be chosen as a unit cell provided that translation along either of the cell directions repeats exactly the chosen unit. However, the unit cell is normally selected to be the simplest of these repeating units. Hence in fig. 6, the unit cell could be chosen as **A** for which displacements to either edge of the square by the dimension of the unit cell produce a new position which is indistinguishable, in terms of cell content and environment, from the original one. The parallelogram **B** is also a suitable unit cell choice, as it has the same area as **A** and shows the full translation symmetry. Square **D** is also an acceptable choice of unit cell in terms of demonstrating translational symmetry of the array but is larger than **A** and **B**.

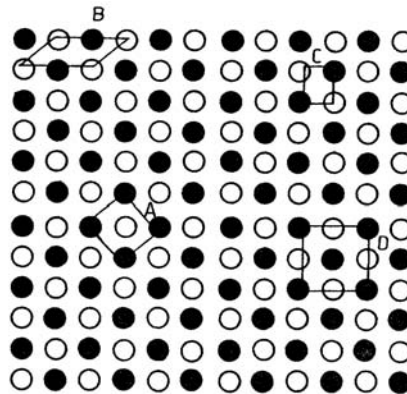


Fig. 6. Two dimensional unit cells

However, parallelogram **C** is not a unit cell as translation parallel to one side by the length of the parallelogram places a corner originally at a site \bullet on a \circ site; i.e., the cell does not show the translational symmetry of the ion array. There is never one unique unit cell that is correct. There are always many that could be chosen and the choice depends both on convenience and convention.

An increasing level of symmetry along with various relationships between the cell parameters leads to the seven crystal systems.

Table 1. Seven Crystal systems

Unit Cell Dimensions	Crystal class	Example
$a = b = c, \alpha = \beta = \gamma = 90^\circ$	Cubic	NaCl, $MgAl_2O_4$, $C_{60}K_3$
$a = b \neq c, \alpha = \beta = \gamma = 90^\circ$	Tetragonal	K_2NiF_4 , TiO_2 , $BaTiO_3$ (298 K)
$a \neq b \neq c, \alpha = \beta = \gamma = 90^\circ$	Orthorhombic	$YBaCu_3O_7$
$a \neq b \neq c, \alpha = \gamma = 90^\circ; \beta \neq 120^\circ$	Monoclinic	KH_2PO_4
$a \neq b \neq c, \alpha \neq \beta \neq \gamma \neq 90^\circ$	Triclinic	Al_2SiO_5 , $NaAlSi_3O_8$
$a = b \neq c, \alpha = \beta = 90^\circ; \gamma = 120^\circ$	Hexagonal	$LiNbO_3$
$a = b = c, \alpha = \beta = \gamma \neq 90^\circ$	Trigonal / Rhombohedral	$BaTiO_3$ (below $-80^\circ C$)

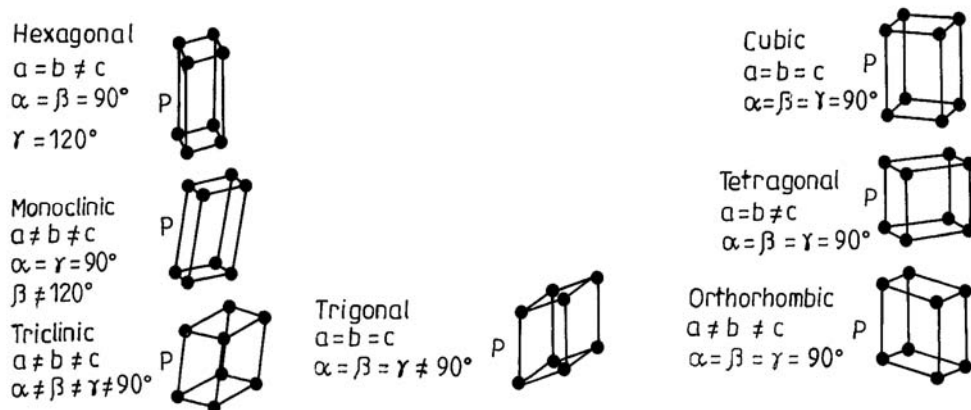


Fig. 7. Seven Crystal Systems

The symmetry requirements of the seven crystal systems are shown in table 2.

Table 2. The symmetry requirements of the seven crystal systems (reproduced from ref. 1)

Crystal System	Required Symmetry
Triclinic	None
Monoclinic	One two fold axis or one symmetry plane
Orthorhombic	Any combination of 3 mutually perpendicular 2-fold axes or plane of symmetry
Trigonal	One 3-fold axis
Hexagonal	One 6-fold axis or one 6-fold improper axis
Tetragonal	One 4-fold axis or one 4-fold improper axis
Cubic	Four 3-fold axes at $109^\circ 28'$ to each other

The combination of the seven crystal systems with the four 3-dimensional lattice types produces **14 possible Bravais Lattices**.

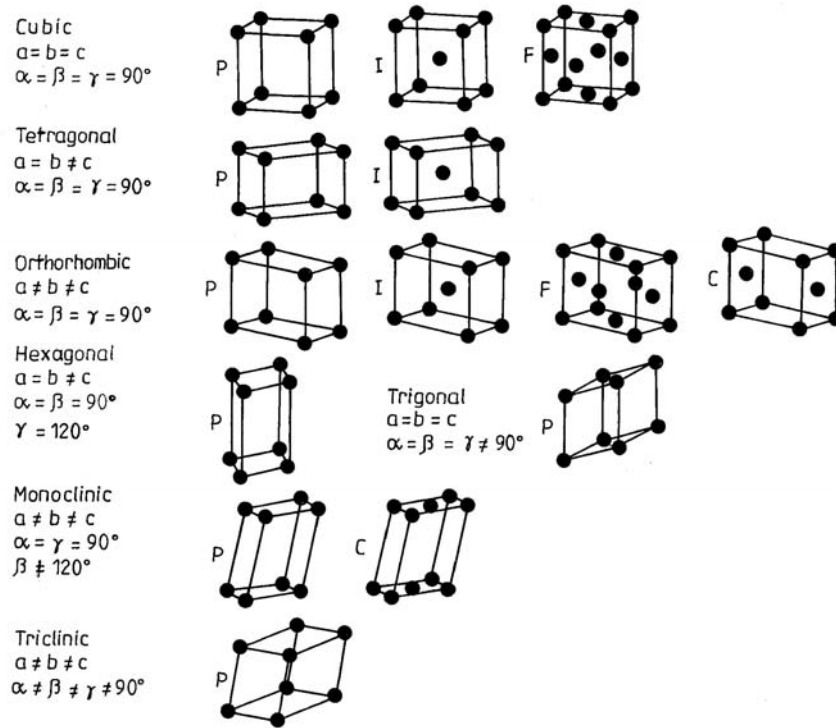


Fig. 8. 14 Bravais Lattices

CLOSE PACKING OF SPHERES

Crystal structures may be described in various ways. The most common way is referring to the unit cell structure. In this approach the structure is given by the size and shape of the unit cell and the positions of the atoms inside the unit cell. However, these informations alone are insufficient to give a revealing picture of the structure in three dimensions. An alternative way of visualizing the structures of many inorganic solids is, in terms of simple packing of spheres, by considering atoms as small rigid spheres. In two dimension, as shown in fig. 9, there are two possible arrangements for a layer of such identical atoms.

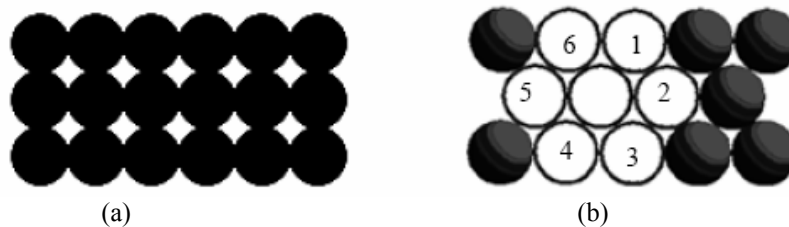


Fig. 9 (a) Square packing of spheres, (b) Close packing of spheres

If each sphere is positioned exactly one over the other, each sphere is in contact with four next nearest spheres as in fig. 9(a). In fig. 9(b), each sphere is positioned at the indentation between the two touching spheres, and forming a triangle. The layer is then formed by continuing this process of positioning spheres in the indentations between those already in place. This way of arrangement each sphere is having six nearest neighbours occupies less space for the same number of spheres compared to the square packing. To build up a structure in the three dimensions, a second layer is to be added.

Primitive Cube

The positioning of the second layer exactly over the first one in the square packing results the simple primitive cube. The stacking sequence is **AAAAA....** It is the least close packed or least efficiently packed structure. It has the unoccupied space of 48%, i.e., the packing efficiency, is 52%. In this arrangement of atoms, each atom or sphere is surrounded by 6 nearest neighbors. Because this structure is inefficient, only one element - polonium, crystallizes in a primitive cubic structure.

Body Centered Cube

In a still better close packing of the square layer, the atoms or spheres in the second layer occupies the dips in the first layer. The staking sequence is **ABABAB....** and results the body centered cube.

Body centered cubic packing is more efficient than simple primitive cubic packing with a packing efficiency of 68%. In this arrangement each sphere is surrounded by 8 nearest neighbors. All of the metals in Group IA (Li, Na, K, and so on), the heavier metals in Group IIA (Ba), and a number of the early transition metals (such as V, Cr, Mo, W, and Fe) pack in a body-centered cubic structure.

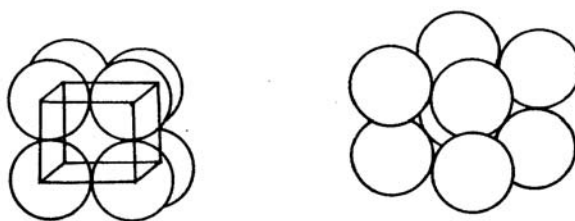


Fig. 10 (a) Primitive Cube, (b) Body centered Cube

Cubic and Hexagonal Close Packing

In the three dimensional stacking of close packed layers of fig. 9(b), the spheres of the second layer sit in half of the dips in the first layer. The layer B sits over the dips marked with small triangle (although it does not make any difference in which hollows or dips the second layer sits, either on the triangles or on the dots).

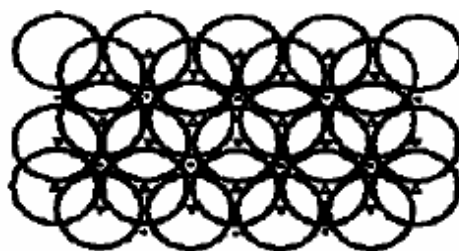


Fig. 11. Close packing of two layers

When the third layer is to be added it has two possibilities; either it could go over the first layer (A layer) directly or over the dips represented by dots. If it occupies over the first layer then the stacking sequence is **ABABAB...** this kind of stacking sequence of the close packed arrangement is called the **hexagonal close packing (hcp)**. When the third layer (C layer) occupies over the dips represented by dots, the stacking sequence is **ABCABCABC....** and is called as the **cubic close packing (ccp)**. Hexagonal close packing and the Cubic close packing are the most efficient ways of packing, since these results in the highest packing efficiency of 74%. In both cases each sphere is surrounded by 12 equidistant nearest neighbours.

As shown in fig. 13, in hcp the first and third layer are occupying the same kind of dips in the second layer. But in ccp, the third layer occupies the dips which are left vacant by the first layer. The unit cell of ccp is fcc (face centered cube).

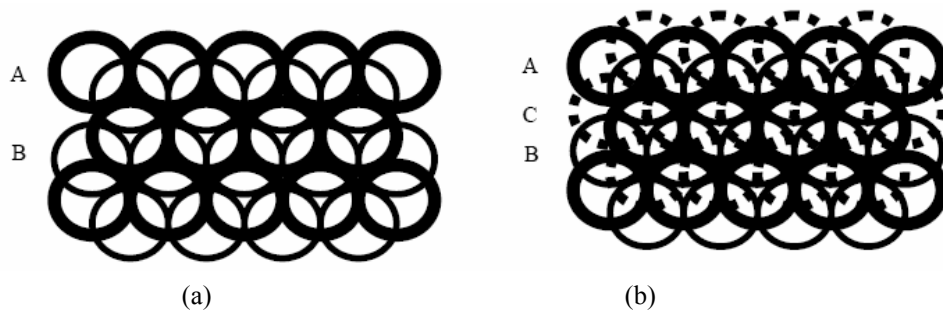


Fig. 12. Close packing of three layers, (a) Hexagonal Close Packing (hcp), (b) Cubic Close Packing (ccp)

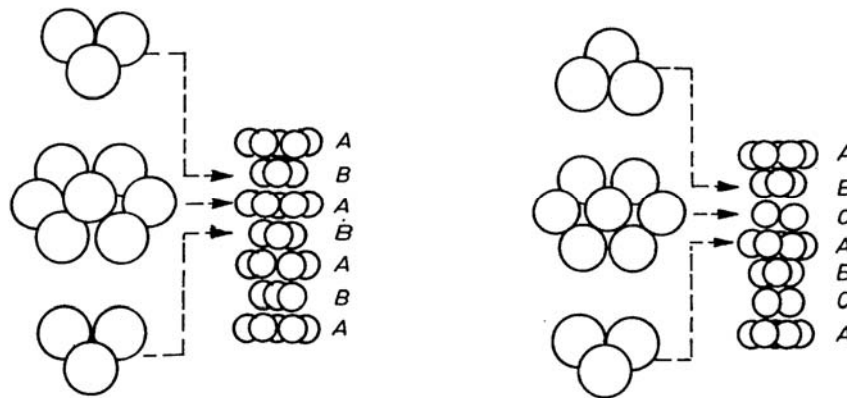


Fig. 13. The stacking sequence of the HCP and CCP close packing

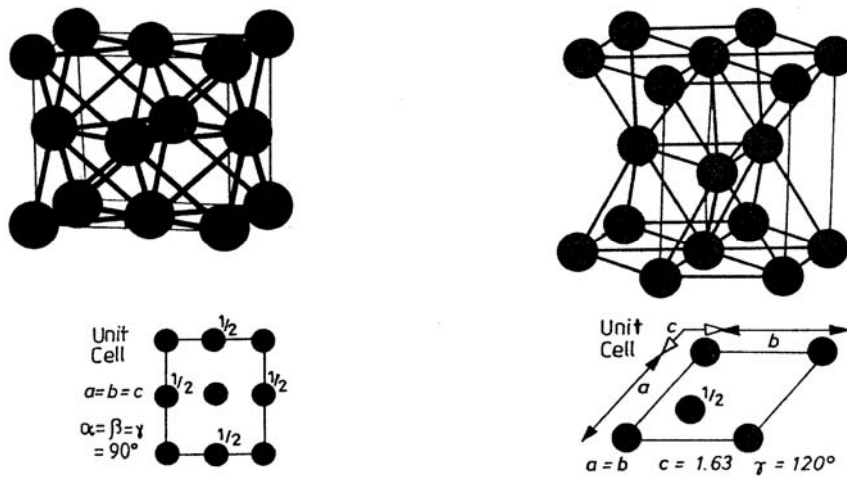


Fig. 14. Unit cell of Cubic and Hexagonal close packing

By seeing the periodic table in fig. 15, it could be seen that most of the elements are having the hcp structure. Next comes the ccp and bcc. Few of them adapt to different structures at different conditions of temperature and pressure. The structures of the actinides are complex and are not included.

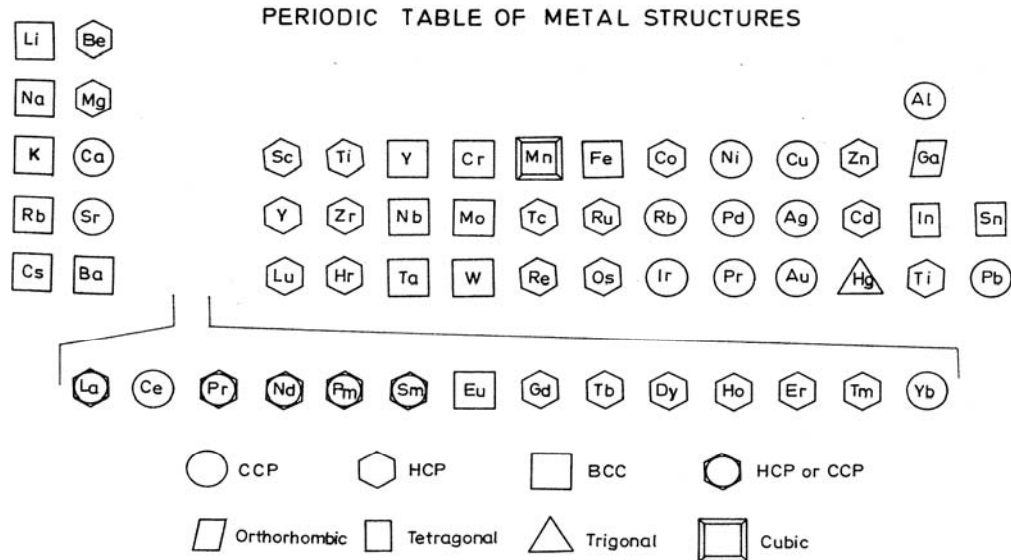


Fig. 15. Packing types among the metals

Holes in Close Packing

In the close packing arrangement of spheres, two kinds of space or holes exist between the spheres. When the hole is formed by three spheres in one plane, and one more capping above or below the plane of the three spheres, such holes are called as **tetrahedral holes**. Each tetrahedral hole is surrounded by four spheres, each lie at the corner of a tetrahedron (fig. 16).

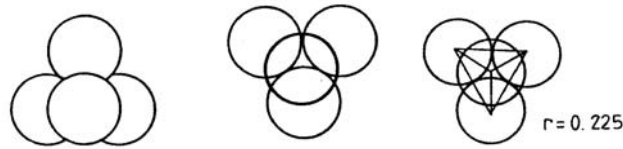


Fig. 16. Tetrahedral hole

When the tetrahedral hole is formed by the capping of the fourth sphere above the plane of the three spheres, it is called as T+. When it is formed by the capping of the fourth sphere below the plane of three spheres, is called as T-.

When the hole is formed by six numbers of spheres, is called an octahedral hole. An octahedral hole is formed by three spheres in one plane and three spheres in another plane which are positioned in a reverse manner. The centers of the spheres of the octahedral hole lie at the corners of an octahedron, hence named as the octahedral holes (fig. 17).

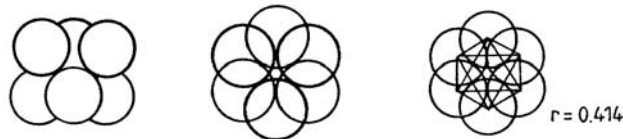


Fig. 17. Octahedral hole

In close packed structures, if the structure is formed by n number of spheres, then there will be n number of **octahedral holes** and $2n$ number of **tetrahedral holes** (n T+ and n T-).

Octahedral holes

In Cubic close packing (CCP) the octahedral holes are on the edge centres and at the body centre. Considering the sharing of the spheres in a unit cell, there are totally four octahedral holes in face centered cubic unit cell of ccp. The positions of the octahedral holes are shown in Fig. 18. The octahedral holes are positioned at $(1/2, 0, 0)$, $(0, 1/2, 0)$, $(0, 0, 1/2)$ and $(1/2, 1/2, 1/2)$.

In hexagonal close packing there are two octahedral holes and are positioned at $(2/3, 1/3, 1/4)$ and $(2/3, 1/3, 3/4)$.

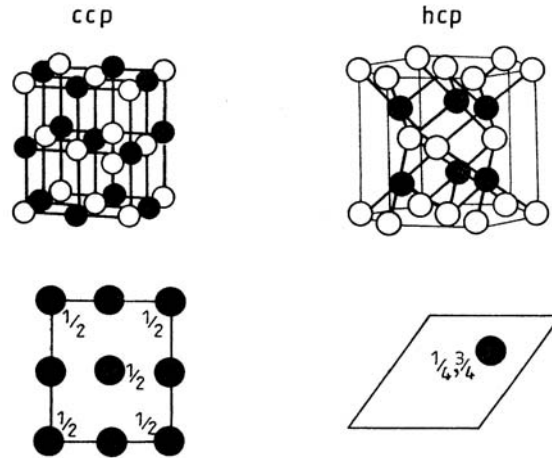


Fig. 18. Position of octahedral holes in close packing

Tetrahedral holes

To visualize tetrahedral holes in ccp, the unit cell fcc could be divided into eight octants. Tetrahedral holes are at the center of each smaller octant. The T⁺ and T⁻ holes are alternatively arranged. The positions of the Tetrahedral holes are shown in Fig. 19. The positions of the T⁺ holes are $(3/4, 1/4, 1/4)$, $(1/4, 3/4, 1/4)$, $(1/4, 1/4, 3/4)$ and $(3/4, 3/4, 3/4)$ with the positions of T⁻ at $(1/4, 1/4, 1/4)$, $(3/4, 3/4, 1/4)$, $(1/4, 3/4, 3/4)$ and $(3/4, 1/4, 3/4)$.

In HCP, there are four tetrahedral holes with T⁺ positioned at $(1/3, 2/3, 1/8)$ and $(0, 0, 5/8)$ and T⁻ positioned at $(0, 0, 3/8)$ and $(1/3, 2/3, 7/8)$.

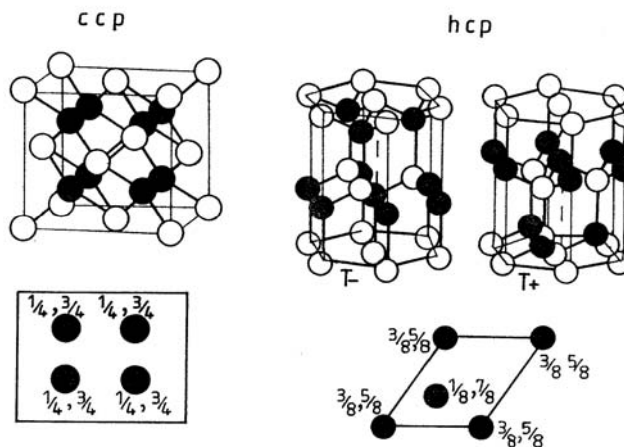


Fig. 19. Positions of Tetrahedral holes in close packing

Ionic crystals

In the formation of ionic crystals, the bigger anions form the close packing arrangement and the smaller cations occupy the holes which are appropriate to their size. Ionic crystals could be classified in terms of stoichiometry in to AX, AX₂ and AX₃ types. In the forthcoming paragraphs only the crystal structures of ionic crystals and adoption of these structures by different compounds are dealt. The coordination environment of the ions in the ionic crystals can be grouped in to as in table 3.

Table 3. Types of Ionic crystals and the coordination number of the ions (reproduced from reference 2)

Ionic crystal type	Coordination number		Structure Type
	A	X	
AX	6	6	NaCl
	8	8	CsCl
AX ₂	6	3	Rutile (TiO ₂)
	8	4	Fluorite (CaF ₂)
AX ₃	6	2	ReO ₃

The occupancy of the holes by the cations, is governed by the **Radius Ratio Rule**.

Radius ratio rule is defined as the ratio of the radius of the cations to the anions.

$$\text{Radius ratio} = \frac{\text{Radius of the cation}}{\text{Radius of the anion}}$$

Depending on the size of the cation, and so the radius ratio, the cations occupy different types of holes as shown in table 4.

Table 4. Effect of metal ion size on the occupancy of hole types

Radius ratio	Coordination number	Holes in which positive ions occupy
0.225 – 0.414	4	Tetrahedral holes
0.414 – 0.732	6	Octahedral holes
0.732 - 1	8	Cubic holes

STRUCTURE TYPE AX : CLOSE PACKING

The simplest type of ionic crystal is an assembly of equal number of cations and anions (AX) as in alkali halides.

Rock Salt (NaCl) Structure

In general for alkali halides except RbF and CsF, the anions will be larger than the cations. Sodium Chloride could be taken as an example and the structure description for sodium chloride can be extended to other alkali halides.

In Sodium chloride, the chloride ions form the fcc arrangement and the sodium ions occupy all the octahedral holes. It could also be considered as the cubic close packing of sodium ions with the filling of chloride ions in all the octahedral holes. It could also be considered as the interpenetration of fcc unit cells of sodium and chloride ions. Both sodium and chloride ions are octahedrally coordinated. Fig. 20 shows the unit cell of sodium chloride, with the chloride ions in the fcc arrangement and sodium ions at the octahedral holes.

Most alkali halides (except CsCl, CsBr, CsI), most oxides / chalcogenides of alkaline earths and many nitrides, carbides, hydrides (e.g. ZrN, TiC, NaH) adopt the Rock salt or Sodium chloride structure.

Spalierite or Zinc blend (ZnS) Structure

Zinc blend is formed by the fcc arrangement of the sulphide ions with the zinc ions occupying half of the tetrahedral holes (T⁺ or T⁻). In Zinc blend both Zinc and sulfide ions are four coordinated.

Zinc Blend structure is formed by Polarizing Cations (Cu⁺, Ag⁺, Cd²⁺, Ga³⁺) and Polarizable Anions (I⁻, S²⁻, P³⁻). e.g., Cu(F, Cl, Br, I), AgI, Zn(S, Se, Te), Ga(P, As), Hg(S, Se, Te).

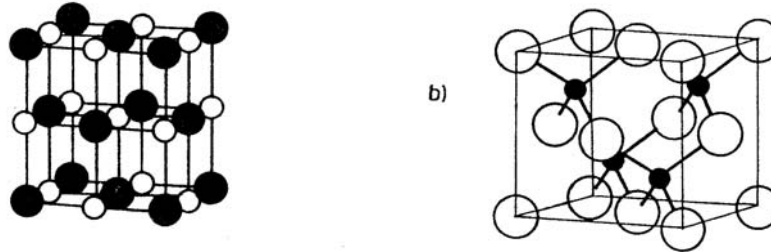


Fig. 20. (a) Unit cell of Sodium chloride (NaCl) or Rock salt structure, (b) Unit cell of Zinc blend (ZnS)

Nickel Arsenide (NiAs) Structure

Nickel arsenide is made up of the hexagonal close packing of arsenide ions with the filling of nickel ions in all octahedral holes. Thus Nickel arsenide is the hcp analogue of Sodium chloride. In Nickel Arsenide, both Nickel and Arsenide are six coordinated (Ni – octahedral and As – trigonal prismatic).

Nickel arsenide structure is adopted by transition metals with chalcogens, As, Sb, Bi, e.g., Ti(S, Se, Te); Cr(S, Se, Te, Sb); Ni(S, Se, Te, As, Sb, Sn).

Wurtzite (ZnS) Structure

Wurtzite is the allotrope of Zinc Blend. In Wurtzite sulfide ions form the hcp arrangement with the filling of zinc ions in half of the tetrahedral holes (T⁺ or T⁻). Both zinc and sulfide ions are tetrahedrally coordinated. Compounds adopting Wurtzite structure are BeO, ZnO and NH₄.

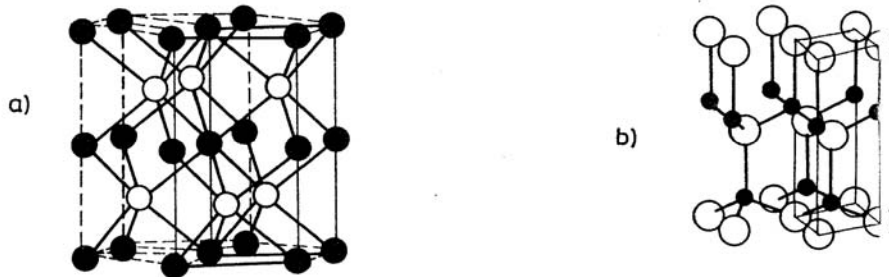


Fig. 21. (a) Unit cell of Nickel Arsenide, (b) Unit cell of Wurtzite (ZnS)

STRUCTURE TYPE AX : NON-CLOSE PACKED STRUCTURE

Caesium Chloride(CsCl) Structure

For the ionic crystals of type AX with radius ratio larger than 0.732, it follows the non-close packed Caesium Chloride structure. In Caesium chloride, chloride ions form the square packing arrangement (or primitive cubic) with the Caesium ion occupying the cubic coordination position (i.e., at the body center). Both Caesium and chloride ions are eight coordinated (cubic coordination).

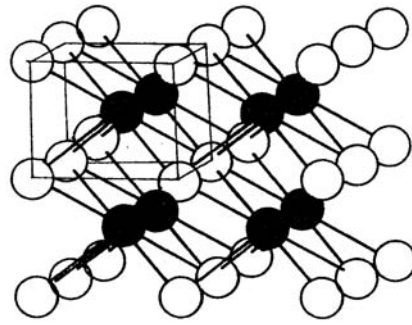


Fig. 22. Unit cell of Caesium chloride

STRUCTURE TYPE AX₂: CLOSE PACKED STRUCTURES

Fluorite (Calcium fluoride, CaF₂) Structure

The ionic crystals of type AX₂ crystallizes with either of the two types; Fluorite (Calcium fluoride, CaF₂) or Rutile (Titanium dioxide, TiO₂). The Fluorite structure is expected if the radius ratio is greater than 0.73, but the Rutile structure when the radius ratio is between 0.414 and 0.732.

In Fluorite structure the calcium ions form the fcc arrangement with the fluoride ions occupying all the tetrahedral holes (Fluorite A-cell). Each Fluoride ion is surrounded by four calcium ions and each calcium ion is surrounded by eight fluoride ions. By moving the unit cell corners to the fluoride ions (Fluorite B-cell), the cubic coordination of the calcium ions could be obviously seen.

Fluorides of large divalent cations, chlorides of Sr, Ba and Oxides of large quadrivalent cations (Zr, Hf, Ce, Th, U) adopt the Fluorite structure.

Anti-Fluorite (Na₂O) Structure

Anti-Fluorite structure results from the reversal of the positions of cations and anions in the Fluorite structure. Oxides and chalcogenides of alkali metals adopt the Anti-Fluorite structure.

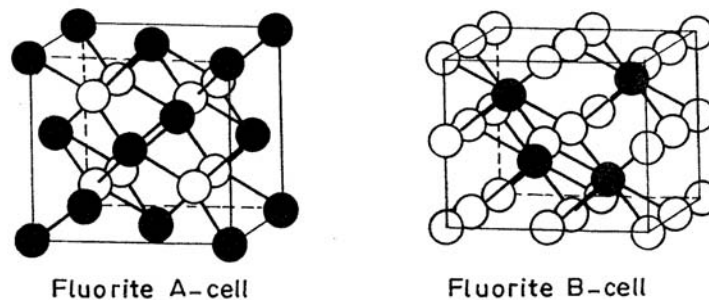


Fig. 23. Unit cell of Fluorite structure

Rutile (TiO₂) Structure

In Rutile structure, oxide ions form the hexagonal close packing with the titanium ions occupying half of the octahedral holes. The coordination around titanium ion is octahedral with slight distortion and around oxygen is equilateral triangle. Because of the distortion the crystal structure is Tetragonal.

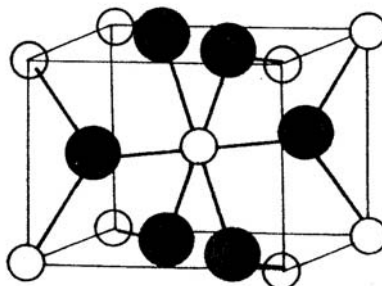


Fig. 24. Unit cell of Rutile (TiO_2)

Majority of transition metal dioxides crystallize with Rutile structure.

STRUCTURE TYPE AX_2 : NON-CLOSE PACKED STRUCTURE(LAYER STRUCTURE)

These structures result, when the holes in alternate layers are completely filled but holes in the next alternate layer are completely not filled.

Cadmium Iodide (CdI_2) Structure

The structure of Cadmium iodide is formed by the hexagonal close packing of iodide ions with the filling of cadmium ions in the octahedral holes of alternate layers. The coordination number of cadmium and iodide ions are 6 and 3.

The Cadmium iodide structure is adopted by iodides of moderately polarising cations; bromides and chlorides of strongly polarising cations; e.g., PbI_2 , FeBr_2 , VCl_2 ; Hydroxides of many divalent cations. e.g., $(\text{Mg},\text{Ni})(\text{OH})_2$; Di-chalcogenides of many quadrivalent cations . e.g., TiS_2 , ZrSe_2 , CoTe_2 .

The structure of Cadmium chloride is the ccp analogue of Cadmium iodide. Chlorides of moderately polarising cations, e.g., MgCl_2 , MnCl_2 and di-sulfides of quadrivalent cations, e.g., TaS_2 , NbS_2 (CdI_2 form as well) adopt to the Cadmium chloride structure.

A characteristic feature of these structures is the unsymmetrical environment of the X ions, which have their A neighbours all to one side and on the other side are in contact with only similar X atoms.

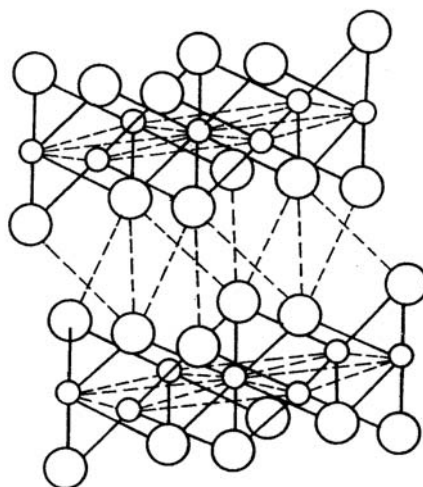


Fig. 25. The layer structure of CdI_2 : small circles represent Cd ions and larger ones the I ions

SUMMARY OF IONIC CRYSTAL STRUCTURES

The hole filling in the cubic close packing arrangement can be summarized as in fig. 26.

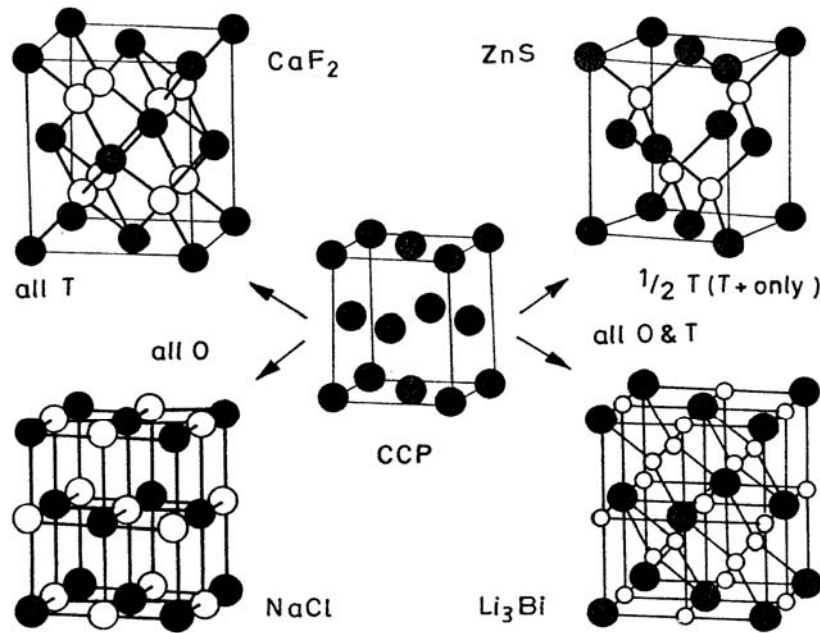


Fig. 26. The possible hole filling in Cubic close packing arrangement

The structures of ionic crystals could be summarized as in table 5.

Table 5. Summary of the structure types of ionic crystals

Formula	Type and fraction of sites occupied	CCP	HCP
AX	All octahedral Half tetrahedral (T+ or T-)	Rock salt (NaCl) Zinc Blende (ZnS)	Nickel Arsenide(NiAs) Wurtzite(ZnS)
AX ₂	All tetrahedral Half octahedral (ordered framework) Half octahedral (Alternate layers full / empty)	Fluorite (CaF ₂), Anti-fluorite (Na ₂ O) Anatase (TiO ₂) Cadmium chloride (CdCl ₂)	Not known Rutile (TiO ₂) Cadmium iodide (CdI ₂)
A ₃ X	All octahedral and all tetrahedral	Li ₃ Bi	Not known
AX ₃	One third octahedral	YCl ₃	BiI ₃

OTHER STRUCTURE TYPES

Perovskite Structure

Perovskites are named after the mineral CaTiO₃, identified by the Russian mineralogist Perovski. These oxides are having the formula unit of ABO₃. The structure is formed by the cubic close packing of A atoms

(bigger) at the corners and Oxygen atoms at the face centers and B atoms (smaller) at the body center. In this structure the bigger cation is 12 coordinated and the smaller cation is 6 coordinated.

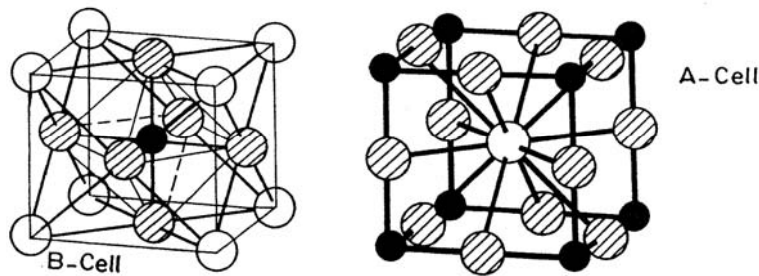


Fig. 27. Unit cell of Perovskite structure

Compounds adopting this structure are NaNbO_3 , BaTiO_3 , CaZrO_3 , SrTiO_3 , SrZrO_3 , YAlO_3 and KMgF_3 .

Spinel Structure

Spinel is named after the mineral MgAl_2O_4 . Spinel has the formula unit of AB_2O_4 . A is a divalent ion and B is trivalent. The structure is formed by the fcc arrangement of oxide ions with A^{2+} ions occupying the tetrahedral holes and B^{3+} ions occupying the octahedral holes. A spinel crystal having $n\text{AB}_2\text{O}_4$ formula unit has $8n$ tetrahedral holes and $4n$ octahedral holes. One-eighth of the tetrahedral holes are occupied by A^{2+} ions and one-half of the octahedral holes by the B^{3+} ions.

The unit cell of Spinel is shown in fig. 28. It has been broken down into eight octants of two types AX_4 and B_4X_4 (each type four), which is shown on the right side of the unit cell. In the spinel unit cell these two types of the octants are alternately arranged. Compounds with this structure are MAl_2O_4 (M is Mg, Fe, Co, Ni, Mn or Zn).

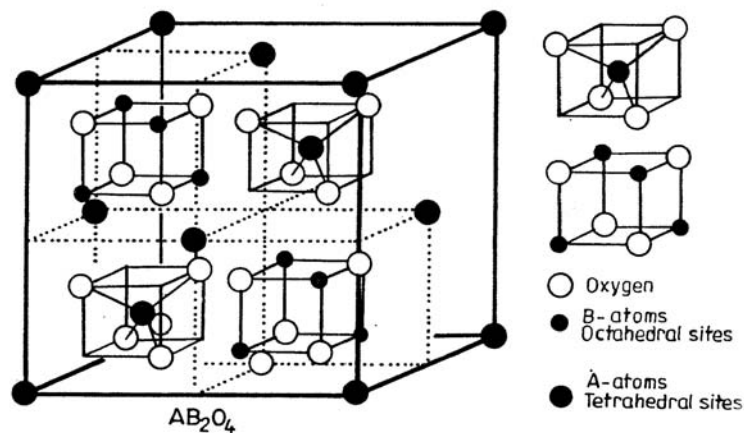


Fig. 28. Unit cell of Spinel structure

In the spinel structure, if half of the B^{3+} ions occupying tetrahedral sites with the remaining half of B^{3+} ions occupying octahedral sites along with A^{2+} ions, then the structure type is called as the Inverse Spinel and are represented by the formula $\text{B}(\text{AB})\text{O}_4$. Examples of inverse spinels are $\text{Fe}(\text{MgFe})\text{O}_4$ and $\text{Fe}(\text{ZnFe})\text{O}_4$.

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CHAPTER – 3

Electric Properties of Solids

INTRODUCTION – METALS, INSULATORS AND SEMICONDUCTORS

Solids may be classified in terms of their resistivity or conductivity as conductors, insulators, or semiconductors. At a first glance, the main difference between metals, semiconductor and insulators is in the magnitude of their conductivities. Metals conduct electricity very easily, $\sigma \sim 10^4$ to $10^6 \text{ ohm}^{-1}\text{cm}^{-1}$, insulators very poorly, or not at all $\sigma \leq 10^{-15} \text{ ohm}^{-1}\text{cm}^{-1}$, and semiconductors lie in between, $\sigma \sim 10^{-15}$ to $10^3 \text{ ohm}^{-1}\text{cm}^{-1}$. The boundaries are somewhat arbitrary and a certain amount of overlap occurs.

In order of conductivity :

Superconductors > conductors > semiconductors > insulators

Conductors are materials capable of carrying electric current, i.e., material which has “mobile charge carriers” (e.g., electrons, ions) e.g., metals, liquids with ions (water, molten ionic compounds), plasma. Insulators are the materials with no or very few free charge carriers; e.g., quartz, most covalent and ionic solids, plastics. Semiconductors are materials with conductivity between that of conductors and insulators; e.g. germanium Ge, silicon Si, GaAs, GaP, InP. Superconductors - certain materials have zero resistivity at very low temperature.

Some Representative Resistivities (ρ)

$R = \rho L/A$, R = resistance, L = length, A = cross section area; ρ = resistivity at 20°C .

Table 1. Typical values of resistivities of materials

Material	Resistivity in $\Omega \text{ m}$	Resistance(in Ω) ($L=1\text{m}$, $\text{diam}=1\text{mm}$)
Aluminum	2.8×10^{-8}	3.6×10^{-2}
Brass	$\approx 8 \times 10^{-8}$	10.1×10^{-2}
Copper	1.7×10^{-8}	2.2×10^{-2}
Platinum	10×10^{-8}	12.7×10^{-2}
Silver	1.6×10^{-8}	2.1×10^{-2}
Carbon	3.5×10^{-5}	44.5
Germanium	0.45	5.7×10^5
Silicon	≈ 640	$\approx 6 \times 10^8$
Porcelain	$10^{10} - 10^{12}$	$10^{16} - 10^{18}$
Teflon	10^{14}	10^{20}
Blood	1.5	1.9×10^6
Fat	24	3×10^7

There is, however, a fundamental difference between the mechanism of conduction in metals, on the one hand, and semiconductors/insulators, on the other. Very simply, the conductivity of most semiconductors/insulators increases with temperature where as that of metals shows a slight but gradual decrease (Fig. 1.).

The conductivity, σ , is given by the equation,

$$\sigma = ne\mu,$$

where n is the number, e , the charge and μ , the mobility of the charge carriers. The temperature dependence of σ in different materials can be understood by considering the temperature dependence of the terms n , e , and μ . For all electronic conductors, e is constant and independent of temperature. The

mobility is similar in most materials in that usually it decreases slightly with increasing temperature due to collisions between the moving electrons and phonons, i.e., lattice vibrations. The main difference between metals, semiconductors and insulators therefore lies in the value of n and its temperature dependence.

- For metals, n is large and essentially unchanged with temperature. The only variable in σ is μ and since μ decreases slightly with temperature, σ also decreases.
- For semiconductors and insulators, n usually increases exponentially with temperature. The effect of this dramatic increase in n more than outweighs the effect of the same decrease in μ . Hence, σ increases rapidly with temperature. Insulators are extreme example of semiconductors in that n is very small at normal temperatures. Thus some insulators become semiconducting at high temperatures where n becomes appreciable and conversely, some semiconductors become more like insulators at low temperatures.

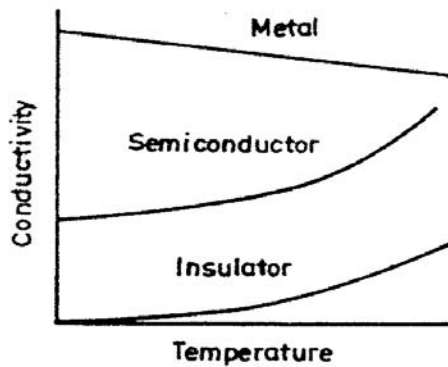


Fig. 1. Effect of temperature on conductivity

BAND THEORY – ELECTRONIC STRUCTURE OF SOLIDS

In MO theory we assumed that atomic orbitals on two atoms could come together to form bonding and antibonding orbitals. If we bring three atoms together we can create a string of atoms with bonding that connects all three. Here we have a bonding orbital, an antibonding orbital, and a curious critter called a nonbonding orbital. Essentially a nonbonding orbital is an orbital that neither increases nor decreases the net bonding in the molecule. The important feature here is that three atomic orbitals in must give three molecular orbitals out. The total number of orbitals must remain constant. If we now go to a huge number of atoms, n , where n is perhaps as big as Avogadro's number, we can see that we're going to have a huge number of bonding and antibonding orbitals. These orbitals will be so close together in energy that they begin to blur creating bands of bonding and bands of antibonding orbitals (Fig. 2.). It is the existence of these bands of orbitals that underlie our understanding of the properties of solids.

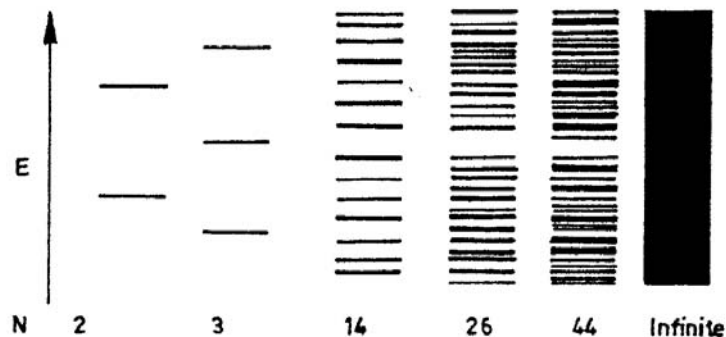


Fig. 2. Splitting of energy levels on molecular orbital theory

The electronic structures of metals, semiconductors and insulators may be easily understood by the energy gap between the bonding bands and the antibonding bands (Fig. 3.). If there is a large gap in energy, the material is called an insulator. If the gap is finite, but small, then the material is a semiconductor, and if there is effectively no gap between the bands, the materials are called conductors. These properties arise because electrons that enter the antibonding band are free to move about the crystal. Such behavior is associated with electrical conduction. To give an idea of the energies involved, typically, the band gap in diamond is 6 eV, while that in Si is 1.1 eV. Diamond is an insulator while the other is semiconductor. Most common semiconductors are either elements from group IV of the periodic table (Si, Ge), or compounds formed from elements on either side of group IV. Thus there are so-called III-V semiconductors (GaAs, GaP, InP, AlAs, GaN, etc.,) and also II-VI semiconductors (ZnSe, CdTe, etc.,).

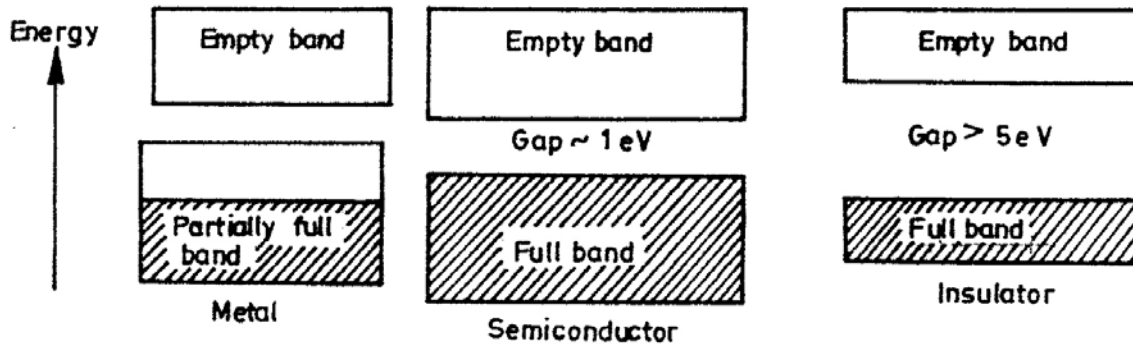


Fig. 3. Band diagram for metals semiconductors and insulators

CONDUCTORS

An electrical conductor is a substance through which electrical current flows with small resistance. It has a cloud of free electrons (at all temperatures above absolute zero). If an electric field is applied electrons will flow causing an electric current. Metals are generally excellent electrical conductors. Few examples are Cu, Al, Au, Fe, Pb, Ag, Ti, U, Zn etc.,

Non metals are also exhibiting conduction and they are termed as non metallic conductors. Silicides, i.e., metal - silicon compounds, are important for microelectronics (ME) technology and used as heating elements. Examples for silicides are MoSi₂, TaSi₂, TiSi₂, CoSi₂, NiSi₂, PtSi & Pd₂Si. Few other non metals that are electronic conductive is HfN TiN TiC TiB₂ and C (Graphite). Indium Tin Oxide (ITO) is a *transparent* conductor with reasonable conductivity (around 1Wcm). It consists of SnO₂ doped with In₂O₃. ITO is technically *very important*, especially for flat panel displays, solar cells and in research (e.g., for the electrical measurements of light-induced phenomena). ITO is one example of conducting oxides; others are TiO, NiO, or ZnO.

Electrical Resistivity of Metals

Resistivity depends on collisions. Quantum mechanics tells us that electrons behave like waves. One of the effects of this is that electrons do not scatter from a perfect lattice. They scatter by defects, which can be:

- atoms displaced by lattice vibrations
- vacancies and interstitials
- dislocations, grain boundaries
- impurities

One can express the total resistivity, as a sum of resistivities due to thermal vibrations, impurities and dislocations.

Electrical Characteristics of Commercial Alloys

The best material for electrical conduction (lower resistivity) is silver. Since it is very expensive, copper is preferred, at an only modest increase in ρ . To achieve low ρ it is necessary to remove gases occluded in the metal during fabrication. Copper is soft. So, for applications where mechanical strength is important, the alloy CuBe is used, which has a nearly as good resistivity as copper. When weight is important one uses Al, which is half as good as Cu. Al is also more resistant to corrosion.

When high resistivity (ρ) materials are needed, like in electrical heaters, especially those that operate at high temperature, nichrome (NiCr) or graphite are used.

SUPERCONDUCTORS

Superconductors are materials that have no resistance to the flow of electricity and are one of the last great frontiers of scientific discovery. The variation of resistance with temperature is shown in fig. 4.

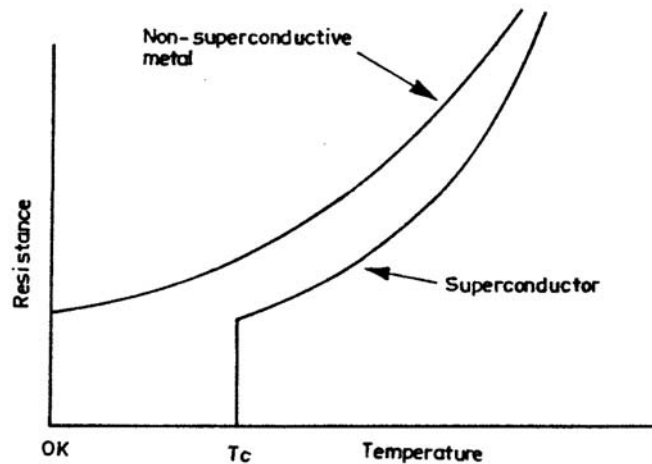


Fig. 4. Variation of resistance with temperature for metals and superconductors

History of Superconductivity

In 1911 superconductivity was first observed in mercury by Dutch physicist Heike Kamerlingh Onnes of Leiden University. When he cooled it to the temperature of liquid helium, 4 degrees Kelvin (-452F, -269°C), its resistance suddenly disappeared. Later, in 1913, he won a Nobel Prize in physics for his research in this area. The next great milestone in understanding how matter behaves at extreme cold temperatures occurred in 1933. Walter Meissner and Robert Ochsenfeld discovered that a superconducting material will repel a magnetic field. In a superconductor the induced currents exactly mirror the field that would have otherwise penetrated the superconducting material - causing the magnet to be repulsed. This phenomenon is known as diamagnetism and is today often referred to as the "Meissner effect". The Meissner effect is so strong that a magnet can actually be levitated over a superconductive material.

In subsequent decades other superconducting metals, alloys and compounds were discovered. In 1941 niobiumnitride was found to superconduct at 16 K. In 1953 vanadium-silicon displayed superconductive properties at 17.5 K. And, in 1962 scientists at Westinghouse developed the first commercial superconducting wire, an alloy of niobium and titanium (NbTi).

The first widely-accepted theoretical understanding of superconductivity was advanced in 1957 by American physicists John Bardeen, Leon Cooper, and John Schrieffer. Another significant theoretical advancement came in 1962 when Brian D. Josephson, a graduate student at Cambridge University, predicted that electrical current would flow between 2 superconducting materials - even when they are separated by a non-superconductor or insulator. His prediction was later confirmed and won him a share of the 1973 Nobel Prize in Physics. This tunneling phenomenon is today known as the "Josephson effect". In 1964 Bill Little of Stanford University had suggested the possibility of organic (carbon-based) superconductors. The first of these theoretical superconductors was successfully synthesized in 1980 by

Danish researcher Klaus Bechgaard of the University of Copenhagen and 3 French team members. $(\text{TMTSF})_2\text{PF}_6$ had to be cooled to an incredibly cold 1.2 K transition temperature (known as T_c) and subjected to high pressure to superconduct.

Then, in 1986, a truly breakthrough discovery was made in the field of superconductivity. Alex Müller and George Bednorz, researchers at the IBM Research Laboratory in Rüschlikon, Switzerland, created a brittle ceramic compound that superconducted at the highest temperature then known : 30 K. What made this discovery so remarkable was that ceramics are normally insulators. They don't conduct electricity well at all. So, researchers had not considered them as possible high-temperature superconductor candidates. The discovery of this first of the superconducting copper-oxides (cuprates) won the 2 men a Nobel Prize the following year. It was later found that tiny amounts of this material were actually superconducting at 58 K, due to a small amount of lead having been added making the discovery even more noteworthy. Müller and Bednorz's discovery triggered a flurry of activity in the field of superconductivity. Researchers around the world began "cooking" up ceramics of every imaginable combination in a quest for higher and higher T_c 's. In January of 1987 a research team at the University of Alabama-Huntsville substituted Yttrium for Lanthanum in the Müller and Bednorz molecule and achieved an incredible 92 K T_c . For the first time a material had been found that would superconduct at temperatures warmer than liquid nitrogen - a commonly available coolant.

One of the pure carbon superconductors is based on the Buckyball - a closed sphere of 60 carbon atoms discovered in 1985. The Buckyball (also called a fullerene) can be doped with alkali metals and made to superconduct at low temperatures. The first was K_3C_{60} in 1991, which has a T_c of 18 K. Other, non-spherical carbon-based superconductors are much more recent. Only two years ago, superconductivity was found in single-walled carbon nanotubes at around 15 K.

The current class of ceramic superconductors with the highest transition temperatures are the mercuric-cuprates. The first synthesis of one of these compounds was achieved in 1993 by Prof. Dr. Ulker Onbasli at the University of Colorado. The world record T_c of 138 K is now held by a thallium-doped, mercuric-cuprate comprised of the elements Mercury, Thallium, Barium, Calcium, Copper and Oxygen. The T_c of this ceramic superconductor was confirmed by Dr. Ron Goldfarb at the National Institute of Standards and Technology-Colorado in February of 1994.

BCS Theory of Superconductivity

Superconductivity was not sufficiently explained until 1957 when John Bardeen and his graduate assistants Leon Cooper and John Schreiffner proposed a microscopic explanation. The BCS Theory makes a crucial assumption at the beginning : that an attractive force exists between electrons. In typical type I superconductors, this force is due to Coulomb attraction between the electron and the crystal lattice. An electron in the lattice will cause a slight increase in positive charges around it. This increase in positive charge will, in turn, attract another electron. These two electrons are known as a Cooper pair. If the energy required to bind these electrons together is less than the energy from the thermal vibrations of the lattice attempting to break them apart, the pair will remain bound. This explains (roughly) why superconductivity requires low temperatures - the thermal vibration of the lattice must be small enough to allow the forming of Cooper pairs. In a superconductor, the current is made up of these Cooper pairs, rather than individual electrons.

So, Cooper pairs are formed by Coulomb interactions with the crystal lattice. This is also what overcomes resistance. Remember, an electron inside the lattice causes a slight increase of positive charge due to Coulomb attraction. As the Cooper pair flows, the leading electron causes this increase of charge, and the trailing electron is attracted by it. This BCS theory prediction of Cooper pair interaction with the crystal lattice has been verified experimentally by the isotope effect. The BCS Theory did exactly what a physical theory should do: it explained properties already witnessed in experiment, and it predicted experimentally verifiable phenomena, though its specific quantitative elements were quite limited in their application (it only explained type I superconductivity).

The type I category of superconductors is mainly comprised of metals and metalloids that show *some* conductivity at room temperature. Type I superconductors - characterized as the "soft" superconductors - were discovered first and require the coldest temperatures to become superconductive. They exhibit a very sharp transition to a superconducting state and "perfect" diamagnetism - the ability to repel a magnetic field completely.

Except for the elements vanadium, technetium and niobium, the type 2 category of superconductors is comprised of metallic compounds and alloys. The recently-discovered superconducting "perovskites" (metal-oxide ceramics that normally have a ratio of 2 metal atoms to every 3 oxygen atoms) belong to this type 2 group. They achieve higher T_c 's than type 1 superconductors by a mechanism that is still not completely understood. Conventional wisdom holds that it relates to the planar layering within the crystalline structure. Although, other recent research suggests the holes of hypocharged oxygen in the charge reservoirs are responsible. (Holes are positively-charged vacancies within the lattice.) Type 2 superconductors - also known as the "hard" superconductors - differ from type 1 in that their transition from a normal to a superconducting state is gradual across a region of "mixed state" behavior. Since a type 2 will allow *some* penetration by an external magnetic field into its surface, this creates some rather novel mesoscopic phenomena like superconducting 'stripes' and 'flux-lattice vortices'.

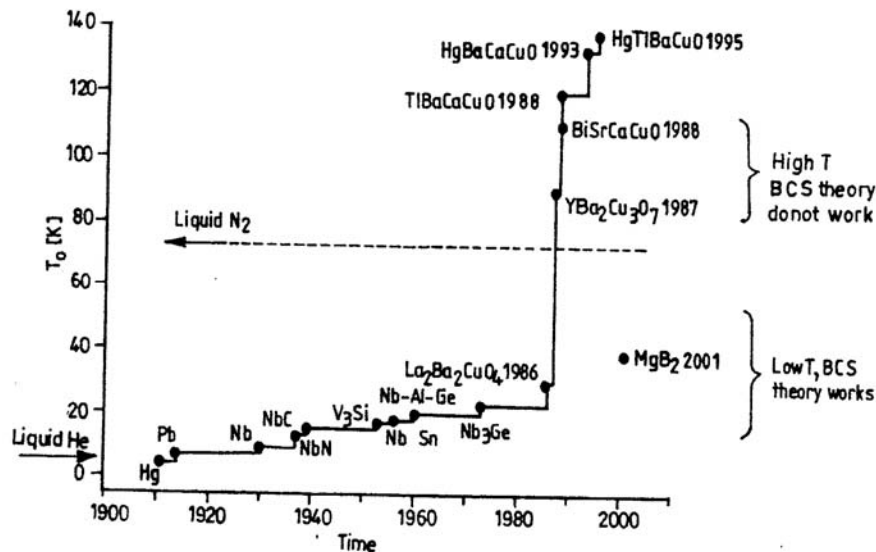


Fig. 5. The time line for the discovery of superconductors

Applications of Superconductors

The potential of superconductors is incredible, and their applications are practically innumerable. They promise to revolutionize electronics as we know them today : making logic gates faster, smaller, and more efficient. This will lead to a leap in miniaturization of consumer electronics and integrated circuits.

Magnetic-levitation is an application where superconductors perform extremely well. Transport vehicles such as trains can be made to "float" on strong superconducting magnets, virtually eliminating friction between the train and its tracks. In 1979 a Japanese mag-lev train set a speed record of 581 kph. The Japanese train had superconducting magnets on the cars themselves, inducing currents in the rails, and creating a repulsive force to levitate the train. Though such a setup requires that the train be moving before it levitates, mag-lev trains should be much safer than traditional trains at high speeds. Although the technology has now been proven, the wider use of MAGLEV vehicles has been constrained by environmental concerns. The world's first MAGLEV train to be adopted into commercial service, shuttled in Birmingham, England, was shut down in 1997 after operating for 11 years.

An area where superconductors can perform a life-saving function is in the field of biomagnetism. Doctors need a non-invasive means of determining what's going on inside the human body. By impinging a strong superconductor-derived magnetic field into the body, hydrogen atoms that exist in the body's water and fat molecules are forced to accept energy from the magnetic field. They then release this energy at a frequency that can be detected and displayed graphically by a computer. Magnetic Resonance Imaging (MRI) was actually discovered in the mid 1940's. But, the first MRI exam on a human being was not

performed until July 3, 1977. And, it took almost five hours to produce one image ! Today's faster computers process the data in much less time.

The Korean Superconductivity Group has carried biomagnetic technology a step further with the development of a double-relaxation oscillation SQUID (Superconducting Quantum Interference Device) for use in Magnetoencephalography. Magnetoencephalography (MEG) is completely noninvasive, non-hazardous technology for functional brain mapping. SQUID's are capable of sensing a change in a magnetic field over a billion times weaker than the force that moves the needle on a compass.

An idealized application for superconductors is to employ them in the transmission of commercial power to cities. In May of 2001 some 150,000 residents of Copenhagen, Denmark, began receiving their electricity through HTS (high-temperature superconducting) material. That cable was only 30 meters long, but proved adequate for testing purposes. Due to the high cost and impracticality of cooling miles of superconducting wire to cryogenic temperatures, this has only happened with short "test runs".

SEMICONDUCTORS

Silicon has been noted that it is an insulator at 0 K. This is because there is insufficient energy available from the lattice to cause a covalent bond to break, so there are no free charges. However, as the temperature of the crystal is raised, there is a finite probability that a small concentration of bonds will gain enough energy to break, releasing an electron to become a free, conduction band electron, while at the same time leaving behind an unfilled covalent bond (empty state in the *valence band*) which in turn can meander around the lattice. At room temperatures there are only few charge carriers. *Pure* semiconductors are poor conductors and are known as *intrinsic* semiconductors.

The conductivity of semiconductors like Si can be increased by adding small, controlled amounts of "impurities" that have roughly the same atomic size, but more or fewer valence electrons than the semimetal. This process is known as *doping*. The doping results in a material that either adds extra electrons to the material (which is then called *N-type* for the extra negative charge carriers) or creates "holes" in the material's crystal structure (which is then called *P-type* because it results in more positive charge carriers).

Assume that a small concentration of group V atoms is added to the *host* Si crystal. These atoms will *substitute* for Si atoms in the lattice. Since they have five rather than four valence electrons, one electron for each impurity atom is unused in the bonding. So the fifth valence electron is responsible for conduction of electricity. Such impurity atom is called a donor. The impure silicon atom is an *n-type* semiconductor since the majority charge carriers are negative electrons. Yet, the overall charge in the crystal is zero since every atom present is electrically neutral.

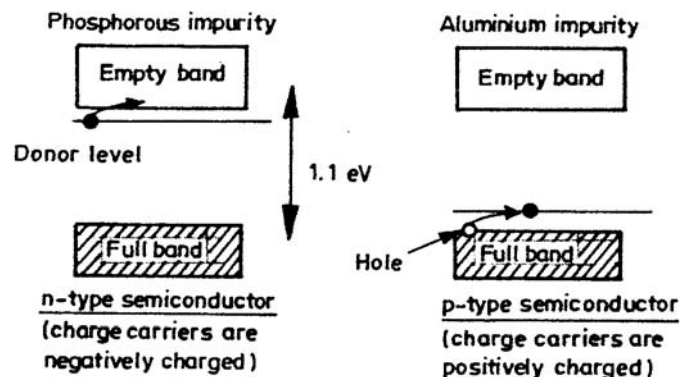


Fig. 6. Band diagram for n-type and p-type semiconductor

When a small concentration of group III atoms is added to the *host* Si crystal these atoms will also substitute for Si atoms in the lattice. Since they have three rather than four valence electrons, one of the four covalent bonds associated with the impurity is unfilled creating a hole. And this hole attracts an electron from the nearby silicon atom, forming another hole. For this reason, the impurity atom is called an

acceptor. The 'impure' silicon is a *p-type* semiconductor because the majority charge carriers causing conduction are positive holes.

When a *p-type* and *n-type* Si are joined together, we have a *p-n* junction. A *p-n* junction has high electron conductivity along one direction, but almost no conductivity along the other! Why? Electrons can cross the *p-n* junction from the *n-type* Si side easily as it can jump into the holes (Fig. 7). However, along the other direction, electrons have to surmount a ~ 1.1 eV barrier (which is impossible at room temperature in the dark). This results in a one-way traffic of electrons.

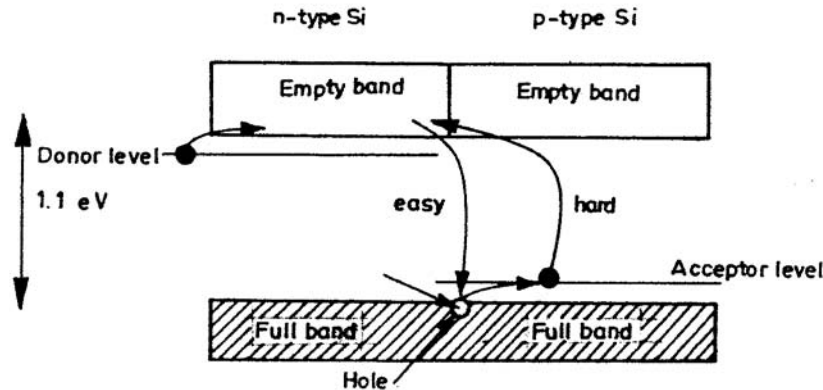
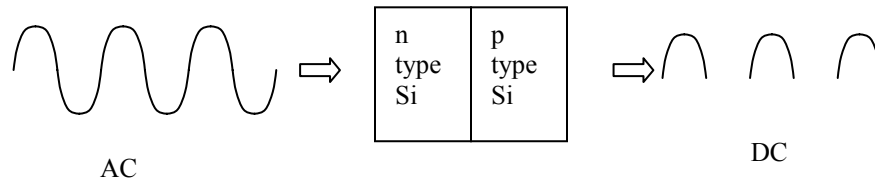


Fig. 7. Operation of *p-n* junction

Applications of Semiconductors

Rectifiers

Rectification is the conversion from alternating current (AC) to direct current (DC). Most electronic equipment requires DC power, and if the equipment draws its power from an AC supply it is necessary to convert the AC supply into a suitable DC voltage source. *Rectifiers* are the main part of a *DC power supply*. Rectifiers also play an important role in signal processing. For example, AM radio is demodulated with the aid of a rectifier.



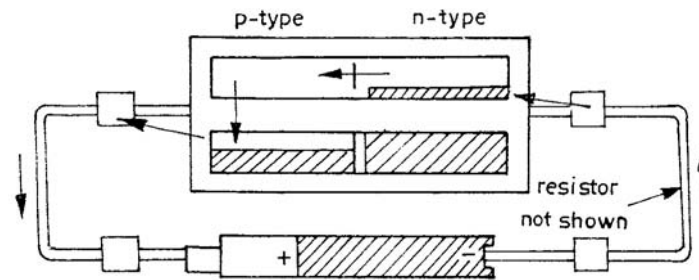
Transistors

The transistor, invented by three scientists at the Bell Laboratories in 1947, rapidly replaced the vacuum tube as an electronic signal regulator. The name "transistor" is a contraction of the two terms transistor-resistor. It regulates current or voltage flow and acts as a switch or gate for electronic signals. It consists of three layers of a semiconductor material, each capable of carrying a current. The transistor's three-layer structure contains an N-type semiconductor layer sandwiched between P-type layers (a PNP configuration) or a P-type layer between N-type layers (an NPN configuration). Transistors are the basic elements in integrated circuits, which consist of very large numbers of transistors interconnected with circuitry and baked into a single silicon. Transistors are more interesting and have more applications than diodes. Two types of transistors are widely used: *Bipolar Junction transistors* (BJTs), is an active semiconductor device formed by two P-N junctions whose function is amplification of an electric current and *Field Effect Transistors* (FETs), are so named because a weak electrical signal coming in through one electrode creates an electrical field through the rest of the transistor. This field flips from positive to negative when the

incoming signal does, and controls a second current traveling through the rest of the transistor. The field modulates the second current to mimic the first one - but it can be substantially larger. Most of today's transistors are "MOS-FETs", or Metal Oxide Semiconductor Field Effect Transistors. They were developed mainly by Bell Labs, Fairchild Semiconductor, and hundreds of Silicon Valley, Japanese and other electronics companies.

Light Emitting Diodes (LEDs)

In order to convert electrical current into light, an LED must have a *p*-type semiconductor in contact with an *n*-type semiconductor. This combination of the two types of semiconductors is known as a *p-n junction*, or a **diode**. The *p*-type semiconductor has extra space for electrons in its valence band, and no electrons in its conduction band, while the *n*-type semiconductor has a full valence band (no space) and extra electrons in its conduction band. If the circuit is constructed such that electrons flow into the *n*-type side of the *p-n* junction from the power source, they will occupy the conduction band, since there is no space in the valence band of an *n*-type semiconductor. As electrons continue to come into the conduction band, they will be pushed to the *p*-type side of the *p-n* junction, which has more space to hold electrons. The electrons go into the empty conduction band of the *p*-type side, since they already occupy the higher-energy band in the *n*-type side. However, once the electrons are in the higher-energy band of the *p*-type side, they will fall to the lower-energy band if there is space available for the electrons to occupy in the valence band. Electrons falling from the higher-energy band of orbitals (conduction band) to the lower-energy band of orbitals (valence band) in the *p*-type semiconductor results in the atoms going from a higher-energy state to a lower-energy state (i.e., becoming more stable). As the electrons cross the band gap, energy related in magnitude to the size of the band gap is released in the form of light.



The diagram shows the path of electrons moving through a circuit containing a *p-n* junction. Electrons flow from the negative pole of the battery to the *n*-type semiconductor, where they occupy the higher-energy (conduction) band. The electrons then move into the conduction band of the *p*-type semiconductor and fall into the empty orbitals of the valence band, which releases energy in the form of light. The electrons then move through the wire back to the positive pole of the battery, and re-circulate. The color of the light emitted depends on the size of the band gap. Few examples are InGaN (yellow-green), GaN (blue), SiC (blue). LEDs are used extensively as indicator lamps, and as picture elements in color matrix displays for lap-top computers, etc.

Laser diode (LD)

Laser diodes are complex semiconductors that convert an electrical current into light. Laser action (with the resultant monochromatic and coherent light output) can be achieved in a *p-n* junction formed by two doped gallium arsenide layers. The two ends of the structure need to be optically flat and parallel with one end mirrored and one partially reflective. The length of the junction must be precisely related to the wavelength of the light to be emitted. The junction is forward biased and the recombination process produces light as in the LED (incoherent). Above a certain current threshold the photons moving parallel to the junction can stimulate emission and initiate laser action. It has more efficient light output than LED. They possess high radiance (i.e., they emit lots of light in a small area). They have a very long life, offering high reliability and they can be modulated (turned off and on) at high speeds. Used also for

reading/writing reflective spots on CD-ROM disks and laser printers. Laser diodes are typically constructed of GaAlAs (gallium aluminum arsenide) for short-wavelength devices. Long-wavelength devices generally incorporate InGaAsP (indium gallium arsenide phosphide).

INSULATORS

An insulator is distinguished from a metal by its vanishing conductivity at low temperature. In contrast to what happens in metals, the electronic charge in insulators cannot flow freely under an applied field. Electrons are tightly bound to atoms in other words, electrons are *localized* in insulators.

Diamond is the hardest naturally occurring substance known. It has a structure in which every carbon is linked to four other carbons in a pyramidal three dimensional arrangement, which gives it strength and rigidity. Due to its large band gap and purity, diamond is an excellent electrical insulator.

Cubic-Boron nitride has the same structure and comes next to diamond in terms of hardness. Boron nitride consists of a three dimensional array of alternate boron and nitrogen atoms, chemically bonded together, and can exist in two forms that mimic those of pure carbon, i.e. diamond and graphite. Like diamond, cubic-BN is also used as an abrasive, especially for iron and steel cutting tools.

Silicon dioxide (SiO_2) is another example for insulator and it is used in refractive pieces (lenses, prisms...) as thickening agent in medicines, for making precision measurement equipment (balances, gravimeters, galvanometers...) and in detergents.

Aluminum trioxide (Al_2O_3) because of its insulating behavior it is used as furnace liner tubes as electronic substrates, used as laboratory instrument tubes and sample holders.

Silicon nitride (Si_3N_4) another insulating material used as cutting tools. Engine moving parts — valves, turbocharger rotors are made using silicon nitride.

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CHAPTER - 4

Optical Properties of Solids

Photons are among the most widely used tools for the investigation of matter. Optical properties are intimately related to photons since they are responsible for either the cause or the effect of an optical property of the material. Solid state materials are of great technological importance. A set of solid state materials exhibit characteristic response when they are exposed to light, a form of energy. Absorption, reflection, transmission and emission of radiation can be regarded as few of the many optical properties which are exhibited by solid state materials.

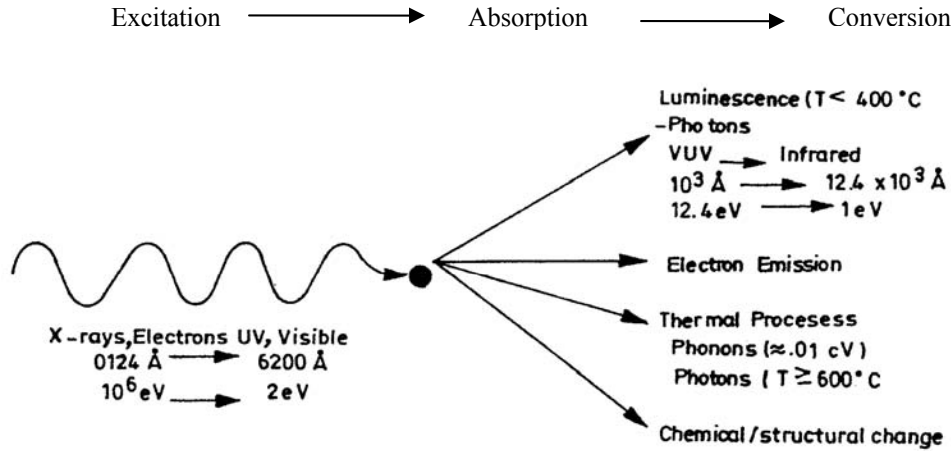


Fig. 1. Conversion of Excitation Energy in Solids

Table 1. Overview of the Electromagnetic Spectrum (reproduced from ref. 10)

Type of radiation	Wavelength λ (m)	Frequency F (Hz)	Methods of Generation	Methods of Detection
Radio wave Microwave	> 0.1 0.1 to 0.001	< 3×10^9 3×10^9 to 3×10^{11}	Electronics Klystron, magnetron, Gunn diode, maser	Electronics Diodes
Infrared radiation Visible light	0.001 to 7×10^{-7} 7×10^{-7} to 4×10^{-7}	3×10^{11} to 4.3×10^{14} 4.3×10^{14} to 7.5 $\times 10^{14}$	LEDs, laser, thermal Incandescence, arc lamp, vapor lamp, LEDs, fluorescence, laser	Diodes, photoconductor Photography, detectors, photoconductors, Photocells
Ultraviolet light X-ray	4×10^{-7} to 10^{-9} 10^{-9} to 10^{-11}	7.5×10^{14} to $3 \times$ 10^{17} 3×10^{17} to $3 \times$ 10^{19}	Arc lamp, laser, synchrotron X-ray tube, radioactivity, synchrotron	Photography, detectors, photocells Photography, detectors, scintillation counters
Gamma ray	< 10^{-11}	> 3×10^{19}	Radioactivity	Photography, detectors, scintillation counters

Understanding the electromagnetic spectrum is the necessary prelude to assimilate optical properties. When a solid absorbs photons or charged particles, a number of energy conversion processes are possible, as illustrated in fig. 1.

Optical properties of solid state materials are important for many reasons. They provide unambiguous information related to the electronic band structure and lattice modes of materials. They can be successfully employed to probe impurities and imperfections in solids. The properties are important for technological applications, such as the design of lasers, light-emitting diodes, nonlinear-optical crystals, and so on.

The types of radiation along with their wavelength and frequency ranges, and typical methods of generating and detecting the radiation are listed. The applications are innumerable and much of the technology of the present century has been involved with employing EM radiation for such diverse applications as communications, unraveling the mysteries of nature, and medical instrumentation. Progress is still being made. A brief overview of the electromagnetic (EM) spectrum is provided in table 1.

One of the phenomena among the various conversions shown in fig. 1 is the Luminescence process. Luminescent materials are a new challenge.

Luminescence

It can be defined as the event of emission of light from any substance occurring from the electronically excited states. Luminescent materials are also called phosphors which consist of a host material constituting the bulk of the phosphor. The characteristic luminescence properties are obtained by adding (“doping”) relatively small amounts of foreign ions to the host material.

Activator

A foreign ion which when incorporated into a host lattice gives rise to a center which can be excited to luminescence.

Sensitizer

A sensitizer is a foreign ion incorporated into a host lattice and is capable of transferring its energy of excitation to a neighbouring activator, thus inducing luminescence.

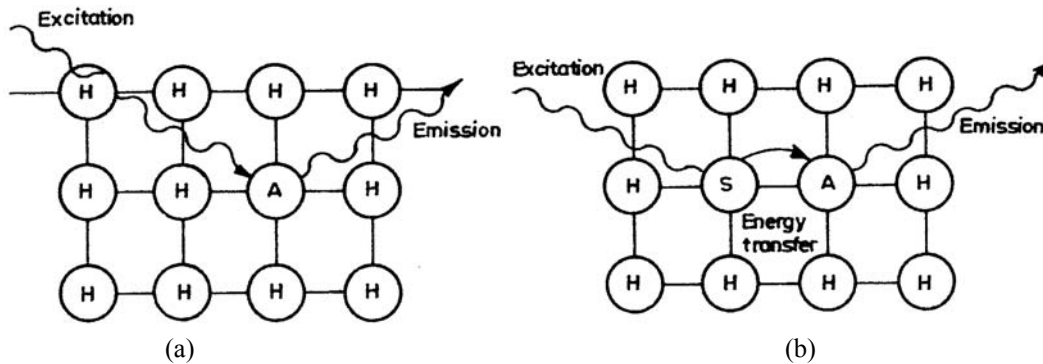


Fig. 2 (a) Diagrammatic representation of the role in the luminescence process of an activator (A) doped in a host (H) lattice, (b) Diagrammatic representation of the role in the luminescence process of a sensitizer (s) and its relationship to an activator (A) and the host lattice (H). (reproduced from ref. 9)

A schematic representation of a phosphor which contains an activator is shown in fig. 2 (a). The activator creates a center which absorbs excitation energy and converts it into visible radiation. For example : $\text{Al}_2\text{O}_3:\text{Cr}^{3+}$ (ruby) and $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$. The role of a sensitizer is illustrated in fig. 2(b). It may so happen in some instances that the activator with a desired emission may be incapable of absorbing or may have insignificant absorption for the available excitation energy. In such a case it may be possible to use a sensitizer which absorbs the excitation energy and then transfers this energy to the activator, which can then emit its characteristic luminescence. For example : $\text{Ca}_5(\text{PO}_4)_3\text{F}:\text{Sb}^{3+}, \text{Mn}^{2+}$. This is a lamp phosphor. Ultraviolet radiation is not absorbed by Mn^{2+} ion, but only by Sb^{3+} and so Sb^{3+} is the sensitizer here.

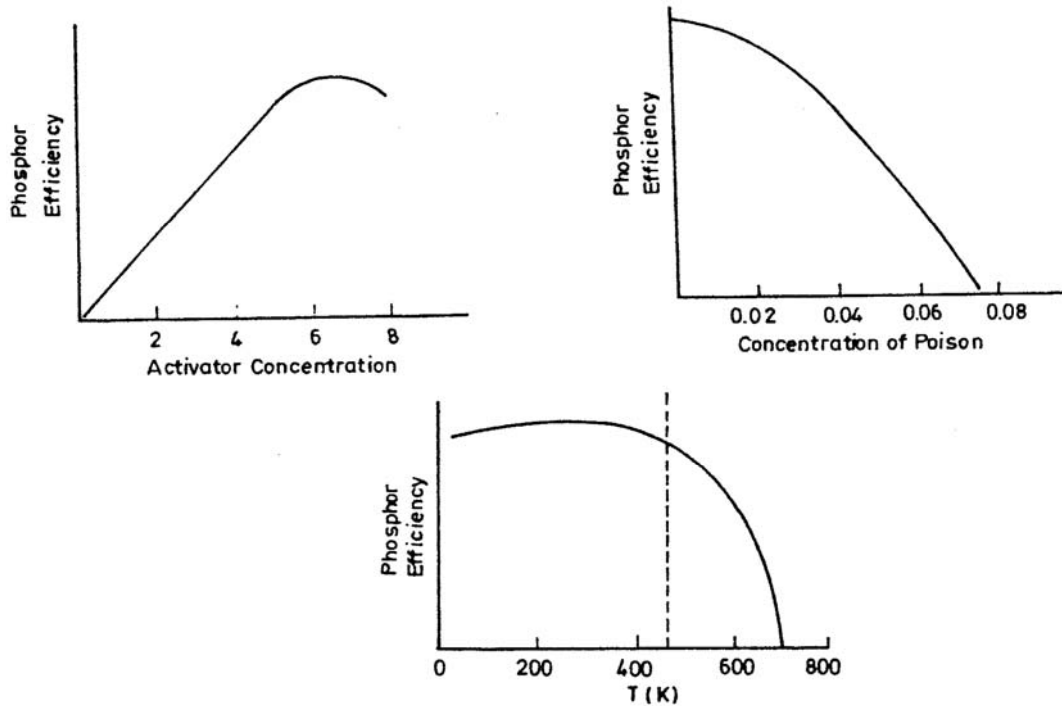


Fig. 3. The effect of (a) activator concentration on phosphor efficiency, (b) poison centers on phosphor efficiency, (c) temperature on phosphor efficiency (reproduced from ref. 9)

The effect of the concentration of activator on the phosphor efficiency is shown in fig. 3(a). The conversion efficiency of a phosphor is an important consideration in commercial applications. This efficiency is usually expressed as either an energy conversion efficiency $\rho E = E_{\text{emitted}}/E_{\text{incident}}$, or quantum conversion efficiency $\rho E = Q_{\text{emitted}}/Q_{\text{incident}}$. If one has a phosphor consisting of an activator incorporated into a host, then one might expect the luminescence emission intensity to increase with increase in the activator concentration. That is, by increasing the activator concentration one would be effectively increasing the absorption of the incident excitation energy by the phosphor. This expected behaviour is true at lower concentrations of activator (say 10%), but as the concentration of activator is increased still further one finds that there is an optimum concentration above which the phosphor efficiency actually decreases.

The effect of concentration of poison on the phosphor efficiency is shown in fig. 3(b). Phosphors can be very sensitive to the presence of foreign ions other than the beneficial sensitizers and activators. If the phosphor is contaminated with the wrong kind of impurity, it may have only a fraction of its potential efficiency. This phenomenon should be kept in mind when undertaking a work to synthesize new phosphors.

The effect of temperature on the phosphor efficiency is shown in fig. 3(c). Phosphors are generally characterized by a transition temperature, T_B above which luminescence efficiency decreases rapidly to vanishingly small values.

Effect of activator on the emission spectra

Activator play a key role in governing the emission property of the luminescent material. Examples of emission spectra of ZnS phosphors activated with a variety of cations are shown in fig. 4. Each activator gives a characteristic spectrum and colour to ZnS.

Classification brings in order and systematics in any branch of study. Luminescence can be classified in to two types based on their life times. One is fluorescence and the other is phosphorescence. The life time of fluorescence emission is $\approx 10^{-8}$ sec and it will take place as long as the source of excitation is present.

Unlike fluorescence, phosphorescence emission has longer life time ranging from 10^{-3} to few seconds and the emission of light continues even after removal of the exciting source.

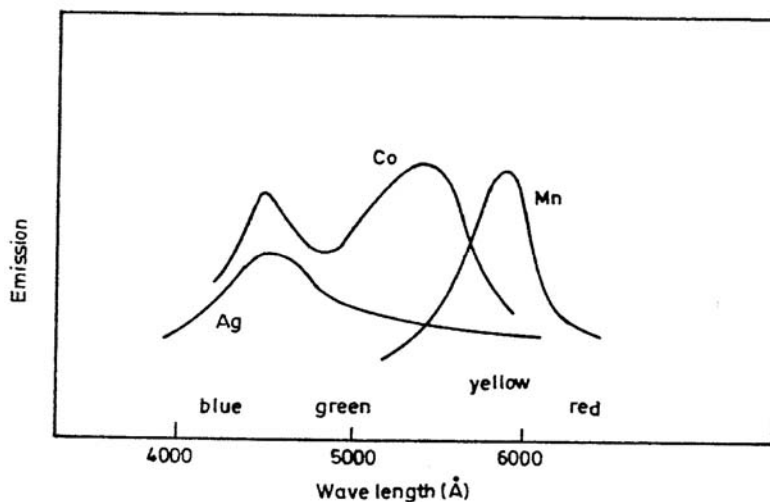


Fig. 4. Luminescence spectra of activated ZnS phosphors after irradiation with UV light (reproduced from ref. 4)

Jablonski Diagram

The process which occur between the absorption and emission of light are usually illustrated by Jablonski diagram. Jablonski diagrams are often used as the starting point for discussing light absorption and emission. These diagrams are named after Professor Alexander Jablonski who is regarded as the father of fluorescence spectroscopy.

A typical Jablonski diagram is shown in fig. 5. The singlet ground, first and second electronic states are depicted as S_0 , S_1 , and S_2 respectively. At each of these electronic energy levels the fluorophores can exist in a number of vibrational energy levels. The transitions between states are depicted as vertical lines to illustrate the instantaneous nature of light absorption.

Following light absorption, several processes usually occur. A fluorophore is usually excited to some higher vibrational level of either S_1 or S_2 .

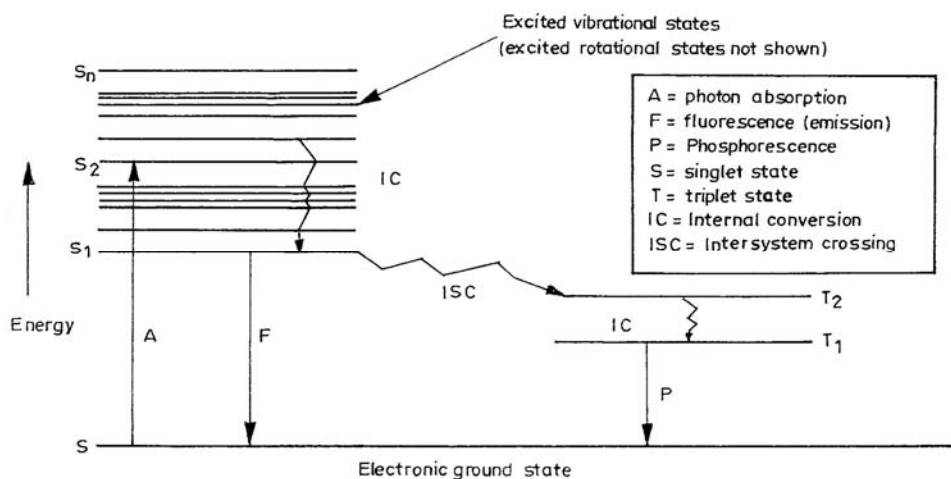


Fig. 5. One form of Jablonski diagram

Internal Conversion : Molecules in condensed phases rapidly relax to the lowest vibrational level of S_1 . This process is called internal conversion and generally occurs in 10^{-12} s or less. Since fluorescence lifetimes are typically near 10^{-8} s, internal conversion is generally complete prior to emission. Hence, fluorescence emission generally results from a thermally equilibrated excited state, that is, the lowest energy vibrational state of S_1 .

Inter System Crossing : Molecules in the S_1 state can also undergo a spin conversion to the first triplet state, T_1 . Emission from T_1 is termed as phosphorescence and is generally shifted to longer wavelength (lower energy) relative to fluorescence. Conversion of S_1 to T_1 is called inter system crossing. Transition from T_1 to the singlet ground state is forbidden and as a result, the rate constants for triplet emission is several orders of magnitude smaller than those for fluorescence. Molecules containing heavy atoms such as bromine and iodine are frequently phosphorescent. The heavy atoms facilitate intersystem crossing and thus enhance phosphorescence quantum yields.

Stokes Shift : Examination of the Jablonski diagram reveals that the energy of the emission is typically less than that of absorption. Hence fluorescence typically occurs at lower energies or longer wavelength. In other words, the energy of the emitted light is generally less than that of the exciting radiation and is therefore, of longer wavelength. This effective increase in wave length is known as the Stokes shift.

An interesting consequence of emission to higher vibrational ground states is that the emission spectrum is typically a mirror image of the absorption spectrum of the S_0 to S_1 transition. This similarity occurs because electronic excitation does not greatly alter the nuclear geometry. Hence, the spacing of the vibrational energy levels of the excited states is similar to that of the ground state. As a result, the vibrational structures seen in the absorption and the emission spectra are similar.

Franck Condon Principle and its Implication : It states that electronic transitions take place in times that are very short compared to the time required for the nuclei to move significantly.

The absorption of a photon is a practically instantaneous process, since it involves only the rearrangement of practically inertia-free electrons. The nuclei are enormously heavy as compared to the electrons. Thus, during light absorption, that occurs in Femto seconds, electrons can move, not the nuclei. The much heavier atomic nuclei have no time to readjust themselves during the absorption act, but have to do after it is over, and this readjustment brings them into vibrations. In simpler words it can be said that the nuclei do not move during the electronic transition. As a consequence of Franck Condon principle an electronic transition is always represented by a straight line.

Based on the source of excitation, luminescence processes can be classified into a variety of types and few of them are listed in table 2.

Luminescence can be excited by many types of energy. Photoluminescence is excited by electromagnetic (often ultraviolet) radiation, cathodoluminescence by a beam of energetic electrons, electroluminescence by an electric voltage, triboluminescence by the mechanical energy, X-ray luminescence by X-rays, chemiluminescence by the energy of a chemical reaction, and so on.

Table 2. Types of luminescence depending on the source of excitation

Type	Source of excitation
Photoluminescence	Electromagnetic radiation
Cathodoluminescence	Energetic electrons or cathode rays
Electroluminescence	Applied voltage
Tribo(mechano)luminescence	Mechanical energy such as grinding, stress, etc.,
Chemiluminescence	Chemical reaction energy
Bioluminescence	Biochemical energy
Radioluminescence	Nuclear radiation, X-ray, etc.,
Sonoluminescence	Sound waves
Thermally stimulated (or) Thermoluminescence	Thermal stimulation of emission which is excited by other means

Anti Stokes Phosphors

Anti-Stokes phosphors are a relatively new class of phosphors. These exhibit the remarkable property of emitting light or photons of higher energy (shorter wave length) than the incident exciting radiation. The typical reason for this being, the process of excitation takes place in two or more stages, as shown schematically in fig. 6. Using these it is possible to convert infrared radiation into higher energy visible light.

The best studied anti-Stokes phosphors todate are host structures such as YF_3 , $\text{NaLa}(\text{WO}_4)_2$, which have been doubly doped with Yb^{3+} as a sensitizer and Er^{3+} as an activator.

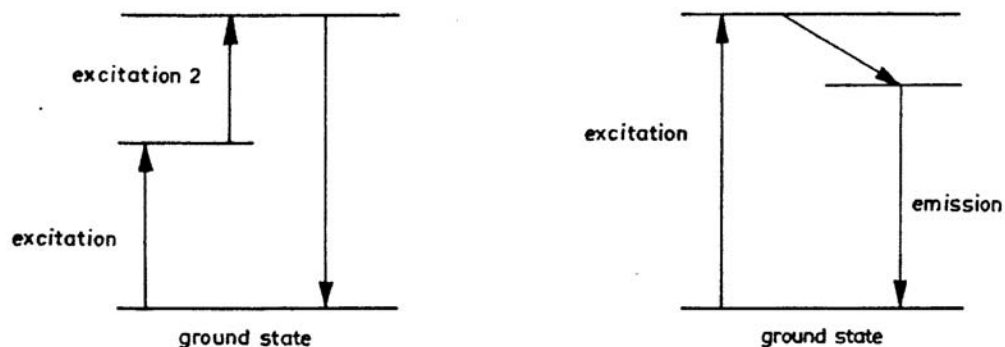


Fig. 6. Schematic representation of (a) anti-Stokes and (b) normal luminescence phenomena (reproduced from ref. 4)

APPLICATIONS OF PHOSPHORS

Phosphors are important constituents of energy efficient fluorescent lamps, cathode ray tubes used in televisions, oscilloscopes, and displays, and in X-ray detectors used in diagnostic equipment. Not just any phosphor will do in these applications; thus, the solid state chemist must meet the challenge of developing a phosphor with the necessary properties of a high efficiency for the excitation energy, desired emission spectrum, and long term chemical stability.

PHOSPHORS IN FLUORESCENT LAMPS

Photoluminescence is used in fluorescent lamps. The lamp consists of a glass tube in which a low pressure mercury discharge generates ultraviolet radiation. The lamp phosphor is applied to the inner side of the tube. This phosphor converts the ultraviolet radiation into white light. The efficiency of conversion of electricity to light is in a fluorescent lamp considerably higher than in an incandescent lamp.

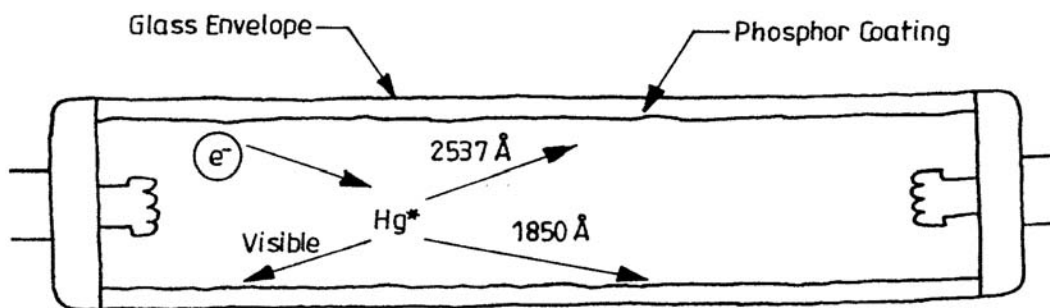


Fig. 7. Schematic design of a fluorescent lamp (reproduced from ref. 9)

The basic elements of a fluorescent lamp are shown in fig. 7. When the current is passed through the lamp envelope, the gaseous mercury atoms are excited to upper energy states which then return to the ground state with an accompanying emission of radiation. Depending on the level to which an atom is excited it may emit in the visible or in the ultraviolet (2537 Å or 1850 Å). Most of the emission from the mercury arc lies in the ultraviolet. Consequently, the glass envelope is coated on the inside with a phosphor which efficiently converts the ultraviolet radiation into visible radiation. Since we are conditioned to the visible spectrum of the sun, we would not react favourably to highly efficient lamps with emission spectra radically different from that spectrum. As a result, a fluorescent lamp must contain a phosphor which provides an emission approximating white light.

A phosphor used extensively in commercial fluorescent lamps is calcium halophosphate doped with manganese and antimony, $\text{Ca}_5(\text{PO}_4)_3\text{F}_{1-x}\text{Cl}_x:\text{Mn}^{2+}:\text{Sb}^{3+}$. In this phosphor the Sb^{3+} plays the role both of a sensitizer and an activator and Mn^{2+} are illustrated in fig. 8. The blue emission of the Sb^{3+} and the yellow emission of the Mn^{2+} combine to produce an emission spectrum that approximates white light.

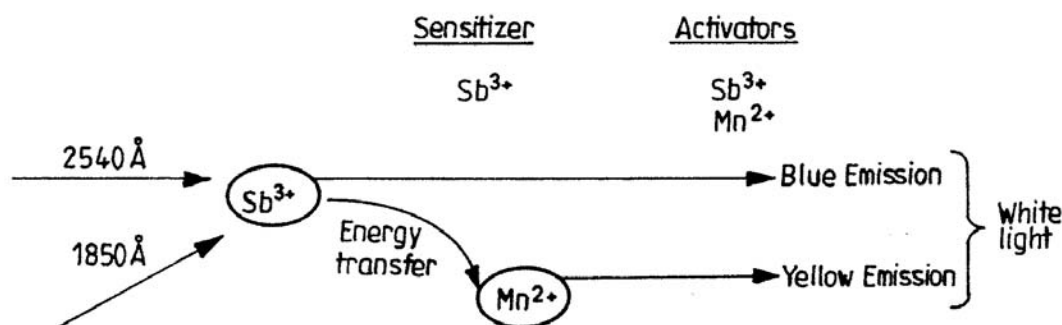


Fig. 8. The role of Sb^{3+} and Mn^{2+} in the commercial fluorescent lamp phosphor, calcium halophosphate, $\text{Ca}_5(\text{PO}_4)_3\text{F}_{1-x}\text{Cl}_x:\text{Mn}^{2+}:\text{Sb}^{3+}$ (reproduced from ref. 9)

Table 3. Some lamp phosphor materials

Phosphor	Activator	Colour
Zn_2SiO_4 , Willemite	Mn^{2+}	Green
Y_2O_3	Eu^{3+}	Red
$\text{CaMg}(\text{SiO}_3)_2$, diopside	Ti	Blue
CaSiO_3 , wallastonite	Pb, Mn	Yellow-orange
$(\text{Sr}, \text{Zn})_3(\text{PO}_4)_2$	Sn	Orange
$\text{Ca}_5(\text{PO}_4)_3(\text{F}, \text{Cl})$ fluorapatite	Sb, Mn	White

PHOSPHORS IN MEDICAL RADIOGRAPHY

Rontgen discovered X rays in 1895, and realized almost immediately that this type of radiation is not very efficient at exposing photographich film, because the film does not absorb the X rays effectively. As a consequence long irradiation times are required. This is bad for the patient. The patient is a moving object; he breathes and may, in addition, make other movements, so that sharp pictures can only be obtained if the irradiation time is short.

CaWO_4 , a luminescent material, can absorb X-rays efficiently and convert their energy into radiation which is able to blacken the photographich film. This material was proposed by Pupin in 1896. CaWO_4 served for some 75 years in the so called X-ray intensifying screens, an absolute record for a luminescent material. A scheme picture of X-ray photography with this method is given in fig. 9. The requirements for X-ray phosphors to be used in intensifying screens are the following : high X-ray absorption and high density, a high conversion efficiency for X-ray to light conversion, an emission spectrum which covers the film sensitivity (in practice blue or green), stability, and an acceptable cost

price. Although CaWO_4 has been used for a long time, it did not satisfy these requirements. It has been replaced by rare-earth doped materials. The first commercial rare-earth X-ray phosphor was $\text{BaFCl} : \text{Eu}^{2+}$ proposed by the Du Pont company. This material has a higher X-ray absorption and a better conversion efficiency than CaWO_4 . Even more surprising was the invention of the tantalite-based phosphors which are physically similar to CaWO_4 .

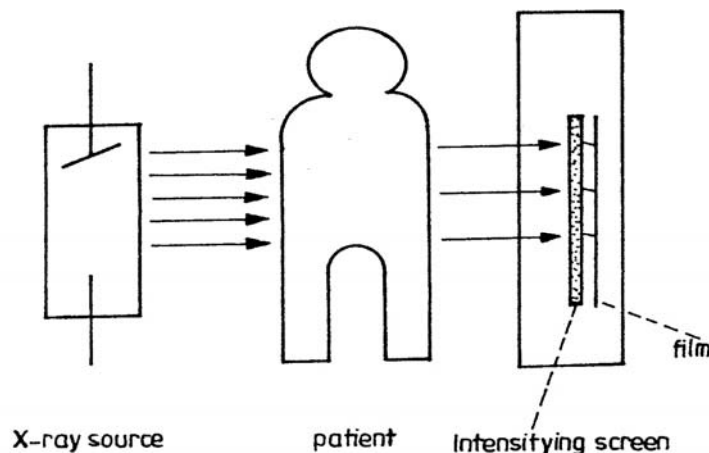


Fig. 9. Schematic representation of a medical radiography system based on the use of an intensifying screen (reproduced from ref. 1)

LUMINESCENCE IMMUNOASSAY

The luminescence of rare earth complexes can be applied in immunology, which is a method for determining biological species, especially for clinical applications. The method is superior to many other methods as far as sensitivity and specificity are concerned. Although the whole of the presentation deals with solid state materials only, this application is mentioned here in view of the interesting aspects of the luminescent species involved, though the whole of the determination is performed in aqueous media.

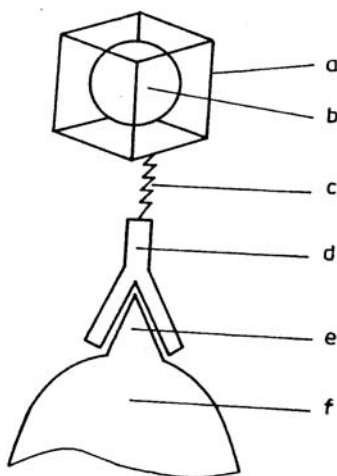


Fig. 10. Schematic representation of luminescence immunoassay with a rare-earth cryptate. (a) Cryptand; (b) luminescent rare earth ion; (c) connection to antibody; (d) antibody; (e) antigene; (f) biomolecule; (reproduced from ref. 1)

The immunological method based on the use of luminescent labels is usually called fluoroimmunoassay. In this method the luminescent label is coupled chemically to an antibody which binds in a specific way to a given biomolecule or organism. In this way the presence of luminescence can be related to the presence of certain molecules or organisms. Since the whole of the determination is carried out in aqueous media, the rare-earth ion has to be shielded from its direct environment. Otherwise its luminescence is strongly quenched by the water molecules. There are several ways of preventing this and in all of these a cage is built around the luminescent ion. The principle of luminescence immunoassay is shown in a schematic way in fig. 10.

Solid state materials find immense applications based on their optical property in the field of lasers too.

LASERS

The physical basis of optical-quantum generators, or lasers, is the amplification of light by stimulated emission of radiation. In systems in a state of thermal equilibrium, stimulated absorption of light is predominant. This is because lower-energy states are more numerous. For stimulated emission of radiation to be predominant, the thermal equilibrium should be shifted so that there will be more higher-energy than lower-energy states. Then the electro-magnetic field will cause excited active center, which may be atoms, ions, excitons or molecules to jump from the higher energy to the lower energy states.

In the ensuing interaction with the atomic systems the radiation will gain in intensity, provided the number of excited energy states is sufficient for the emission of quanta to exceed the absorption. The difference in density between the excited and ground states of an amplifying medium (the population inversion density, or the population inversion or the inverted population, is the key factor deciding whether the amplification or generation of light by stimulated emission of radiation is possible at all.

Population inversion

For reasonable probability of occurrence of stimulated emission population inversion need to be created. The population of the upper level (N_2) should be greatly increased relative to that of the lower level (N_1). This is called population inversion. This situation is, in some sense, contrast to the Boltzmann distribution corresponding to thermal equilibrium. Such a situation cannot be created by merely raising the temperature of the system.

The important question one has to pose now is “How to achieve population inversion ?”

To attain a population inversion the atoms within the laser medium must be excited or pumped into a non-equilibrium distribution through the application of a large amount of energy to the medium from an external source.

Population inversion can be obtained in several ways. In solid state lasers (those using crystal), the active atoms are usually excited by optical pumping. Optical pumping is nothing but exposing the material to high-intensity light. Optical pumping causes the material to absorb energy. As a result the atoms are raised to excited energy states and undergo radiative or non-radiative transitions to produce the desired population inversion. The materials having absorbing centres with an appropriate set of discrete energy levels suitable for population inversion are called active media. Apart from optical radiation, pumping a collection of atoms can be achieved by other methods such as collisions within an electrical discharge, passage of a current, electron bombardment and the release of chemical energy.

A gas discharge flash tube can be used to achieve population inversion in solid-state lasers. The light produced by the flash tube is concentrated onto the laser rod by the chamber enclosing the pumping systems, or simply the pump. Flash tubes are energized by banks of storage capacitors charged from a.c. main via step-up transformers and rectifiers.

Laser rod is the key element in the conversion of electrical energy into the energy of excited atoms. Although a population inversion can be obtained in a great number of solid-state materials, the most frequently used ones are ruby, neodymium-doped glass yttrium-aluminum-garnet (Nd: YAG) and dysprosium doped fluorite. Though many other active materials are there, practically they are not used because of lack of know-how or low efficiency.

The active medium exhibiting optical gain over a narrow range of wave lengths is the heart of every laser. The three important features of any laser in general are the energy level structure, the active medium and the pumping method employed to achieve the necessary population inversion.

The energy level structure and its significance

Population inversion cannot be achieved by a simple two level energy system involving energy level E_1 and E_2 (lower and upper energy levels). It is because even with very intense irradiation the populations of the upper and the lower levels can only be made equal. Optical pumping and other pumping methods in general require a three- or a four level energy systems. Some lasers may operate with even more than four level energy systems.

The first operational laser, namely, the ruby laser has a three-level arrangement in which the laser medium is illuminated by intense radiation from a flash tube and a large number of atoms are pumped into the upper level E_2 from the ground state E_0 by absorption of radiation of frequency ν . From E_2 the atoms decay into level E_1 and a population inversion occurs between the level E_1 and E_0 when N_1 exceeds N_0 where N_1 and N_0 are number of atoms in E_1 and E_0 respectively. For the inversion to occur with the minimum pumping, the transition of atoms from E_2 to E_1 should be rapid. Note that the level E_2 is not directly involved in the amplification process.

In spite of the very fact that the first laser is operated on a three-level energy system, it requires very high pumping power. It is because, E_0 , the terminal state, of the laser transition, is the ground state in this case. Thus more than half of the total number of atoms must be pumped from the ground state into the excited state before a population inversion can be achieved. In other words, the energy required to pump half of the total number of atoms in the system into E_1 via E_0 is wasted. As a result the three-level system is inherently inefficient.

The pumping requirements can be greatly reduced by using the four level energy system which is seen for instance in the Nd: YAG laser. For deeper insight into the phenomenon and the process of population inversion and its dependence on energy level system of the active component the reader is directed to [11].

Heat Generation in Lasers

A specific feature of solid-state lasers is the generation of a considerable amount of heat during the lasing action. This heat may bring about changes in the geometry of the laser elements, thermal stresses and distortions. Depending on operating conditions and the set-up of the optical system, heat liberation may affect the characteristics of the laser beam in a variety of ways and in an unpredictable manner. The non-uniform heating of the laser is one of the major factors that can heavily distort the wave front of the out put radiation. To maintain the temperature of the laser within the tolerable limits, it is important to cool the optical elements during the lasing action or to bring them back to the original temperature before the start of a next lasing cycle.

Laser Action Control

Lasing action control poses a multitude of problems which cannot be successfully solved by a single type of device. A multiplicity of shutters and reflectors are used. For instance, optico-mechanical Q-switches are used in cases where the inherent time lag is not an obstacle. Q switching is a technique for obtaining short, intense bursts of radiation from lasers.

Optical Laser elements

Laser Pumps : In solid-state lasers, a population inversion is obtained by optical pumping with a flash tube or a continuous lamp. For better efficiency, the flash tube and the laser rod are combined in a laser pumping cavity where the light emitted by the flash tube is focused by reflection onto the laser rod.

Laser Rods : The laser materials used in solid-state lasers may be solid or ionic crystals, glass or organic compounds doped with suitable elements. The dopants most often used are the ions of transition group metals, rare-earth metals and actinides. In most cases, a dopant ion is introduced through isomorphous

substitution of a host ion. The energy level structure of active centers is above all determined by dopant atoms. Though several laser materials based on inorganic ionic materials are available only few have been widely used. This is because laser materials should have a high efficiency, low beam divergence and stability of emission with time. A very important property of a laser material is its ability to operate at room temperature.

The First Laser System

The ruby laser was the first laser system to be discovered. The essential component of the ruby laser is the single crystal of Al_2O_3 doped with a small amount, 0.05 wt%, of Cr^{3+} . The Cr^{3+} ions substitute for Al^{3+} ions in the distorted octahedral sites of the corundum crystal structure. On addition of Cr_2O_3 to Al_2O_3 , the colour changes from white, in Al_2O_3 , to red, at low Cr^{3+} levels, to green, for larger Cr^{3+} contents.

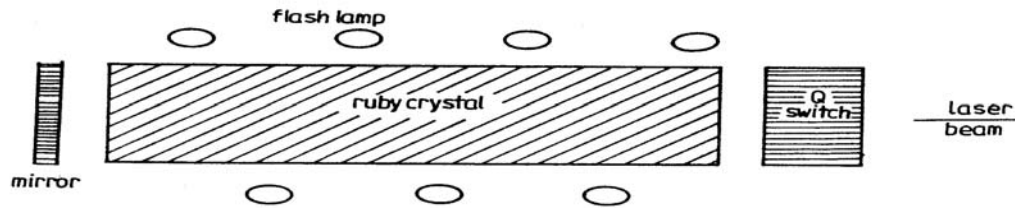


Fig. 11. Design of a ruby laser

The design of a ruby laser is shown schematically in fig. 11. It contains a ruby crystal rod, several centimeters long and 1 to 2 cm in diameter. The flash lamp is shown as being wrapped around the ruby rod. Alternatively, it may be placed alongside the rod; the two are then arranged inside a reflection cavity such that the rod is effectively irradiated from all sides. At one end of the rod is a mirror for reflecting the light pulse back through the rod. At the other end is a device known as a Q switch which may either allow the laser beam to pass out of the system or may reflect it back through the rod for another cycle. The Q switch may simply be a rotating mirror timed to allow out the laser beam when it has reached its optimum intensity: as the light pulse passes back and forth along the rod, it builds up in intensity as more of the active centres are stimulated to emit radiation that is coherent with the initial pulse.

APPLICATIONS OF LASERS

Lasers find applications in diverse fields. Jeff Hecht gave an exhaustive and interesting account of different types of lasers and their applications [12].

Laser Tracking System : Laser tracking system has been employed in bouncing laser beams from an earth band laser off a retroreflector placed on the moon to precisely measure the distance between moon and earth. In an analogous way the position of satellites can be tracked by Lasers.

Types of Lasers used for Tracking Systems : Both pulse and continuous wave (CW) have been successfully employed for this particular application. Solid lasers as well as semiconductor lasers are used in pulsed mode whereas Noble gas atomic lasers and ionic and molecular lasers are used in CW operation.

The characteristics of lasers used in tracking systems are given in table 4. The Ar laser is considerably more powerful than the He-Ne and the CO_2 laser in orders of magnitude more powerful than the Ar. The CO_2 laser is, however, a very large unit consisting of an oscillator and two amplifiers. The GaAs laser is particularly small and rugged. The ruby and Nd lasers can also be rugged, but cooling and alignment problems become increasingly critical as energy and pulse-repetition rate are increased and beam divergences is limited to small angles.

The lasers vary widely in their operating wavelength as shown in the table. Those in the visible band have the advantage of being in a region where efficient detection is easily achieved. The Nd-glass laser converts its near-IR radiation into the visual band by using a frequency double. All the lasers except the CO_2 laser are in a wavelength region where the human eye is particularly sensitive to retinal damage.

The overall efficiencies of the various lasers are very different. Over all efficiency is defined as the output optical energy (or power) . The GaAs and CO₂ lasers are the only ones with efficiency above 1%. The list of application of lasers is endless.

Table 4. Characteristics of Lasers used in Tracking systems (reproduced from ref. 7) : CW Lasers

Type	Wave length (μm)	Efficiency %	Power (W)
CO ₂	10.6	12-15	1400
He-Ne	0.633	10 ⁻³ - 10 ⁻⁴	0.05
Ar	0.514	0.1	5

Pulsed Lasers

Type	Wave length (μm)	Efficiency %	Energy (J)
Nd:YAG	1.06	0.1	0.02
GaAs	0.9	4	10 ⁻⁴
Ruby	0.694	0.013	7
Nd-glass	0.57	0.04	20

To conclude the presentation with the words of Sir William Henry Bragg, “The infinite variety in the properties of solid materials we find in the world is really the expression of the infinite variety of the ways in which the atoms and molecules can be tied together and of the strength of those ties.”

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CHAPTER - 5

Dielectric Properties of Solids

The term *dielectric* is used in broad sense, as relating to various electrical phenomena, primarily in ceramics and polymers. Dielectric materials are electrical insulators and they are used principally in capacitors and electrical insulators. The dielectric materials for the practical application should possess the following properties : (a) high dielectric strength, i.e., they should be able to withstand high voltages without undergoing degradation and becoming electrically conducting, (b) low dielectric loss, i.e., in an alternating electric field, the loss of electrical energy, which appears as heat should be minimized.

Experimentally, dielectric properties may be defined by the behaviour of the material in a parallel plate capacitor. This is a pair of conducting plates, parallel to one another and separated by a distance, d , that is small compared with the linear dimensions of the plates (Fig. 1.).

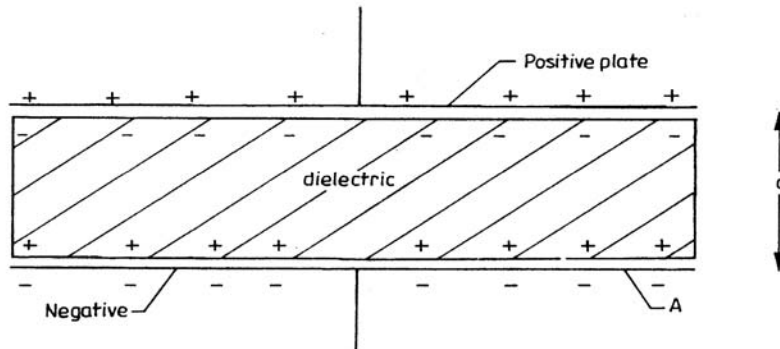


Fig. 1. Dielectric materials between the plates of a parallel plate capacitor

Table 1. Atomic polarizability of the Halogen ions, Noble gas atoms and Alkali metal ions

Halogens		Noble Gases		Alkali Metals	
F ⁻	1.2	He	0.2	Li ⁺	0.03
Cl ⁻	3	Ne	0.4	Na ⁺	0.2
Br ⁻	4.5	Ar	1.6	K ⁺	0.9
I ⁻	7	Kr	2.5	Rb ⁺	1.7
		Xe	4.0	Cs ⁺	2.5

Table 2. Static Dielectric constant for selected covalent and covalent-Ionic crystals

Crystal	ϵ_0	Crystal	ϵ_0
C	5.7	ZnO	4.6
Si	12.0	ZnS	5.1
Ge	16.0	ZnSe	5.8
Sn	23.8	ZnTe	8.3
SiC	6.7	CdS	5.2
GaP	8.4	CdSe	7.0
GaAs	10.9	CdTe	7.0
GaSb	14.4	BeO	3.0
InP	9.6	MgO	3.0
InAs	12.2		
InSb	15.7		

With a vacuum between the plates, the capacitance C_0 is defined as $C_0 = \epsilon_0 A / d$, where ϵ_0 = permittivity of free space, $8.854 \times 10^{-12} \text{ Fm}^{-1}$, and A = area of the plates. Since ϵ_0 = constants, the capacitance depends

only on the dimensions of the capacitor. On applying a potential difference, V , between the plates, a quantity of charge, Q_0 , is stored on them, given by $Q_0 = C_0 V$. A dielectric substance is placed between the plates and the same potential difference applied, the amount of charge stored increases to Q_1 and the capacitance therefore increases to C_1 . The dielectric constant or relative permittivity, ϵ' , is: $\epsilon' = C_1/C_0$. ϵ' depends on the degree of polarization or charge displacement that can occur in the material. For air, $\epsilon' \sim 1$. For most ionic solids, $\epsilon' = 5$ to 10 ; for ferroelectric materials such as BaTiO_3 , $\epsilon' = 10^3$ to 10^4 .

The polarizability, α , of the dielectric is defined by $p = \alpha E$, where p = dipole moment induced by the local electric field, E . The polarizability and dielectric constant of some selected substances are given in the table. 1 and 2 respectively.

Polarizability has four possible components and is given by the summation:

$$\alpha = \alpha_e + \alpha_i + \alpha_d + \alpha_s$$

These four components are as follows :

1. The electronic polarizability, α_e , arises from the displacement of the electron shell relative to the positive charged nucleus. Electronic polarizability occurs in all solids and in some, such as diamond, it is the only contributor to the dielectric constant since ionic, dipolar and space charge polarizabilities are absent.
2. The ionic polarizability, α_i , contribution comes from the displacement of a charged ion with respect to other ions (separation of anions and cations in a solid). It is the principal source of polarization in ionic crystals.
3. Dipolar polarizability, α_d , arises from the molecules with a permanent electric dipole moment that can change orientation in an applied electric field. In materials such as HCl or H_2O that contain permanent electric dipoles. These dipoles may change their orientation and they tend to align themselves with an applied electric field. The effect is usually very temperature dependent since the dipoles may be 'frozen in' at low temperatures.
4. Space charge polarizability, α_s , occurs in materials that are not perfect dielectrics but in which some long range charge migration may occur. For instance, in NaCl , cations migrate preferentially towards the negative electrode by means of crystal defects such as cation vacancies; consequently, an electrical double layer builds up at the electrode- NaCl interface. When such effects are significant, the material is better regarded as an ionic conductor or solid electrolyte than as a dielectric. Apparent dielectric constants as high as 10^6 to 10^7 may be measured in these materials (corresponding to double-layer capacitances of $\sim 10^{-6}$ F), but these values have no significance in the conventional dielectric sense. The magnitude of α usually decreases in the order of polarization as follows $(4) > (3) > (2) > (1)$, not all materials show all types of polarization.

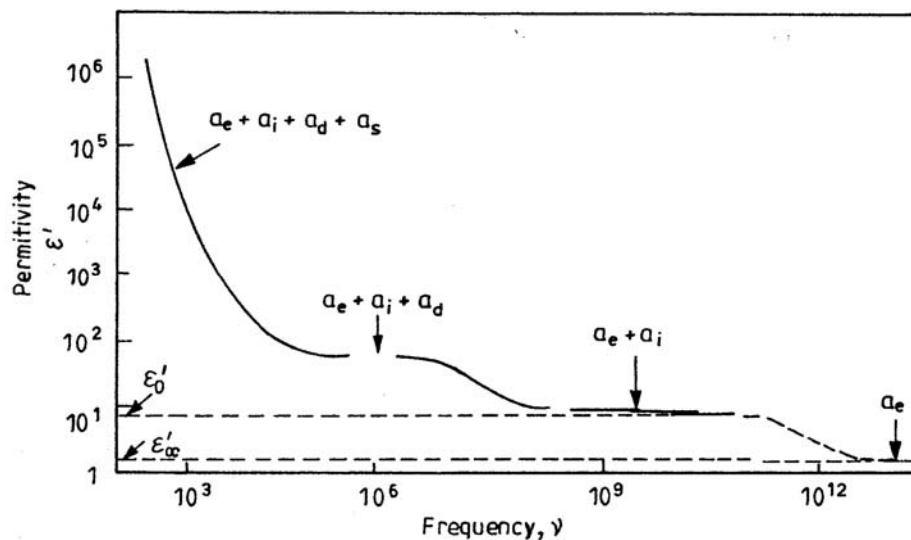


Fig. 2. Polarization effect in a dielectric

Experimentally, the four contributions to α and ϵ' may be separated by making measurements over a wide range of a.c. frequencies using a combination of capacitance bridge, microwave and optical measurement (Fig. 2).

At low frequencies, e.g., audiofrequencies ($\sim 10^3$ Hz), all four (if present) may contribute to α . At radio frequencies, ($\sim 10^6$ Hz), space charge effects may not have time to build up in most ionic conductor materials and are effectively 'relaxed out'. At microwave frequencies ($\sim 10^9$ Hz) dipoles do not usually have time to reorient themselves and are effectively and are effectively relaxed out.

Table 3. Important properties of the selected dielectric materials

Materials	Dielectric Constant		Dielectric Strength 10^6 V/m	Tan δ at 10^6 Hz	Resistivity ohmcm
	at 60 Hz	at 10^6 Hz			
Polyethylene	2.3	2.3	20	0.00010	10^{16}
Teflon	2.1	2.1	20	0.00007	10^{18}
Polystyrene	2.5	2.5	20	0.00020	10^{18}
PVC	3.5	3.2	40	0.05000	10^{12}
Nylon	4.0	3.6	20	0.04000	10^{15}
Rubber	4.0	3.6	24		
Phenolic	7.0	4.9	12	0.0500	10^{12}
Epoxy	4.0	3.6	18		10^{15}
Paraffin wax		2.3	10		10^{13} - 10^{19}
Fused silica	3.8	3.8	10	0.00004	10^{11} - 10^{12}
Soda lime glass	7.0	7.0	10	0.00900	10^{15}
Al ₂ O ₃	9.0	6.5	6	0.00100	10^{11} - 10^{13}
TiO ₂		14-114	8	0.00020	10^{13} - 10^{18}
Mica		7.0	40		10^{13}
BaTiO ₃		2000-5000	12	~ 0.0001	$\sim 10^8$ - 10^{15}
Water		78.3			10^{14}

In good dielectric materials which do not contain contributions from α_s and α_d , the limiting low frequency permittivity, ϵ'_{∞} , is composed mainly of α_i and α_e polarizations. ϵ'_{∞} may be obtained from a.c. capacitance bridge measurements in which the value of the capacitance is determined with and without the dielectric substance placed between the plates of the capacitor or cell ($\epsilon' = C_1/C_0$). The value of ϵ'_{∞} which

contains only α_c contributions may be obtained from refractive index measurements (visible light frequencies). Ceramic crystals having mixed ionic and covalent bonds can be obtained from ϵ_0 and ϵ_∞ relationship, where $\epsilon_0/\epsilon_\infty$ is large indicates that there is a substantial ionic component to the bond. If the ratio were close to 1, it would indicate a largely covalent bond. Detailed information about dielectrics, measurements are usually made over a range of frequencies covering the audiofrequency, radiofrequency and microwave regions. The results are plotted as Cole-Cole complex Permittivity diagrams or as the dielectric loss factor, $\tan\delta$. The values for the various materials are given in the table 3.

FERROELECTRIC MATERIALS

Ferroelectric materials are distinguished from ordinary dielectrics by having extremely large permittivities and the possibility of retaining some residual electrical polarization after an applied voltage has been switched off. Illustrated as :

- 1) As the potential difference applied across a dielectric substance is increased, a proportional increase in the induced polarization, P (note capitalized), or stored charge, Q , occurs.
- 2) With ferroelectrics, the simple linear relation between Q (or P) and V does not hold. Instead, more complicated behaviour with a hysteresis loop is observed.

Ferroelectric materials show spontaneous polarization which is given by the value of the dipole moment per unit volume or by the value of the charge per unit area on the surface perpendicular to the axis of spontaneous polarization. The axis of spontaneous polarization is usually along a given crystal axis. They possess regions with uniform polarization called ferroelectric domains. Within a domain, all the electric dipoles are aligned in the same direction. There may be many domains in a crystal separated by interfaces called domain walls. A ferroelectric single crystal, when grown, has multiple ferroelectric domains as shown in fig. 3. A single domain can be obtained by domain wall motion made possible by the application of an appropriate electric field. A very strong field could lead to the reversal of the polarization in the domain, known as domain switching.

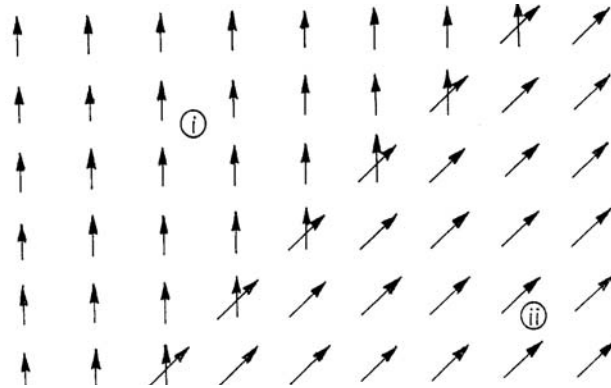


Fig. 3. Ferroelectric domains separated by a domain wall or boundary

The polarization reversal can be observed by measuring the ferroelectric hysteresis as shown in fig. 4. As the electric field strength is increased, the domains start to align in the positive direction giving rise to a rapid increase in the polarization (OB). At very high field levels, the polarization reaches a saturation value (P_{sat}). The polarization does not fall to zero when the external field is removed. At zero external field, some of the domains remain aligned in the positive direction, hence the crystal will show a remnant polarization P_r . The crystal cannot be completely depolarized until a field of magnitude OF is applied in the negative direction. The external field needed to reduce the polarization to zero is called the coercive field strength E_c .

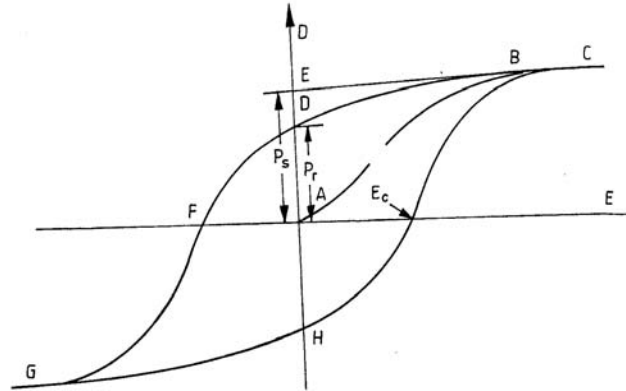


Fig. 4. Polarization vs. Electric Field (P-E) hysteresis loop for a typical ferroelectric crystal

All ferroelectric materials have a transition temperature called the Curie point (T_c). At a temperature $T > T_c$ the crystal does not exhibit ferroelectricity, while for $T < T_c$ it is ferroelectric. On decreasing the temperature through the Curie point, a ferroelectric crystal undergoes a phase transition from a non-ferroelectric phase to a ferroelectric phase. If there are more than one ferroelectric phases, the temperature at which the crystal transforms from one ferroelectric phase to another is called the transition temperature. Fig. 5 shows the variation of the relative permittivity, ϵ_r with temperature as a BaTiO_3 crystal is cooled from its paraelectric cubic phase to the ferroelectric tetragonal, orthorhombic, and rhombohedral phases. Near the Curie point or transition temperatures, thermodynamic properties including dielectric, elastic, optical, and thermal constants show an anomalous behavior. This is due to a distortion in the crystal as the phase structure changes. The temperature dependence of the dielectric constant above the Curie point ($T > T_c$) in ferroelectric crystals is governed by the Curie-Weiss law : $\epsilon = \epsilon_0 + C/(T-T_0)$, where ϵ is the permittivity of the material, ϵ_0 is the permittivity of vacuum, C is the Curie constant and T_0 is the Curie temperature. The Curie Temperature, T_0 is different from the Curie point T_c . T_0 is a formula constant obtained by extrapolation, while T_c is the actual temperature where the crystal structure changes. Examples of ferroelectric materials and their Curie temperature are given in table 4.

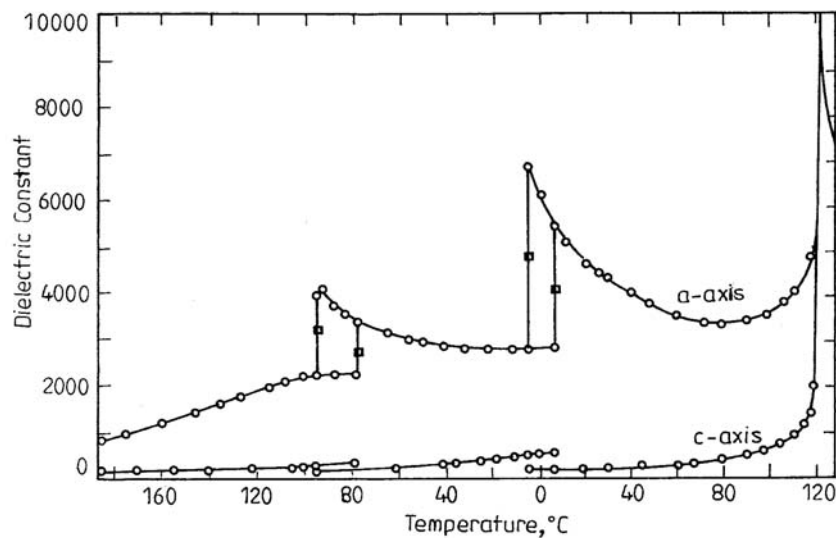


Fig. 5. Variation of dielectric constants (a and c axis) with temperature for BaTiO_3

Table 4. Examples of ferroelectric materials and their Curie temperature

Materials	T_c (°C)
Barium titanate BaTiO_3	120
Rochelle salt $\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$	- 18 to 24
Potassium niobate KNbO_3	434
Potassium dihydrogen phosphate KH_2PO_4	- 150
Lead titanate PbTiO_3	490
Lithium niobate LiNbO_3	1210
Bismuth titanate $\text{Bi}_4\text{Ti}_3\text{O}_{12}$	675
Gadolinium molybdate GMO , $\text{Gd}_2(\text{MoO}_4)_3$	159
Lead zirconate titanate $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$, PZT	depends on x

The four main types of structures which shows ferroelectric property are : (1) the corner sharing oxygen octahedra, (2) compounds containing hydrogen bonded radicals, (3) organic polymers and (4) ceramic polymer composites. A large class of ferroelectric crystals are made up of mixed oxides containing corner sharing octahedra of O^{2-} ions schematically shown in fig. 6. Inside each octahedron is a cation B^{b+} where 'b' varies from 3 to 6. The space between the octahedra are occupied by A^{a+} ions where 'a' varies from 1 to 3. In prototypic forms, the geometric centers of the A^{a+} , B^{b+} and O^{2-} ions coincide, giving rise to a non-polar lattice. When polarized, the A and B ions are displaced from their geometric centers with respect to the O^{2-} ions, to give a net polarity to the lattice. These displacements occur due to the changes in the lattice structure when phase transitions take place as the temperature is changed. The formation of dipoles by the displacement of ions will not lead to spontaneous polarization if a compensation pattern of dipoles are formed which give zero net dipole moment. The corner sharing oxygen octahedra includes the perovskite type compounds, tungsten bronze type compounds, bismuth oxide layer structured compounds, and lithium niobate and tantalate.

Perovskites

Perovskite is a family name of a group of materials and the mineral name of calcium titanate (CaTiO_3) having a structure of the type ABO_3 . Many piezoelectric (including ferroelectric) ceramics such as Barium Titanate (BaTiO_3), Lead Titanate (PbTiO_3), Lead Zirconate Titanate (PZT), Lead Lanthanum Zirconate Titanate (PLZT), Lead Magnesium Niobate (PMN), Potassium Niobate (KNbO_3), Potassium Sodium Niobate ($\text{K}_x\text{Na}_{1-x}\text{NbO}_3$), and Potassium Tantalate Niobate ($\text{K}(\text{Ta}_x\text{Nb}_{1-x})\text{O}_3$) have a perovskite type structure and their behaviour is listed in table 5.

Table 5. Perovskite type structure compounds and their behaviour

Compounds	Behaviour
CaTiO_3	Dielectric
BaTiO_3	Ferroelectric
$\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$	Relaxor ferroelectric
$\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$	Piezoelectric
$(\text{Ba}_{1-x}\text{La}_x)\text{TiO}_3$	Semiconductor
$(\text{Y}_{1/3}\text{Ba}_{2/3})\text{CuO}_{3-x}$	Superconductor
Na_xWO_3	Mixed conductor ; electrochromic
$\text{SrCeO}_3 - \text{H}$	Protonic conductor
ReCoO_{3-x}	Mixed conductor
$(\text{Li}_{0.5-3x}\text{La}_{0.5+x})\text{TiO}_3$	Lithium ion conductor
LaMnO_{3-x}	Giant magneto - resistance

Barium Titanate (BaTiO_3)

Barium titanate (BaTiO_3) has a paraelectric cubic phase above its Curie point of about 120°C . In the temperature range of 120°C to 0°C the ferroelectric tetragonal phase with a c/a ratio of ~ 1.01 is stable. The spontaneous polarization is along one of the $[001]$ directions in the original cubic structure. Between 0°C and -90°C , the ferroelectric orthorhombic phase is stable with the polarization along one of the $[110]$ directions in the original cubic structure. On decreasing the temperature below -90°C the phase transition from the orthorhombic to ferroelectric rhombohedral phase leads to polarization along one of the $[111]$ cubic directions.

The spontaneous polarization on cooling BaTiO_3 below the Curie point T_c is due to changes in the crystal structure. As shown in fig. 7, the paraelectric cubic phase is stable above 130°C with the center of positive charges (Ba^{2+} and Ti^{4+} ions) coinciding with the center of negative charge (O^{2-}). On cooling below the Curie point T_c , a tetragonal structure develops where the center of Ba^{2+} and Ti^{4+} ions are displaced relative to the O^{2-} ions, leading to the formation of electric dipoles. Spontaneous polarization developed is the net dipole moment produced per unit volume for the dipoles pointing in a given direction.

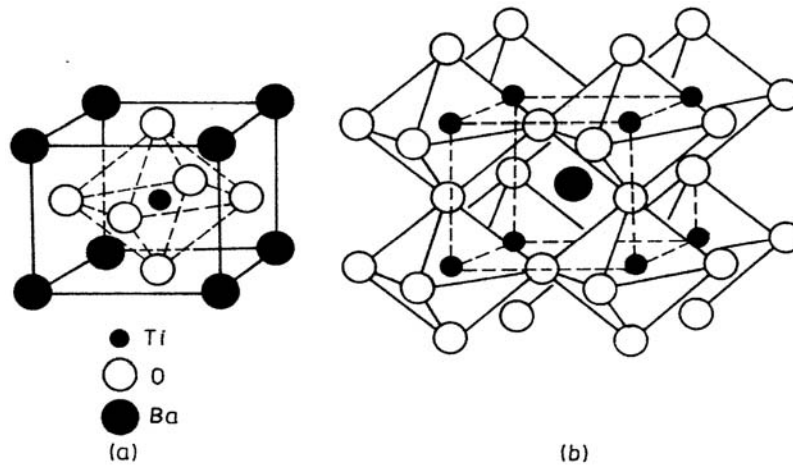


Fig. 6. (a) A cubic ABO_3 (BaTiO_3) perovskite-type unit cell and (b) three dimensional network of corner sharing octahedra of O^{2-} ions

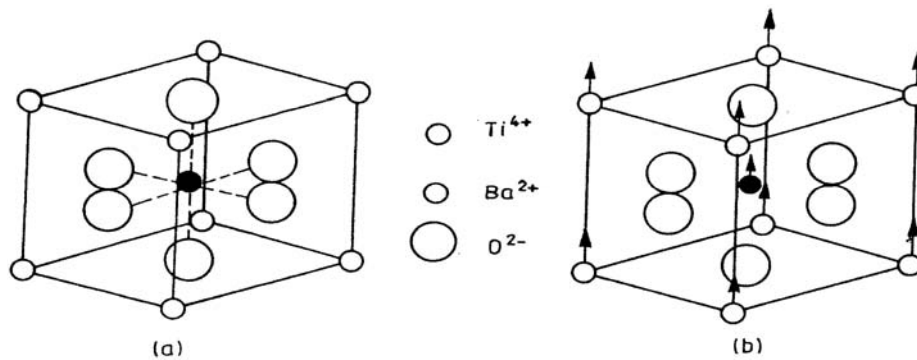


Fig. 7. The crystal structure of BaTiO_3 (a) above the Curie point the cell is cubic, (b) below the Curie point the structure is tetragonal with Ba^{2+} and Ti^{4+} ions displaced relative to O^{2-} ions

Various A and B site substitutions in different concentrations have been tried to see their effect on the dielectric and ferroelectric properties of BaTiO_3 . Sr^{2+} substitutions to the A site have been found to reduce the Curie point linearly towards room temperature. The substitution of Pb^{2+} for Ba^{2+} raises the Curie point.

The simultaneous substitution into both A and B sites with different ions can be used to tailor the properties of BaTiO₃. The dielectric properties of BaTiO₃ are found to be dependent on the grain size. Figure 8 shows the variation of dielectric constant with temperature for BaTiO₃ ceramics with a fine (~1 mm) and coarse (~50 mm) grain size. Large grained BaTiO₃ (~50 mm) shows an extremely high dielectric constant at the Curie point. This is because of the formation of multiple domains in a single grain, the motion of whose walls increases the dielectric constant at the Curie point. For a BaTiO₃ ceramic with fine grains (~1 mm), a single domain forms inside each grain. The movement of domain walls are restricted by the grain boundaries, thus leading to a low dielectric constant at the Curie point as compared to coarse grained BaTiO₃. The room temperature dielectric constant (ϵ_r) of coarse grained (~10 mm) BaTiO₃ is found to be in the range of 1500-2000. On the other hand, fine grained (~1 mm) BaTiO₃ ceramics exhibit a room temperature dielectric constant between 3500-6000. The grain size effect on the dielectric constant at room temperature has been explained by the internal stresses in fine grained BaTiO₃ must be much greater than the coarse grained ceramic, thus leading to a higher permittivity at room temperature.

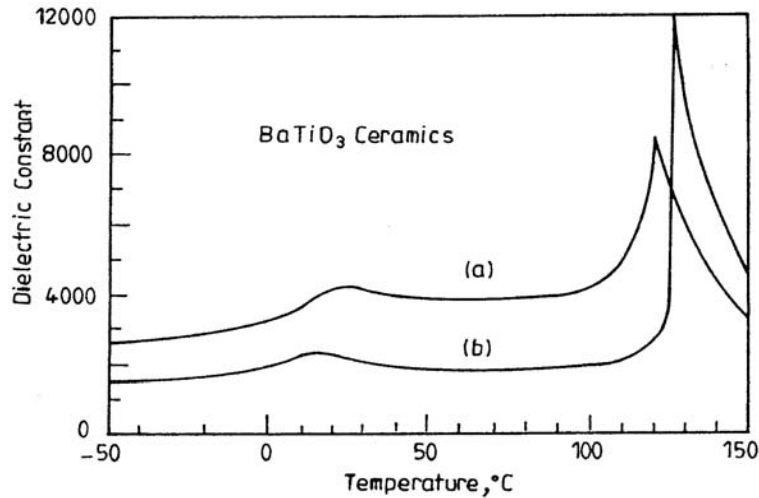


Fig. 8. The variation of the relative permittivity (ϵ_r) with temperature for BaTiO₃ ceramics with (a) 1 mm grain size and (b) 50 mm grain size

At the room temperature ϵ_r reached a peak value at a critical grain size of ~0.7 mm. The enhanced dielectric constant was due to the increased 90° domain wall density. The mobility of the 90° domain walls in very fine grained BaTiO₃ is hindered and only less than 25 % of the ϵ_r was achieved. As the BaTiO₃ ceramics have a very large room temperature dielectric constant, they are mainly used multilayer capacitor applications. The grain size control is very important for these applications.

ANTIFERROELECTRIC MATERIALS

A related type of spontaneous polarization occurs in antiferroelectric materials.

In the antiferroelectric materials the individual dipoles generally arrange themselves so as to be antiparallel to adjacent dipoles as a result, the net spontaneous polarization is zero as seen from the fig. 9 (b).

Above the antiferroelectric Curie temperature, the materials revert to normal paraelectric behaviour. Examples of antiferroelectrics, with their Curie temperatures, are : lead zirconate, PbZrO₃, (233 °C); sodium niobate, NaNbO₃, (638 °C); and ammonium dihydrogen phosphate, NH₄H₂PO₄, (125 °C). The electrical characteristics of antiferroelectrics are rather different to those of ferroelectrics. The antiferroelectric state is a non-polar one and no hysteresis loop occurs, although large increases in permittivity occur close to T_c (for PbZrO₃, $\epsilon' \sim 100$ at 200 °C and ~ 3000 at 230 °C). The antiparallel arrangement of dipoles in the antiferroelectric state is only slightly more stable than the parallel arrangement in the ferroelectric state and a small change in conditions may lead to a phase transition. For example, application of an electric field to PbZrO₃ causes it to change from an antiferroelectric to a ferroelectric structure.

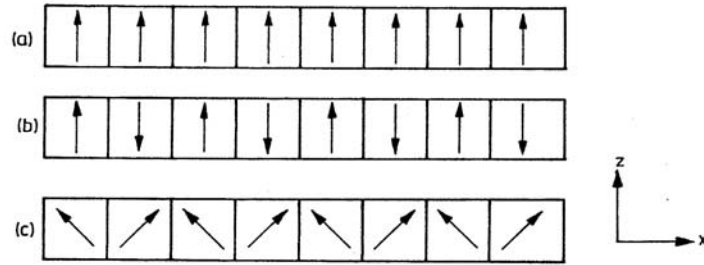


Fig. 9. Dipole orientation (schematic) in (a) a ferroelectric, (b) an antiferroelectric and (c) a ferroelectric

FERRIELECTRIC

A related type of polarization phenomenon in which the structure is antiferroelectric only in certain direction(s) (Fig. 9(c)); where in the x direction, the net polarization is zero and the structure is antiferroelectric, in the z direction, a net spontaneous polarization occurs. This type of structure is known as ferroelectric. Examples like $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ and lithium ammonium tartarate monohydrate.

PYROELECTRICITY

Pyroelectric crystals are related to ferroelectric ones in that they are non-centrosymmetric and exhibit a net spontaneous polarization, P_s . Unlike ferroelectrics, however, the direction of P_s cannot be reversed by an applied electric field. P_s is usually temperature dependent $\Delta P_s = \pi \Delta T$, where π is the pyroelectric coefficient. Pyroelectricity arises mainly because the thermal expansion that occurs on heating changes the sizes (i.e., lengths) of the dipoles. the pyroelectric effect in a crystal is often not detectable under constant temperature conditions but becomes apparent only when the crystal is heated, thereby changing P_s .

PIEZO-ELECTRICITY

Under the action of an applied mechanical stress, piezoelectric crystals polarize and develop electrical charges on opposite crystal faces. As is the case for ferro- and pyroelectricity, the crystal must belong to one of the non-centrosymmetric point groups. The occurrence of piezoelectricity depends on the crystal structure of the material and the direction of applied stress (Fig. 10), e.g., quartz develops a polarization when subjected to a compressive stress along [100] but not when stressed along [001].

The polarization, P , and stress, s , are related to the piezoelectric coefficient, d , $P = d \sigma$. Many crystals that contain tetrahedral groups, e.g. ZnO , ZnS , are piezoelectric since application of a shearing stress distorts the tetrahedra. One of the most important piezoelectrics is PZT, lead zirconate titanate, which is a series of solid solutions between PbZrO_3 and PbTiO_3 . These solid solutions are also antiferroelectric and ferroelectric at certain compositions, as shown by a partial phase diagram as shown in fig 11. The best piezoelectric compositions occur at $x \sim 0.5$.

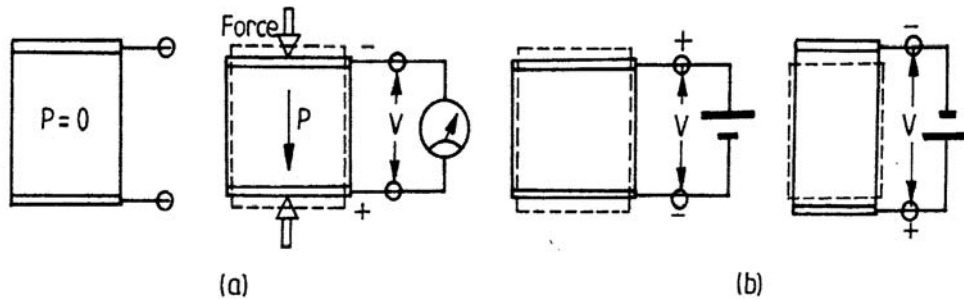


Fig. 10 (a). Direct piezoelectric effect - applied stress causes a voltage to appear, (b) converse piezoelectric effect - an applied voltage leads to development of strain

RELATIONSHIP BETWEEN FERRO-, PIEZO- AND PYROELECTRICITY

All three of these properties are concerned with polar effects in crystals and, obviously, they have a great deal in common. Many materials may be included in the general class of dielectrics in which their properties, especially electrical properties, are influenced by electric fields.

Piezoelectrics are a subclass of dielectrics. Piezoelectrics develop an electric charge when mechanically stressed; conversely, piezoelectrics generate mechanical stresses under the action of an applied electric field. A subclass of piezoelectrics is pyroelectrics, materials that are spontaneously polarized and therefore exhibit a net dipole moment. Some pyroelectric materials are also ferroelectric because the spontaneous polarization can be reversed under the action of an applied electric field. By definition, therefore, ferroelectric materials are also pyroelectric and piezoelectric; further, pyroelectric materials are also piezoelectric. The reverse does not hold, however; i.e. not all piezoelectric materials are pyroelectric, etc.

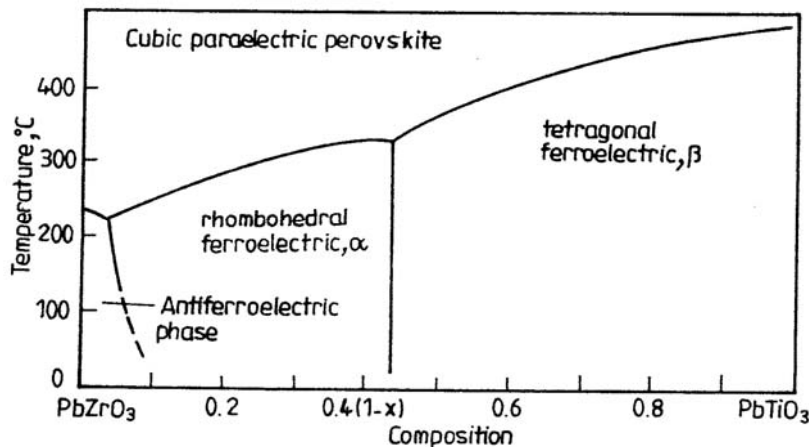


Fig. 11. Phase diagram for the PZT (lead zirconate titanate) system

APPLICATIONS OF FERRO-, PIEZO- AND PYROELECTRICS

Applications of these materials are considered together because they overlap considerably and, in some cases, more than one property may be involved in a particular application. Applications are very varied, especially of ferroelectrics.

The main commercial application of ferroelectrics is in capacitors. Because ferroelectrics have a high permittivity or dielectric constant, ϵ' , usually in the range 10^2 to 10^4 , they can be used in the construction of large capacitors. - The main commercial materials are BaTiO_3 and PZT (lead zirconate titanate) which are used in the form of dense, polycrystalline ceramics. By contrast, conventional dielectrics such as TiO_2 or MgTiO_3 have ϵ' in the range of 10 to 100. Hence, for a given volume, a BaTiO_3 capacitor has 10 to 1000 times the capacitance of a dielectric capacitor.

An important use of certain ferroelectrics such as BaTiO_3 and PbTiO_3 , which does not depend directly on their ferroelectricity, is in PTC thermistors (i.e. positive temperature coefficient thermally sensitive resistors). In most non-metallic materials, the electrical resistivity decreases with increasing temperature, i.e., the resistivity has a negative temperature coefficient (NTC). However, some ferroelectrics including BaTiO_3 , show an anomalous and large increase in resistivity as the temperature approaches the ferroelectric-paraelectric transition temperature, T_c . In a BaTiO_3 thermistor, the resistivity increases dramatically as it heats and consequently the current switches off. Applications include (a) thermal and current overload protection devices, in which the thermistor acts as a reusable fuse, and (b) time delay fuses.

Pyroelectric crystals are : (a) used mainly in infrared radiation detectors, (b) they can be made spectrally sensitive by coating the probe surface of the crystal with appropriate absorbing material, (c) for detectors, it

is desirable to maximize the ratio π/ϵ' , which means that ferroelectric materials with high dielectric constant are not suitable, (d) the best detector material found to date is triglycine sulphate.

Piezoelectric crystals have been used as transducers for converting mechanical to electrical energy, and vice versa. (a) Applications are diverse, e.g., as bimorphs in microphones, earphones, loudspeakers and stereo pick-ups, (b) as fuses, solenoid ignition systems and cigarette lighters, sonar generators and ultrasonic cleaners, (c) More complex devices are used in transformers, filters and oscillators. Most of these applications use PZT ceramics, quartz, Rochelle salt or $\text{Li}_2\text{SO}_4 \cdot \text{H}_2\text{O}$.

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CHAPTER – 6

Magnetic Properties of Solids

INTRODUCTION

Magnetism is the force of attraction or repulsion in a material. A magnet is an object made of certain materials, which create a magnetic field. A magnet produces a vector field, the magnetic field, at all points in the space around it. It can be defined by measuring the force the field exerts on a moving charged particle, such as an electron. Magnetic field is the region around a magnet characterized by the existence of a detectable magnetic force at every point in the region and by the existence of magnetic poles.

MAGNETIC DIPOLE MOMENT

When a magnet is placed in an electric (E) or magnetic (B) field, equal but opposite forces arise on each side of the dipole creating a torque τ tending to align its axis in the direction of the field (Fig. 1.). This torque increases with the strength of the poles and their distance apart. Magnetic dipole moment is the product of the strength of either pole in a magnetic dipole with the distance separating them. The direction of the dipole moment corresponds to the direction from the negative to the positive charge or from the south to the north pole.

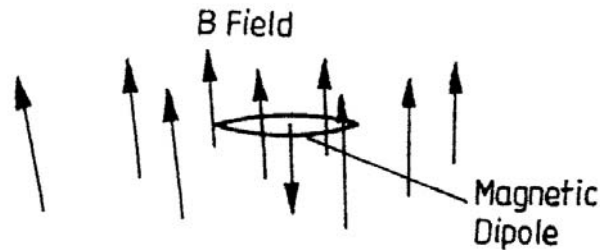


Fig. 1. Magnetic dipole and Magnetic field

MAGNETIZATION

A magnetic field H will be produced at the center of the loop given by

$$H = \frac{i}{2r} \quad [\text{Amperes/meter, A/m}]$$

The current loop has a magnetic moment, m, associated with it

$$m = i \times \text{Area} \quad [\text{Am}^2]$$

The intensity of magnetization, M or J, is magnetic moment per unit volume.

$$M = \frac{m}{v} \quad [\text{A/m}]$$

MAGNETIC FLUX DENSITY

Flux (Φ) is a measure of the number of these lines - the total amount of magnetism. Flux density or strength of a magnetic field is simply the total flux divided by the cross sectional area of the part through which it flows.

$$B = \Phi / A, \text{ Tesla}$$

MAGNETIC PERMEABILITY

It represents the tendency of magnetic lines of force to pass through the medium relative to the tendency of the same lines of force to pass through the air or vacuum. The magnetic permeability, μ , of a particular material is defined as the ratio of flux density to field strength.

$$\mu = B / H \text{ Henry m}^{-1}$$

For vacuum, μ is taken as 1

$\mu < 1$, it is diamagnetic

$\mu > 1$, it is paramagnetic

$\mu \gg 1$, it is ferromagnetic

SUSCEPTIBILITY

Susceptibility is a measure of how magnetizable a substance can become in the presence of a magnetic field. It is the quantitative measure of the response of a material to an applied magnetic field. It can be calculated from the ratio of magnetization to magnetic field.

$$k = M/H \quad [\text{dimensionless}]$$

The mass susceptibility

$$c = k/\text{density} \quad [\text{m}^3/\text{kg}]$$

Molar Susceptibility

$\chi_M = \chi \cdot M$, M is the molecular weight of the substance

Magnetic permeability and susceptibility are related as,

$$\mu = 1 + 4 \pi \chi$$

ELECTRONS - SOURCE OF MAGNETIC MOMENT

A magnetic field can be created with moving charges, such as a current-carrying wire. A magnetic field can also be created by the spin magnetic dipole moment, and by the orbital magnetic dipole moment of an electron within an atom. Each electron constitutes a magnetic dipole. An electron circulating around the nucleus would constitute a current loop and produce a magnetic dipole field. The revolving electron rotates on its own axis to give magnetic spin. The magnitude of the resulting spin moment, μ_s , is 1.73 Bohr Magnetons (BM), where the Bohr Magnetons is defined as

$$1 \text{ BM} = eh/4\pi mc$$

where, e = electron charge

h = Planck's constant

m = electron mass

c = velocity of light

The formula used for calculating μ_s for a single electron is $\mu_s = g [s(s+1)]^{1/2}$, where s is the spin quantum number, $1/2$, and g is the gyromagnetic ratio, ~ 2.00 . Substituting for s and g gives $\mu_s = 1.73 \text{ BM}$ for a single electron.

For atoms or ions that contain >1 unpaired electron, the overall spin moment is given by

$$\mu_s = s [S(S+1)]^{1/2}$$

where S is the sum of the spin quantum numbers of the individual unpaired electrons.

The motion of an electron around the nucleus may, in some materials, give rise to an orbital moment that contributes to the overall magnetic moment. In cases where the orbital moment makes its full contribution,

$$\mu_{s+L} = [4S(S+1) + L(L+1)]^{1/2}$$

where L is the orbital angular momentum quantum number for the ion. In practice, in solid materials, the last equation does not hold because the orbital angular momentum is either wholly or partially quenched. This happens when the electric fields of the surrounding atoms or ions may restrict the orbital motion of the electrons. The ways in which these magnetic dipoles interact with each other and with the external fields is important in the interpretation of the spectroscopic behaviour of atoms and molecules.

CLASSIFICATION OF MAGNETIC MATERIALS

One consequence of the closeness of atoms in a solid is that properties of the individual atoms or molecules can interact cooperatively to produce effects not found in fluids. The magnetic dipoles can interact with each other and can show cooperative spin behaviour. In certain materials, however this interaction does not happen and the spins remain isolated. So in general, magnetic materials can be classified on the basis of their spin interaction as follows :

Isolated Spin Behaviour

1. Paramagnetic
2. Diamagnetic

Cooperative Spin Behaviour

1. Ferromagnetic
2. Antiferromagnetic
3. Ferrimagnetic

Paramagnetism

There are several theories of paramagnetism, which are valid for specific types of material. The Langevin model, which is true for materials with non-interacting localised electrons, states that each atom has a magnetic moment which is randomly oriented (can be seen in the fig. 2.) as a result of thermal agitation.

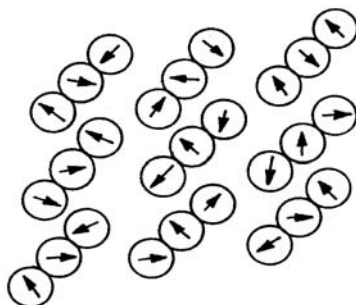


Fig. 2. Spin alignment in a paramagnet

The application of a magnetic field creates a slight alignment of these moments and hence a low magnetisation in the same direction as the applied field (Fig. 3a). As the temperature increases, then the thermal agitation will increase and it will become harder to align the atomic magnetic moments and hence the susceptibility will decrease (Fig. 3b). This behaviour is known as the Curie law and is shown below in the equation, where C is a material constant called the Curie constant.

$$\chi = \frac{C}{T}$$

Materials which obey this law are materials in which the magnetic moments are localised at the atomic or ionic sites and where there is no interaction between neighbouring magnetic moments. The hydrated salts of the transition metals, e.g. $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, are examples of this type of behaviour as the transition metal ions, which have a magnetic moment, are surrounded by a number of non-magnetic ions / atoms, which prevent interaction between neighbouring magnetic moments.

In fact the Curie law is a special case of the more general Curie-Weiss law, which incorporates a temperature constant (θ) and derives from Weiss theory, proposed for ferromagnetic materials, that incorporates the interaction between magnetic moments. In the equation below θ can either be positive, negative or zero. Clearly when $\theta = 0$ then the Curie-Weiss law equates to the Curie law.

$$\chi = \frac{C}{T - \theta} \quad (\text{Curie - Weiss law})$$

When θ is non-zero then there is an interaction between neighbouring magnetic moments and the material is only paramagnetic above a certain transition temperature. If θ is positive then the material is ferromagnetic below the transition temperature and the value of θ corresponds to the transition temperature (Curie temperature, T_C). If θ is negative then the material is antiferromagnetic below the transition temperature (Néel temperature, T_N), however, the value of θ is not related to T_N .

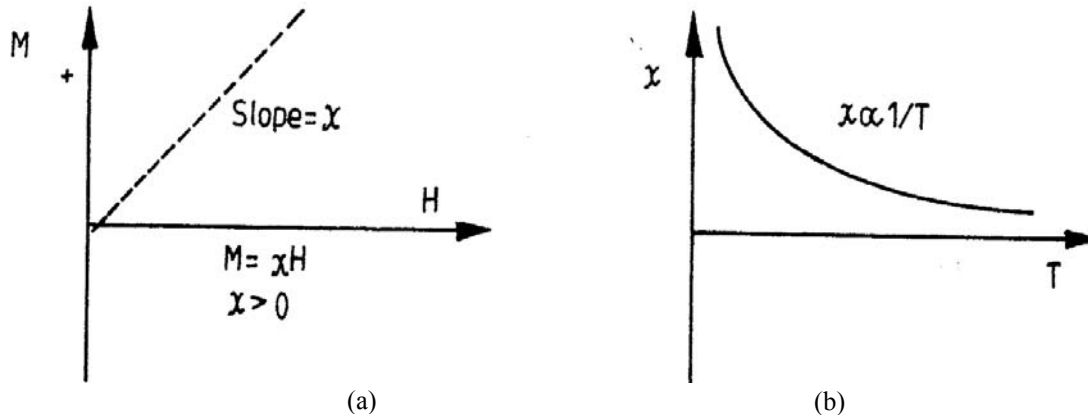


Fig. 3 (a) Increase in magnetization when external field is applied, (b) Effect of temperature on susceptibility for a paramagnet

Diamagnetism

It is due to the non-cooperative behaviour of orbiting electrons when exposed to an applied magnetic field. In a diamagnetic material the atoms have no net magnetic moment when there is no applied field. Under the influence of an applied field (H), the spinning electrons precess and this motion, which is a type of electric current, produces a magnetisation (M) in the opposite direction to that of the applied field (Fig. 4a). All materials have a diamagnetic effect, however, it is often the case that the diamagnetic effect is masked by the larger paramagnetic or ferromagnetic term. The value of diamagnetic susceptibility is independent of temperature (Fig. 4b).

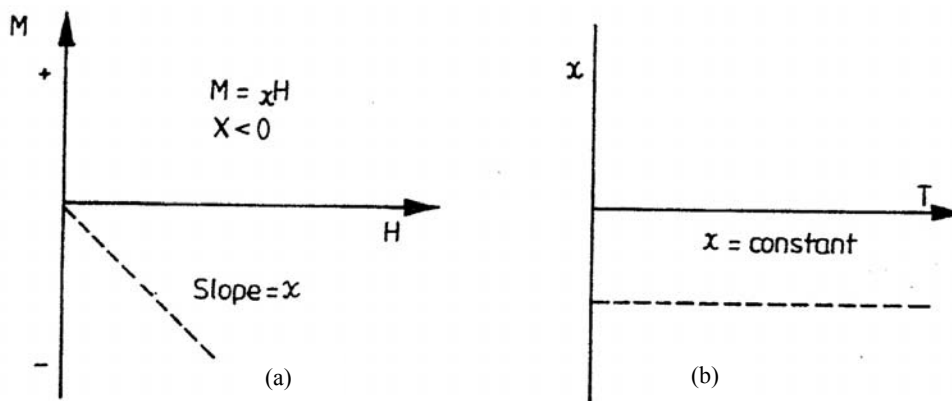


Fig. 4 (a) Increase in magnetization when external field is applied, (b) Effect of temperature on susceptibility

Ferromagnetism

Ferromagnetism is only possible when atoms are arranged in a lattice and the atomic magnetic moments can interact to align parallel to each other. This effect is explained in classical theory by the presence of a molecular field within the ferromagnetic material, which was first postulated by Weiss in 1907. This field is sufficient to magnetise the material to saturation. In quantum mechanics, the Heisenberg model of ferromagnetism describes the parallel alignment of magnetic moments (Fig. 5.) in terms of an exchange interaction between neighbouring moments.

Weiss postulated the presence of magnetic domains within the material, which are regions where the atomic magnetic moments are aligned. The movement of these domains determines how the material responds to a magnetic field and as a consequence the susceptibility is a function of applied magnetic field. Therefore, ferromagnetic materials are usually compared in terms of saturation magnetisation (magnetisation when all domains are aligned) rather than susceptibility.

Ferromagnetic materials get their magnetic properties not only because their atoms carry a magnetic moment but also because the material is made up of small regions known as magnetic domains. In each domain, all of the atomic dipoles are coupled together in a preferential direction. Ferromagnetic materials are said to be characterized by "spontaneous magnetization" since they obtain saturation magnetization in each of the domains without an external magnetic field being applied. Even though the domains are magnetically saturated, the bulk material may not show any sign of magnetism because the domains developed by themselves are randomly oriented relative to each other.

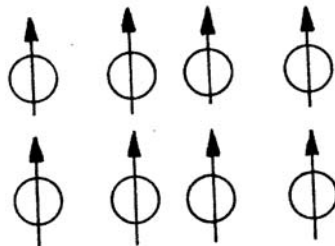


Fig. 5. Spin alignment in a ferromagnet

Ferromagnetic materials become magnetized when the magnetic domains within the material are aligned. This can be done by placing the material in a strong external magnetic field or by passing electrical current through the material. Some or all of the domains can become aligned. The more domains that are aligned, the stronger the magnetic field in the material. When all of the domains are aligned, the material is said to be magnetically saturated. When a material is magnetically saturated, no additional amount of external magnetization force will cause an increase in its internal level of magnetization.

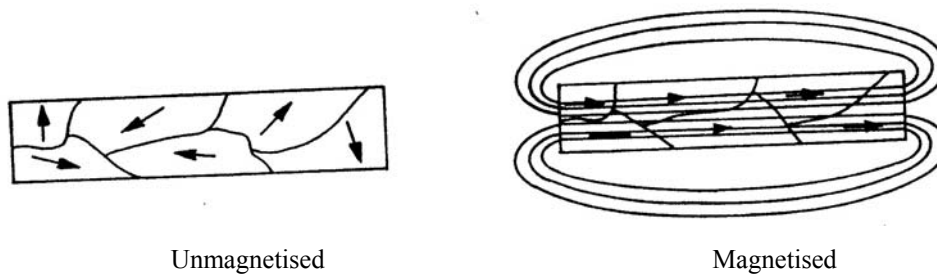


Fig. 6. A ferromagnet (a) in absence of external magnetic field, (b) in presence of external magnetic field

As ferromagnetic materials are heated, the thermal agitation of the atoms means that the degree of alignment of the atomic magnetic moments decreases and hence the saturation magnetisation also decreases. Eventually the thermal agitation becomes so great that the material becomes paramagnetic; the temperature of this transition is the Curie temperature, T_C (Fig. 7.).

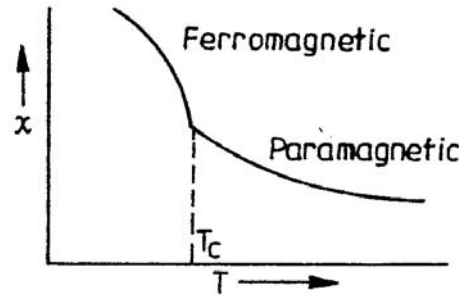


Fig. 7. Effect of temperature on susceptibility in a ferromagnet

Antiferromagnetism

Antiferromagnetic materials are very similar to ferromagnetic materials but the exchange interaction between neighbouring atoms leads to the anti-parallel alignment of the atomic magnetic moments (Fig. 8).

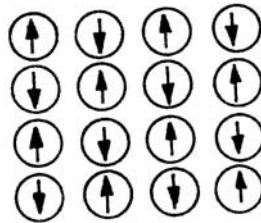


Fig. 8. Spin alignment in an antiferromagnetic material

Therefore, the magnetic field cancels out and the material appears to behave in the same way as a paramagnetic material. Like ferromagnetic materials these materials become paramagnetic above a transition temperature, known as the Néel temperature, T_N (Fig. 9).

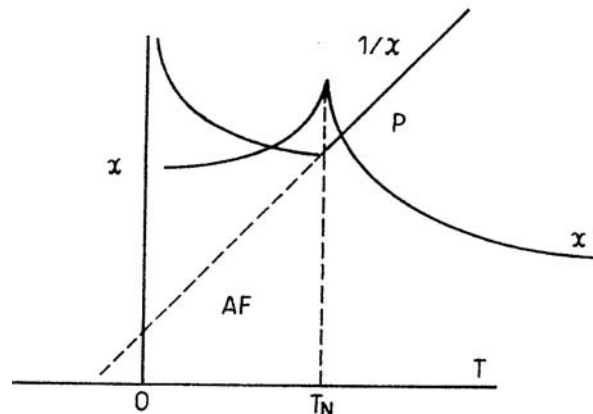


Fig. 9. Effect of temperature on an antiferromagnetic material

Antiferromagnets obey Curie-Weiss law and θ is negative for antiferromagnetic materials.

Ferrimagnetism

Within these materials the exchange interactions lead to parallel alignment of atoms in some of the crystal sites and anti-parallel alignment of others (Fig. 10). The material breaks down into magnetic domains, just

like a ferromagnetic material and the magnetic behaviour is also similar, although ferrimagnetic materials usually have lower saturation magnetisation.

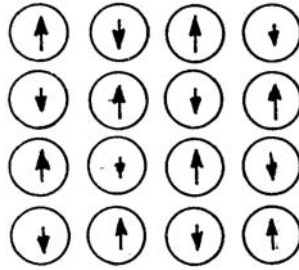


Fig. 10. Spin alignment in a ferrimagnet

Almost every item of electronic equipment produced today contains some ferrimagnetic material : loudspeakers, motors, deflection yokes, interference suppressors, antenna rods, proximity sensors, recording heads, transformers and inductors.

Hysteresis

Hysteresis is well known in ferromagnetic materials. When an external magnetic field is applied to a ferromagnet, the ferromagnet absorbs some of the external field. Even when the external field is removed, the magnet will retain some field: it has become magnetized. When a ferromagnetic material is magnetized in one direction, it will not relax back to zero magnetization when the imposed magnetizing field is removed. It must be driven back to zero by a field in the opposite direction. If an alternating magnetic field is applied to the material, its magnetization will trace out a loop called a hysteresis loop (Fig. 11).

The relationship between magnetic field strength and magnetic flux density is not linear in such materials. If the relationship between the two is plotted for increasing levels of field strength, it will follow a curve up to a point where further increases in magnetic field strength will result in no further change in flux density. This condition is called magnetic saturation.

If the magnetic field is now reversed and increased linearly, the plotted relationship will again follow a similar curve back towards and beyond zero flux density but offset from the original curve by an amount called the remanent flux density or remanence. The cause of the offset is the fact that ferromagnetic materials will tend to retain some of the magnetism induced in them and this has to be overcome each time the magnetic field across the substance reverses.

If this relationship is plotted for all strengths of applied magnetic field the result is a sort of S-shaped loop. The 'thinness' of the middle bit of the S describes the amount of hysteresis.

The loop is generated by measuring the magnetic flux \mathbf{B} of a ferromagnetic material while the magnetizing force \mathbf{H} is changed. A ferromagnetic material that has never been previously magnetized or has been thoroughly demagnetized will follow the dashed line as \mathbf{H} is increased. As the line demonstrates, the greater the amount of current applied ($\mathbf{H}+$), the stronger the magnetic field in the component ($\mathbf{B}+$). At point "a" almost all of the magnetic domains are aligned and an additional increase in the magnetizing force will produce very little increase in magnetic flux. The material has reached the point of magnetic saturation. When \mathbf{H} is reduced back down to zero, the curve will move from point "a" to point "b." At this point, it can be seen that some magnetic flux remains in the material even though the magnetizing force is zero. This is referred to as the point of retentivity on the graph and indicates the remanence or level of residual magnetism in the material. (Some of the magnetic domains remain aligned but some have lost their alignment). As the magnetizing force is reversed, the curve moves to point "c", where the flux has been reduced to zero. This is called the point of coercivity on the curve. (The reversed magnetizing force has flipped enough of the domains so that the net flux within the material is zero). The force required to remove the residual magnetism from the material, is called the coercive force or coercivity of the material. As the magnetizing force is increased in the negative direction, the material will again become magnetically saturated but in the opposite direction (point "d"). Reducing \mathbf{H} to zero brings the curve to point "e." It will have a level of residual magnetism equal to that achieved in the other direction. Increasing \mathbf{H} back in the positive direction will return \mathbf{B} to zero. Notice that the curve did not return to the

origin of the graph because some force is required to remove the residual magnetism. The curve will take a different path from point "f" back the saturation point where it will complete the loop. From the hysteresis loop, a number of primary magnetic properties of a material can be determined.

Retentivity - A measure of the residual flux density corresponding to the saturation induction of a magnetic material. In other words, it is a material's ability to retain a certain amount of residual magnetic field when the magnetizing force is removed after achieving saturation. (The value of **B** at point b on the hysteresis curve.)

Residual Magnetism or **Residual Flux** - The magnetic flux density that remains in a material when the magnetizing force is zero. Note that residual magnetism and retentivity are the same when the material has been magnetized to the saturation point. However, the level of residual magnetism may be lower than the retentivity value when the magnetizing force did not reach the saturation level.

Coercive Force - The amount of reverse magnetic field which must be applied to a magnetic material to make the magnetic flux return to zero. (The value of **H** at point c on the hysteresis curve.)

Permeability, μ - A property of a material that describes the ease with which a magnetic flux is established in the component.

Reluctance - Is the opposition that a ferromagnetic material shows to the establishment of a magnetic field. Reluctance is analogous to the resistance in an electrical circuit. In a magnetic system, hysteresis is seen in a ferromagnetic material that tends to stay magnetized after an applied field force has been removed, if the force is reversed in polarity.

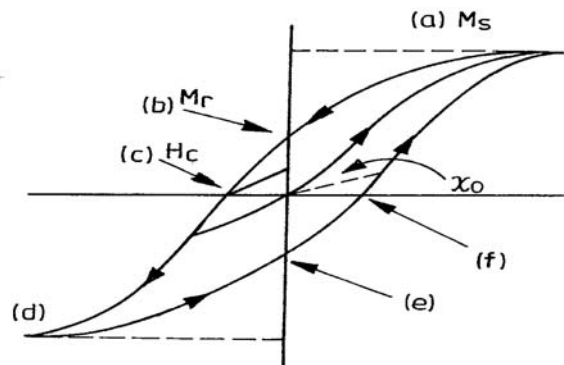


Fig. 11.Hysteresis loop

Hard Magnets

Hard magnets, also referred to as permanent magnets, are magnetic materials that retain their magnetism after being magnetised. Practically, this means materials that have an intrinsic coercivity of greater than $\sim 10 \text{ kA m}^{-1}$. It is believed that permanent magnets have been used for compasses by the Chinese since ~ 2500 BC. However, it was only in the early twentieth century that high carbon steels and then tungsten / chromium containing steels replaced lodestone as the best available permanent magnet material. These magnets are permanent magnets due to the pinning of domain walls by dislocations and inclusions. The movement of dislocations within a material is often hindered by the same factors that effect the motion of domain walls and as a consequence these steels are mechanically very hard and are the origin of the term hard magnet. These magnets have an energy product of approximately 8 kJ m^{-3} . Hard magnets find their applications in Automotives (Starter motors, Injection pumps, Fans and controls for windows, Loudspeakers, Eddy current brakes, Alternators), Telecommunications (Microphones, Telephone ringers, Electro-acoustic pick-ups, Switches and relays), Data Processing (Disc drives and actuators, Stepping

motors, Printers), Consumer Electronics (DC motors for showers, Washing machines, Drills, Low voltage DC drives for cordless appliances, Loudspeakers for TV and Audio, TV beam correction and focusing device, Compact-disc drives, Home computers, Video recorders, Clocks) and in fields such as electronic and instrumentation, industrial, astro and aerospace and biosurgicals.

Soft Magnets

Soft magnetic materials are those materials that are easily magnetised and demagnetised. They typically have intrinsic coercivity less than 1000 Am^{-1} . They are used primarily to enhance and/or channel the flux produced by an electric current. The main parameter, often used as a figure of merit for soft magnetic materials, is the relative permeability (m_r , where $m_r = B/m_oH$), which is a measure of how readily the material responds to the applied magnetic field. The other main parameters of interest are the coercivity, the saturation magnetisation and the electrical conductivity.

The types of applications for soft magnetic materials fall into two main categories; AC and DC. In DC applications the material is magnetised in order to perform an operation and then demagnetised at the conclusion of the operation, e.g. an electromagnet on a crane at a scrap yard will be switched on to attract the scrap steel and then switched off to drop the steel. In AC applications the material will be continuously cycled from being magnetised in one direction to the other, throughout the period of operation, e.g., a power supply transformer. A high permeability will be desirable for each type of application but the significance of the other properties varies.

For DC applications the main consideration for material selection is most likely to be the permeability. This would be the case, for example, in shielding applications where the flux must be channelled through the material. Where the material is used to generate a magnetic field or to create a force then the saturation magnetisation may also be significant.

For AC applications the important consideration is how much energy is lost in the system as the material is cycled around its hysteresis loop. The energy loss can originate from three different sources : 1. hysteresis loss, which is related to the area contained within the hysteresis loop; 2. eddy current loss, which is related to the generation of electric currents in the magnetic material and the associated resistive losses and 3. anomalous loss, which is related to the movement of domain walls within the material. Hysteresis losses can be reduced by the reduction of the intrinsic coercivity, with a consequent reduction in the area contained within the hysteresis loop. Eddy current losses can be reduced by decreasing the electrical conductivity of the material and by laminating the material, which has an influence on overall conductivity and is important because of skin effects at higher frequency. Finally, the anomalous losses can be reduced by having a completely homogeneous material, within which there will be no hindrance to the motion of domain walls.

Applications of Magnetic Materials

The magnetic storage of data is very important for modern life - magnetic tape was originally used for analogue sound storage but is now used to store both analogue and digital information and this is no longer limited to tape which has slow access times. Magnetic discs (floppies, hard disks) offer rapid storage and access of ever increasing amounts of information. We use a wide variety of plastic cards with magnetic strips, e.g., bank cards, debit cards, credit cards, account cards etc., to manage (mismanage?) our financial affairs, for security access, e.g., telephone cards, travel tickets (e.g., London Underground).

Scientists are now developing newer magnetic materials for computers. The disc drive storage system is mechanical and still quite slow, unlike chip (RAM) storage of data which is "instantaneous". But whilst discs retain the information when the power is off, chips forget everything without power. The race is now on to produce M-RAM, or magnetic random access memory, which will retain information permanently in so-called non-volatile memory. This is possible with the development of new magnetic materials in which the magnetic properties of individual molecular magnets can be controlled on a molecular or nanotechnological scale.

In the television tube the deflection of the electron beams that "paint" the picture on the television screen is accomplished using magnetic fields.

The magnetic properties of certain atomic nuclei can be used in chemistry in nuclear magnetic resonance (NMR) spectroscopy, which is a valuable tool in molecular structure determination. A development of this technique is magnetic resonance imaging (MRI) that has rapidly become a powerful

imaging technique in the medical world for scanning internal organs. Both techniques rely on the fact that some atomic nuclei behave like little magnets and can either align themselves for or against the field of a powerful magnet - applied radio frequency waves can cause the nuclei to flip between the for and against states and the radio frequency required to do this can give information about the environment of an atomic nucleus.

The repulsive force between like poles of magnets can be used for magnetic levitation which engineers are trying to exploit in modern train systems.

Nuclear fusion of light elements has the potential to generate vast amounts of energy at low cost. In conventional nuclear fusion the positively charged atomic nuclei must be heated to very high temperatures in order to give them enough kinetic energy to collide by overcoming the repulsion between their positive charges - the required temperatures (100 000 000 °C) are so high that the gaseous matter cannot be stored in any normal material and scientist are looking at ways of storing this very hot matter or plasma in magnetic bottles in which the plasma is suspended in a powerful magnetic field without physical contact.

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CHAPTER - 7

Surfaces and solids

INTRODUCTION

A surface is defined as the outer or the topmost boundary of an object or it is the two dimensionally extended outer boundary of a three-dimensional object. Among different states of matter, solid state is having a well-defined surface. A liquid is not having an inherent boundary but can be created which will vary with the container. In other words we can tell that creation and the stretching of the surfaces are equivalent processes in the case of liquids. Hence the energetics governed by the surface energy is identical to the surface tension, in the case of liquids. In solids by adding atoms or increasing the interatomic distances of surface atoms, the surface area can be enhanced unlike liquids. Hence surface tension and surface energy are entirely different in solids. A surface is formed by the breaking of many lattice bonds, which causes the formation of unfavourable energetics (+ve free energy) enhancing the surface energy. Minimization of this surface energy can be done either by reducing the amount of surface area exposed or by predominantly exposing surface planes, which have a low surface free energy or by altering the local surface atomic geometry in a way, which reduces the surface free energy. For a surface to be stable either it should have a high surface atom density or the surface atoms should have a higher coordination number. A liquid prefers the spherical geometry to reduce its surface tension. In a similar way solid surface tends to saturate its coordination by the mere process of adsorption.

Table 1. Surface depth regimes (reproduced from ref. 2)

Surface depth	Examples of definitive role
Outer mono layer ≈ 0.1 nm	Heterogeneous catalysis, surface tension control (contact angle) Selective adsorption, Electrochemical systems, Biological systems, Sensors
Thin film ≈ 0.1 – 100 nm	Emulsions, Tribological control (Friction), Antireflection coatings, Lipid membranes, Langmuir Blodgett films, Interference filters, Release agents
Near surface 0.1 – 10 μm	Semiconductor devices, Surface hardening, Polymer biodegradation, Controlled release membranes, Osmosis devices, Photo graphic film, Optical recording media, Aerosols
Thick layers > 10 μm	Anti-corrosion coatings, (Anodizing, Electro plates, Paints), Phosphors, Adhesives Electro winning, Magnetic recording media, Surface cladding

Importance of various depth regimes of the solid surface can be understood from the information given in table 1. The relevance to the solid surfaces is evident from the elaborate account of its applications in science and technology utilizing the electrical, magnetic and optical properties.

ADSORPTION – SIGNIFICANCE

The phenomenon of adsorption has been explained and experimentally proved by the surface chemist Irving Langmuir for which he received the Nobel prize in chemistry in 1932. Adsorption can be classified into two types depending on the nature of interaction of the adsorbent and the adsorbate. They are chemisorption and physisorption. In chemisorption the forces involved are the valence forces of the same kind as that of operating in the formation of chemical compounds, whereas in physisorption the forces involved are van der Waals forces and there will not be any significant changes in the electronic orbital patterns of the species involved. Because of rather weak forces involved in physisorption, the adsorbed layers can be removed easily. Chemisorption can happen in two ways; dissociative (atomic) chemisorption and associative (molecular) chemisorption. In dissociative chemisorption as shown in the figure a diatomic molecule will first cleave and then adsorb as atoms. In associative Chemisorption molecular entity as such will get adsorbed.

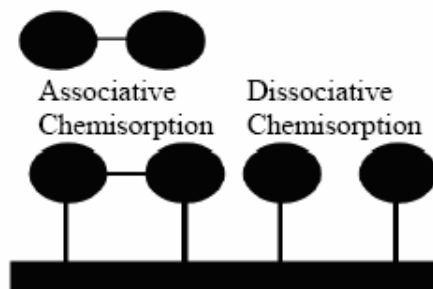


Fig. 1. Types of chemisorption

From the energetics of adsorption it is very clear that chemisorption will yield much stable situation than that in the physisorption. The potential energy diagrams for both the processes are given in the fig. 2.

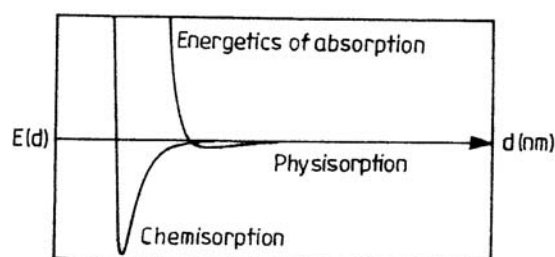


Fig. 2. Energetics of adsorption

A major fraction of the surface reactions are as a consequence of adsorption phenomena because of which it is of great significance. Adsorbed reactants will have to surmount an activation barrier, which is much less than that of the reactions in the bulk as in homogeneous reactions. The energy changes involved in the homogeneous and heterogeneously catalyzed reactions are given below.

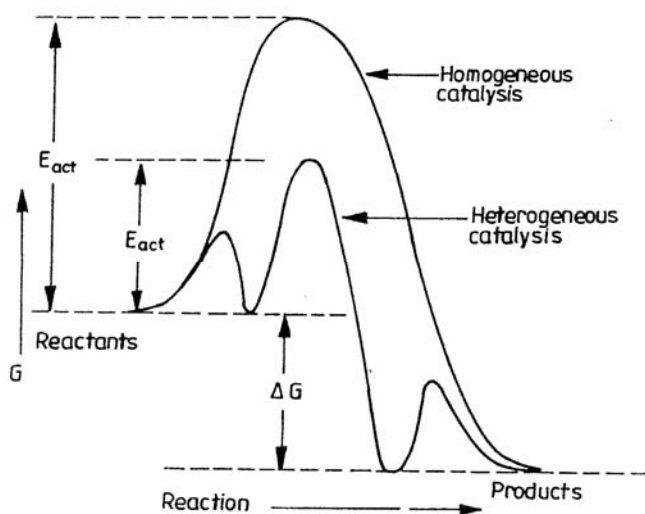


Fig. 3. Potential energy diagram for homogeneous and heterogeneous reactions

In heterogeneous catalysis catalyst is in different phase as that of the reactants. The reactants will first get adsorbed on the active centers of the catalyst surface in suitable positions allowing the rapid reactions. Here the surface anchoring of the reactant on the surface will provide a geometry, which

facilitates the reaction with lower activation energy. In homogeneous catalysis, the products will be in the same phase as that of the catalyst. Here the properly oriented collisions only will yield the products for which the activation energy will be higher. In surface catalyzed reactions, surface area of the catalyst and the active site distribution are the important criteria, which determine the efficiency of the catalyst. For example we can see that the same reactant is undergoing different types of reactions on two different surfaces such as copper and alumina. On copper surface ethanol will undergo dehydrogenation reaction to yield acetaldehyde, where we can see the ethanol OH group atoms are preferentially adsorbed on the adjacent sites yielding the corresponding aldehyde. On alumina alkyl moiety and the oxygen of the OH group is preferably adsorbed thus subsequent cleavage will be enhancing the dehydration yielding ethane as the product. The higher surface area of the catalyst will provide more and more sites for adsorption and hence the reaction will be rapid. In human beings IQ (Intelligence Quotient) will be having a direct relation to the surface area of the brain. If the brain is having more foldings more will be the surface area and more will be the IQ.

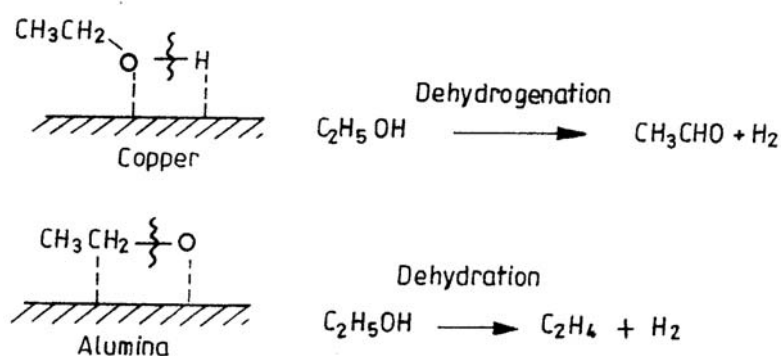


Fig. 4. Surface catalysis

SALIENT FEATURES OF THE SOLID SURFACES

Over Layer Structures

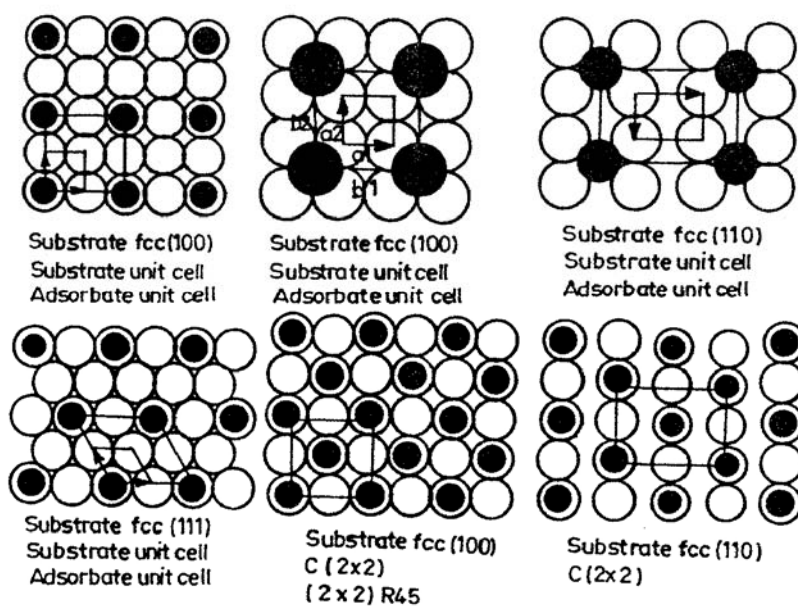


Fig. 5. Over layer structures

Adsorbed species on single crystal surfaces are frequently found to exhibit long-range ordering; that is to say that the adsorbed species form a well defined over layer structure. There are two principal methods for specifying the structure:

- a) Wood's notation
- b) Matrix notation

Ordered surface structures may be described by defining the adsorbate unit cell in terms of that of the underlying substrate using either of the above two notations. According to Wood's notation the lengths of b_1 and b_2 are given as simple multiples of a_1 and a_2 respectively, and this is followed by the angle of rotation of b_1 from a_1 (if this is non-zero). In matrix notation b_1 and b_2 are independently defined as linear combinations of a_1 and a_2 and these relationships are expressed in a matrix format. Similar ways as that of the solid surfaces, over layers are also having definite patterns of arrangement.

Surface Reconstruction

Crystal facets can undergo several types of phase transitions. Few of such types are reconstructive phase transitions, surface roughening, surface melting etc. Reconstructive phase transitions involve breaking and making of new bonds reorganizing the whole crystal structure. In surface reconstruction only the surface is getting reorganized. When the characteristic temperatures for all these processes are well separated; for example when a reconstructed surface first loses its reconstruction order, then roughens at a higher temperature, and finally surface melts just below the bulk melting temperature. Optical properties of silicon nano clusters are due to the reconstruction and the oxidation of the surface. Reconstruction of the solid surfaces is extremely important in the field of catalysis where reconstruction will lead to active phases, which will be specific for the chemisorption step. In the case of CO oxidation over pt (110) surface, it has been found to exist a missing row reconstruction due to which there will be an interplay of (1x1) and (1x2) adsorbate geometry. Surface reconstructions can be divided into two groups: Displacement and misplacement reconstructions. Compared to the unreconstructed configuration, particles on the surface are moved only locally or are transported away completely. Misplacement reconstructed surfaces have typically a different average surface height than their unreconstructed counterparts. The top layers can be interpreted as only partially completed and have long-range positional order.

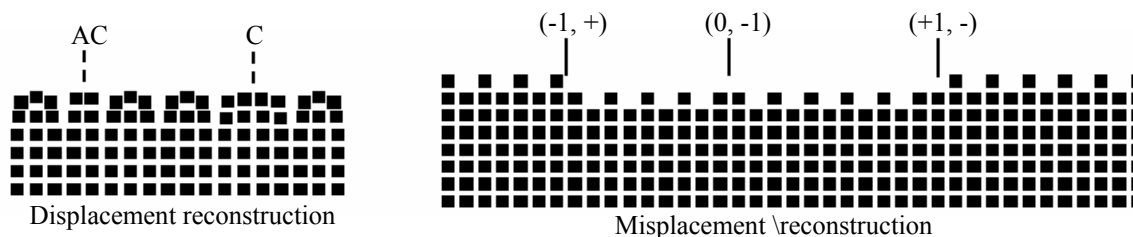


Fig. 6. Surface reconstructions

Segregation

In alloys or solid solutions as the time goes on the material with the lowest surface energy separate out to the surface. This is known as segregation. It can also be affected by adsorption. If a reactant reacts with one component more favourable than other (in the solid solution) and the product has lower surface energy, then it will tend to segregate. That is why the iron in steels always rusts. After long time coin surface will become black in colour due to the Cu segregation to the surface and subsequent reaction with moisture will finally leads to black CuO.

Wetting

It is the phenomenon of the adherent contact of liquids to the surface of solids (or other liquids). The surface energy of the substrate (i.e., the flat surface) is so high that the droplet will tend to spread at the base. The angle of contact is called the contact angle and decides the degree of 'wetting'. It is highly

unrealistic a liquid drop to be always spherical. Wetting of surface has important implications for preventing wear on engines, paintings and buildings, for medical products such as contact lenses, surgical tools and prosthetics, as well as for self-cleaning windows, cars and clothes.

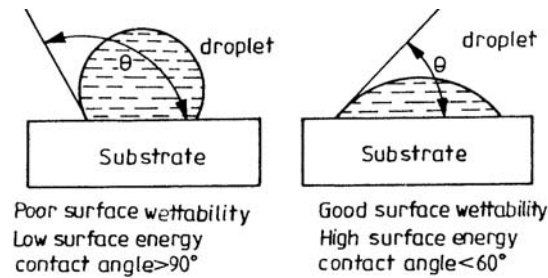


Fig. 7 Surface wetting

There are two types of wetting. Namely complete wetting and partial wetting. A zero contact angle ($\theta = 0$) is the condition for complete wetting of a solid by a liquid (e.g. water on clean glass). Conversely, complete non-wetting dictates an angle of 180° , and this is only possible for a liquid in a liquid.

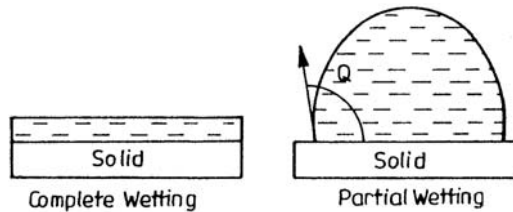


Fig. 8. Types of wetting

Cutting and Polishing

Surface modifications such as cutting and polishing are done in order to make the surface quality excellent and to get the precise angular alignments for example in the case of diamonds. Proportion for an ideal cut for a diamond is given in the following fig. 9. It is termed as ideal because the given dimensions will provide a total internal reflection of the light beams entering into the crystal so as to give a finest look to the diamond. Polishing will provide smooth surfaces which will be having applications in reducing the unfavourable reaction rates such as corrosion, oxidation etc.

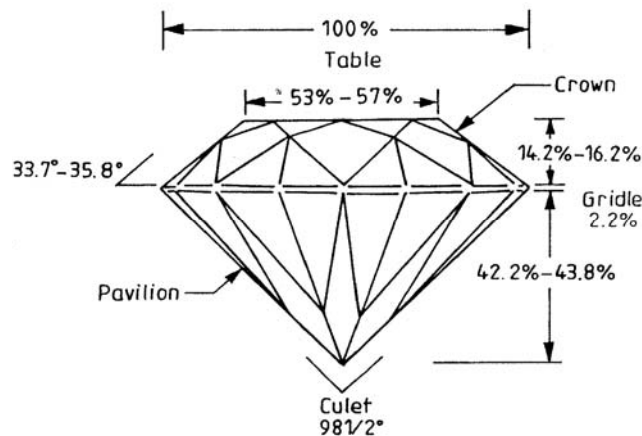


Fig. 9. An ideal cut for a diamond

Corrosion

Corrosion is defined as the process involving the deterioration or degradation of metal components. The best-known case is that of rusting of steel. Corrosion processes are usually electrochemical in nature, like battery. When metal atoms are exposed to an environment containing water molecules they can give up electrons becoming themselves positively charged ions, provided an electrical circuit can be completed. This effect can be concentrated locally to form a pit or sometimes a crack or it can extend across. Corrosion is the disintegration of metal through an unintentional chemical or electrochemical action, starting at its surface. All metals exhibit a tendency to be oxidized, some more easily than others. The corrosion process (anodic reaction) of the metal dissolving as ions generates some electrons, as shown in the figure that are consumed by a secondary process (cathodic reaction). These two processes have to balance their charges. Examples of corrosion processes are given below.

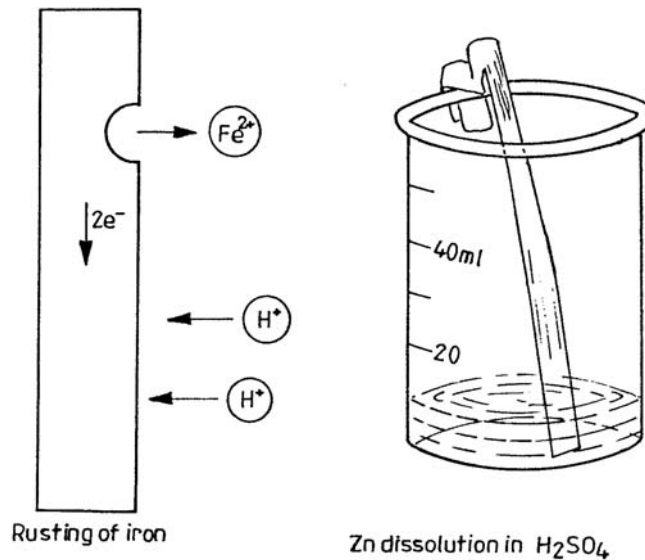


Fig. 10. Corrosion

Corrosion Prevention

Most of the cases corrosion is playing an unfavourable role; hence it is crucial to adopt strategies to prevent corrosion. Best way to prevent corrosion is the passivation by forming thin films of micrometer thickness on the surface. For example Al, stainless steel, Ti, and Si surface will form an oxide coating and will resist the corrosion. Another way is to do Galvanization. It is a process in which Zinc is electroplated on the metal surface, which has to be protected from corrosion. Similar way waxing, painting, oiling etc. are also used for preventing the corrosion.

Sintering

The bonding of adjacent surfaces of particles in a mass of powders, usually metal, by heating is known as sintering. One of the recent methods used for sintering is Selective Laser Sintering, which utilizes CO_2 lasers to selectively fuse together layers of powdered plastic, metal or ceramic materials to create durable materials. For example Chalk pieces, refractory bricks etc. are produced through sintering process. Synthesis of a wide variety of ceramic material can be done by sintering. Self-lubricating properties of many materials can be enhanced through sintering. We can achieve densification and hardening of the materials by the mere process of sintering. In catalysis sintering causes decrease in the activity partly due to the decrease in the surface area of the catalyst for adsorption.

SURFACE CLEANING AND MODIFICATION PROCESSES

ETCHING

It is defined as the modification of the surface by treating with some other chemical compounds. e.g., removing the rust on the iron by acid treatment. Etching can be classified into different types, isotropic etching, anisotropic etching, wet etching, dry etching and infusion etching. In isotropic etching, etching rate is the same in all directions. For example etching of thin film coated on the Si wafer. In anisotropic etching, the rate of etching is different in different directions. Hence it will be having a more control on the resulting shape. Etching rate depends on nature of the plane. In one plane it is faster and in other it is slower. Si and KOH are used as the etching agents. Wet etching is that which uses solutions for etching. Different acidic solutions are used to etch the surface. Dry etching is that in which no solutions are involved. One such type is reactive ion etching, where ions are accelerated towards the material to be etched, and the etching reaction is enhanced in the direction of travel of the ion. Deep trenches and pits (up to ten or a few tens of microns) of arbitrary shape and with vertical walls can be etched in a variety of materials including silicon oxide and nitride. In the case of infusion etching the accelerated ions interact with the surface and thus leave the surface taking the surface atoms. Surface etching is used to detect the cracks. Glass etching is the abrading or roughening of a piece of glass in selected areas in order to produce a design. Glass etching will lead to different glass carvings, which will be used in mirrors, windows, show glasses etc.

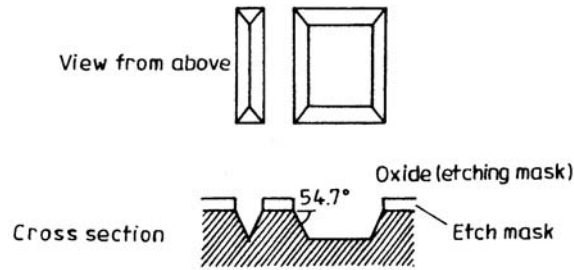


Fig. 11. Etching of the surface

SPUTTERING

Sputtering is a vacuum evaporation process, which physically removes portions of a coating material called the target, and deposits a thin, firmly bonded film onto an adjacent surface called the substrate. The process occurs by bombarding the surface of the sputtering target with gaseous ions under high voltage acceleration. As these ions collide with the target, atoms or occasionally entire molecules of the target material are ejected and propelled against the substrate, where they form a very tight bond. The resulting coating is held firmly to the surface by mechanical forces, although, in some cases, alloy or chemical bond may result. Sputtering has proven to be a successful method of coating a variety of substrates with thin films of electrically conductive or non-conductive materials. One of the most striking characteristics of sputtering is its universality. Since the coating material is passed into the vapor phase by a mechanical rather than a chemical or thermal process, virtually any material can be deposited. Direct current is used to sputter conductive materials, while radio frequency is used for non-conductive materials.

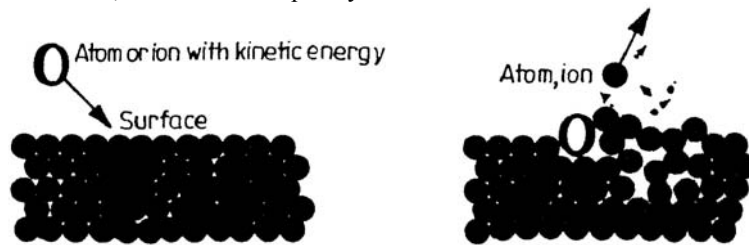


Fig. 12. Sputtering of the surfaces

ULTRASONICATION

This is a method where irradiation with ultra sound waves will enhance the rate of a chemical reaction or it can be used to clean the surface adsorbed atoms on different materials.

SURFACE BLEACHING

To remove the colour from anything as by means of chemical agents or sunlight is known as the bleaching. Bleaching of the surface can be done either by mechanical methods or by chemical methods. For example removal of stain from concrete surfaces is a process of bleaching which can be done either mechanically or chemically. Mechanical methods involve sand blasting, grinding, steam cleaning, brushing, scouring and sometimes, use of blow torches. Chemicals act as solvents to dissolve stains or react with them to form a compound that will not show as a stain. As solvents, they are applied in one of three ways: directly on the surface; by soaking cotton or cloth placed on the concrete (the bandage method); or by making a poultice of the solvent and a finely ground powder such as whiting (calcium carbonate), hydrated lime (calcium hydroxide), talc, fuller's earth (saponite), or diatomaceous earth and spreading it on the stained area in a ¼- to ½-in. layer. Bleaching powder is used so commonly in households. Bleaching powder $[\text{Ca}(\text{OCl})_2]$ is acting as a disinfectant, where chlorine kills pathogens such as bacteria and viruses by breaking the chemical bonds in their molecules. When enzymes in bacteria come in contact with chlorine, one or more of the hydrogen atoms in the molecule are replaced by chlorine. This causes the entire molecule to change shape or fall apart. When enzymes do not function properly, a cell or bacterium will die. Similar way the bleaching of corals is also occurring in the sea, when the temperature of the sea is above 28 °C.

LANGMUIR BLODGETT FILMS (LB FILMS)

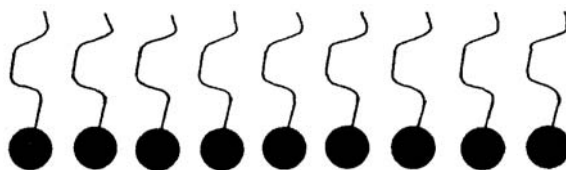


Fig. 13. Langmuir Blodgett films

Spreading amphiphile molecules on a water surface yields monolayers or films where the hydrophobic segments stem at the water/air interface. The molecules can be compressed to give monolayers with controlled density and organization. Langmuir -Blodgett films are obtained from the deposition of monolayers on a solid substrate. Film build-ups can be prepared by multiple dippings of the substrate through the monolayer. Films consisting of 1, 2 or as much as 10,000 monolayers can be encountered. When the molecules are first spread on the water surface, they are loosely packed and form a so-called gas phase. Increasing the surface pressure translates as a transition to a liquid phase. Further increase in pressure brings about a last compressibility change that is associated to a liquid-solid phase transition.

Two different types of substrates can be used, hydrophilic and hydrophobic, out of which hydrophilic substrates are glass and quartz, metal plates composed of oxides of chromium, aluminium or tin, silver and gold (conductive substrates), silicon or gallium arsenide plates (semi conductive). Example for the hydrophobic substrate is mica sheet. Several methods can be adopted for the deposition of the LB films. Once the monolayer is deposited, chemical reactions are possible with these molecules such as removal of aliphatic chain, functionalization of the head groups and preparation of mixed monolayers by spreading two different amphiphiles on the water surface. Various distribution and patterns can thus be obtained. One of the important applications of LB films is in mimicking of cell membranes. The advantage here is that we can tune the properties of the film. Optical properties can be incorporated. This brings out lot more applications in the field of sensors.

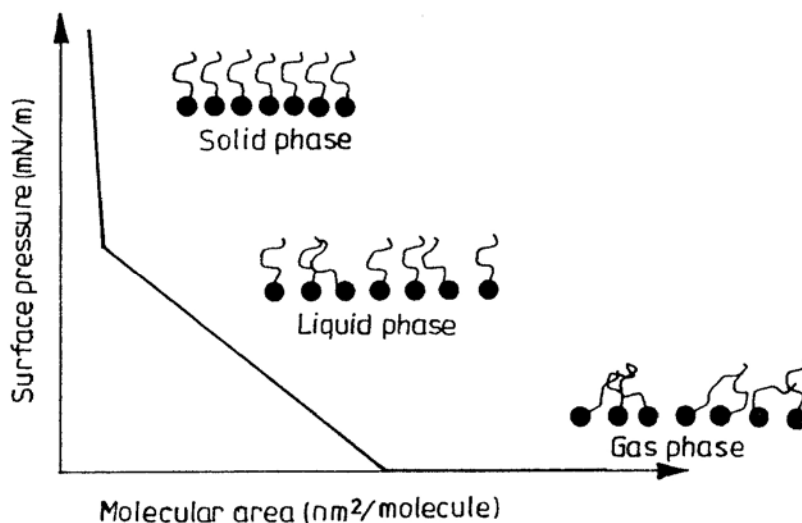


Fig. 14. Phase transitions in LB films

SELF ASSEMBLED MONOLAYERS (SAM)

They are highly ordered ensembles of surfactants spontaneously adsorbed onto solid surfaces. Here the amphiphiles or the surfactants are anchored over the solid surface directly unlike in the case of LB films. e.g., SAM of thiol on gold. The advantages of SAMs over LB films are their ease of preparation and functionalization and its stability. Specific applications of SAM involve the corrosion protection, Light emitting diodes, dental care and detection of elements where we use alkane mono and diphosphonic acid SAMs on iron, ITO modified with polyaniline, organophosphonic acid SAMs on teeth, TC SAMs on gold respectively.

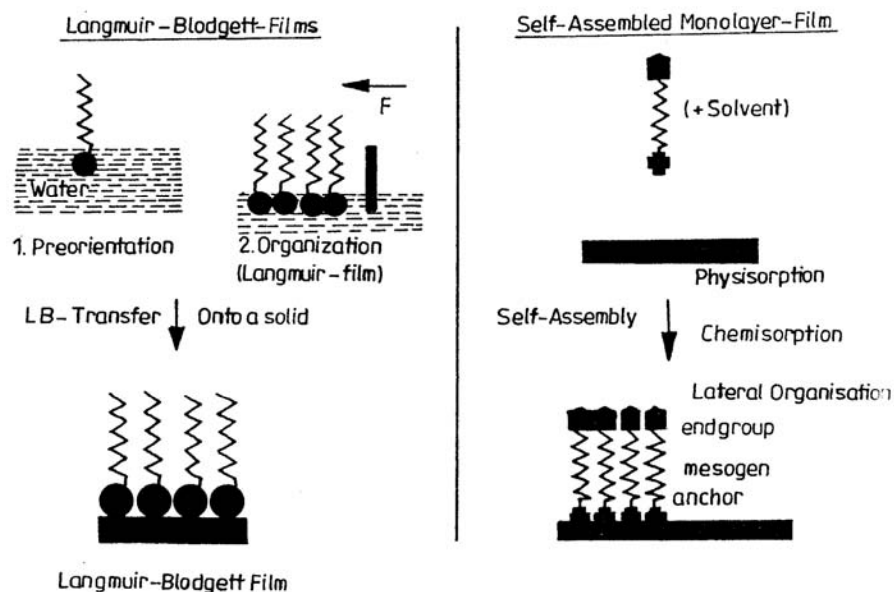


Fig. 15. Schematic formation of SAMs and LB films

SURFACE DEFECTS

Different types of surface defects are given in the figure given below:

Presence of defects on the surface will affect the chemical, electrical and mechanical properties of the solids. Presence of elastic distortions, step growth, existence of surface twins, cracks etc. will increase the surface area and that will be a favorable change for the surface reactions.

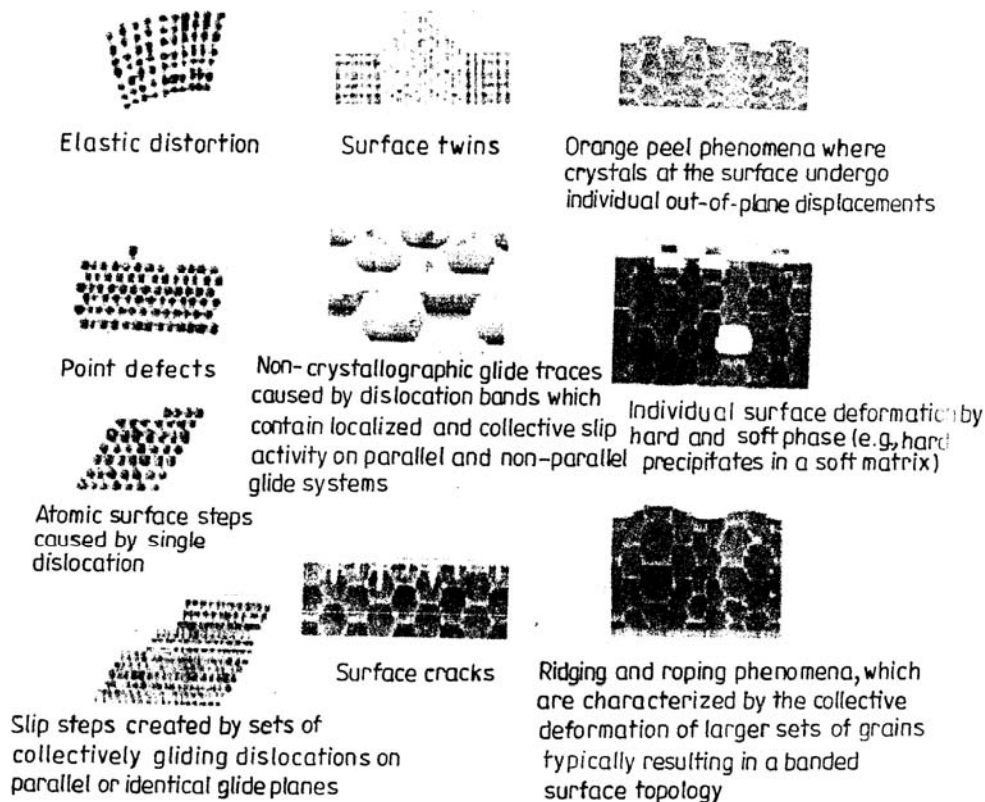


Fig. 16. Surface defects (reproduced from ref. 13)

SURFACE IN DIFFERENT DIMENSIONS

Engineering

The advancement in surface engineering has spread its dimensions from nano chips to the gega dimensions of spacecraft technology. As we can see in the satellites sunshield panel for the passive radiative cooler has been engineered in such a way that it can send the IR images to map out the relevant information. National Aerospace Laboratory Bangalore has contributed a number of such surface engineered technologies to the country such as seal discs for nuclear power plant applications, solar selective coatings for water heating applications, restoration of brake accumulator body of aircraft, rough diamond coatings etc.

Electrochemistry

The role of surfaces in electrochemistry is much wider than that we can think of. All electrochemical reactions that are taking place will be in the interphase of solid electrode and the electrolyte. The nature of the electrode surface is having a crucial role in the rate of electrochemical reactions. That is the reason why coating of the surface prevents the corrosion.

Tribology

It is the science of the mechanisms of friction, lubrication, and the wear of interacting surfaces that are in relative motion. Tribology, the word itself is derived from the Greek word 'tribos' which means to rub. The

field of tribology is of great importance to engineers who design or use mechanical components such as bearings, gears, seals, magnetic recording heads and disks, or prosthetic joints, or who are involved with manufacturing processes. Designing of railway wheels, surface defects and rolling contact fatigue, moving parts of the complex machineries, all these areas are of big concerns in tribology.

Bio surfaces and Interfaces

The significance of solid surfaces comes into play in biology in medicines and prosthetics. Immense amount of care should be taken in designing the implants, drug delivery systems, drugs etc. Pacemakers and artificial bone materials are examples for the development of the biotechnology, where the biosurface chemistry plays a significant role.

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CHAPTER - 8

Energy Storage in Solids

Energy is the driving force for the universe. Energy is a quantitative property of a system which may be kinetic, potential, or other in form. There are many different forms of energy. Energy storage is needed to store electricity, heat and cold, which is produced at times of low demand and low generation cost and from intermittent energy sources such as wind and solar power. It is released at times of high demand and high generation cost or when there is no more generation capacity available. Energy can be stored in many ways: e.g., mechanical energy, kinetic energy, and chemical energy.

DIFFERENT ENERGY STORAGE TECHNOLOGIES

- Batteries
- Fuel cells
- Electromagnetic
- Compressed air
- Super-capacitors
- Pumped hydro storage

Table 1. Energy sources, use of energy and energy storage

Energy sources	Use of energy	Energy storage
Conventional fossil fuels Nuclear Fuels Renewable energy: Biomass, wind, water and solar energy	Electricity Heat Cold Transport Kinetic energy Compressed gas	Flywheels Reversible fuel cells Electromagnetic fields Compressed air Thermal energy Pumped hydro

SOLAR ENERGY

Sunlight or solar energy can be used to generate electricity, provide hot water, and to heat, cool, and light buildings.

Photovoltaic (PV) (solar cell) systems (which directly convert sunlight into electricity, are made of semiconducting materials. The simplest photovoltaic cells power watches and calculators and the like, while more complex systems can light houses and provide power to the electrical grid) convert sunlight directly into electricity. A solar or PV cell consists of semi conducting material that absorbs the sunlight. The solar energy knocks electrons loose from their atoms, allowing the electrons to flow through the material to produce electricity. PV cells are typically combined into modules that hold about 40 cells. About 10 of these modules are mounted in *PV arrays*. PV arrays can be used to generate electricity for a single building or, in large numbers, for a power plant. A power plant can also use a *concentrating solar power system*, which uses the sun's heat to generate electricity. The sunlight is collected and focused with mirrors to create a high-intensity heat source. This heat source produces steam or mechanical power to run a generator that creates electricity.

Solar water heating systems for buildings have two main parts : a solar collector and a storage tank. Typically, a *flat-plate collector*—a thin, flat, rectangular box with a transparent covers—is mounted on the roof, facing the sun. The sun heats an *absorber plate* in the collector, which, in turn, heats the fluid running through tubes within the collector. To move the heated fluid between the collector and the storage tank, a system either uses a pump or gravity, as water has a tendency to naturally circulate as it is heated. Systems that use fluids other than water in the collector's tubes usually heat the water by passing it through a coil of tubing in the tank.

Many large commercial buildings can use solar collectors to provide more than just hot water. Solar process heating systems can be used to heat these buildings. A solar ventilation system can be used in cold climates to preheat air as it enters a building. And the heat from a solar collector can even be used to provide energy for cooling a building.

A solar collector is not always needed when using sunlight to heat a building. Some buildings can be designed for *passive solar* heating. These buildings usually have large, south-facing windows. Materials that absorb and store the sun's heat can be built into the sunlit floors and walls. The floors and walls will then heat up during the day and slowly release heat at night - a process called *direct gain*. Many of the passive solar heating design features also provide *daylighting*. Daylighting is simply the use of natural sunlight to brighten up a building's interior.

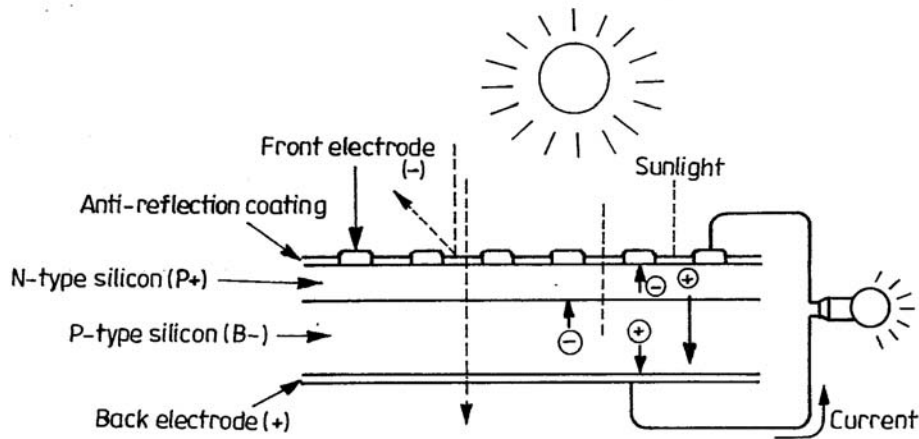


Fig. 1. The Photoelectric Effect.

SPACE APPLICATIONS

Solar arrays work well for generating power in space and power virtually all satellites. Most satellites and spacecraft are equipped with crystalline silicon or high-efficiency Group III-IV cells, but recently satellites have begun using thin-film amorphous-silicon-based solar panels.

ELECTROCHEMICAL, ELECTROSTATIC & ELECTROMAGNETIC ENERGY STORAGE

BATTERIES AND SUPERCAPACITORS

In the field of energy storage, two main parameters are fundamental for storage devices: the energy density and the power density. The first parameter defines the amount of energy that can be stored in a given volume or weight. The power density defines the way this energy can be stored into the device. The more this parameter is high, the longer the time for loading and unloading the amount of needed energy is reduced. The ideal storage device should propose both a high energy density, together with a high power density. This is unfortunately not the case, and compromises have to be done. Considering the battery technologies, the energy density is high, but with a poor power density. The opposite is the main characteristic of capacitors: a limited energy density with a high power density. New components, such as the supercapacitors, offer today an alternative to this dilemma. They are compromises between batteries and conventional capacitors (Fig. 2.). Their main characteristic is to propose both a high energy density together with a high power density. This leads to new applications for energy storage, even if the energy density is still lower than that one of the batteries.

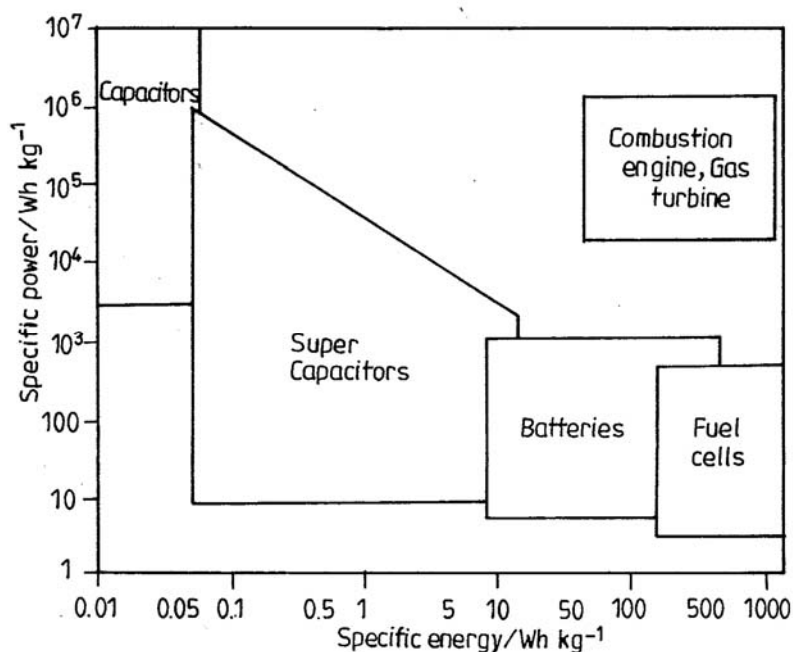


Fig. 2. Simplified Ragone plot of the energy storage domains for the various electrochemical energy conversion systems compared to an internal combustion engine and turbines and conventional capacitors (reproduced from ref. 3.)

LITHIUM – ION BATTERIES

In batteries, electrical energy is generated by conversion of chemical energy through redox reactions at the anode and cathode. As reactions at the anode usually take place at lower electrode potentials than at the cathode, the terms negative and positive electrode (indicated as minus and plus poles) are used.

The lithium ion battery employs a metal oxide material (such as lithium cobalt oxide LiCoO_2), or a material with a tunneled structure (such as lithium manganese oxide LiMn_2O_4) as its positive electrode. The negative electrode is typically a graphitic carbon. During the charge and discharge processes, lithium ions are inserted or extracted from interstitial space between atomic layers within the active material of the battery. During charge, the positive material is oxidized and the negative material is reduced. In this process, lithium ions are de-intercalated from the positive material and intercalated into the negative material. (Intercalated – a reaction where lithium ions are reversibly removed or inserted into a host without a significant structural change to the host). The reverse process is present during a discharge cycle.

The energy density of lithium-ion is typically twice that of the standard nickel-cadmium. There is potential for higher energy densities. The load characteristics are reasonably good and behave similarly to nickel-cadmium in terms of discharge. The high cell voltage of 3.6 volts allows battery pack designs with only one cell. Most of today's mobile phones run on a single cell. A nickel-based pack would require three 1.2 volt cells connected in series.

Lithium-ion is a low maintenance battery, an advantage that most other systems cannot claim. There is no memory effect and no scheduled cycling is required to prolong the battery's life. In addition, the self-discharge is less than half compared to nickel-cadmium, making lithium-ion well suited for modern fuel gauge applications. Lithium-ion cells cause little harm when disposed. Despite its overall advantages, lithium-ion has its drawbacks. It is fragile and requires a protection circuit to maintain safe operation.

CAPACITORS

Capacitors consist of two conductive parallel plates and separated by a dielectric insulator. The plates hold opposite charges which generate an electric field. Unlike in batteries where energy is stored in chemical form, capacitors store energy in the form of field.

The capacitance is defined as $C = (A/d) \epsilon_r \epsilon_0$

where A is the area of the parallel plates d is the distance between them, ϵ_r is the relative permittivity or dielectric constant and ϵ_0 is the permittivity of free space (8.854×10^{-12} F/m).

The energy stored by the capacitor is given by $E = (1/2) C V^2$

SUPERCAPACITORS

In 1997, researchers from CSIRO, Australia developed the first supercapacitor. This is basically a capacitor which is able to hold significantly more charge using thin film polymers for the dielectric layer. The electrodes are made of carbon nanotubes. The energy density of supercapacitors can be four times more compared to the normal capacitor.

Capacitors which store the energy within the electrochemical double-layer at the electrode - electrolyte interface are known under various names which are trade marks or established colloquial names such as 'double layer capacitors', 'supercapacitors', 'ultracapacitors', 'power capacitors', or 'gold capacitors'. 'Electrochemical double-layer capacitor' is the name that describes the fundamental charge storage principle of such capacitors.

However, due to the fact that there are, in general, additional contributions to the capacitance other than double layer effects, we will call these capacitors electrochemical capacitors.

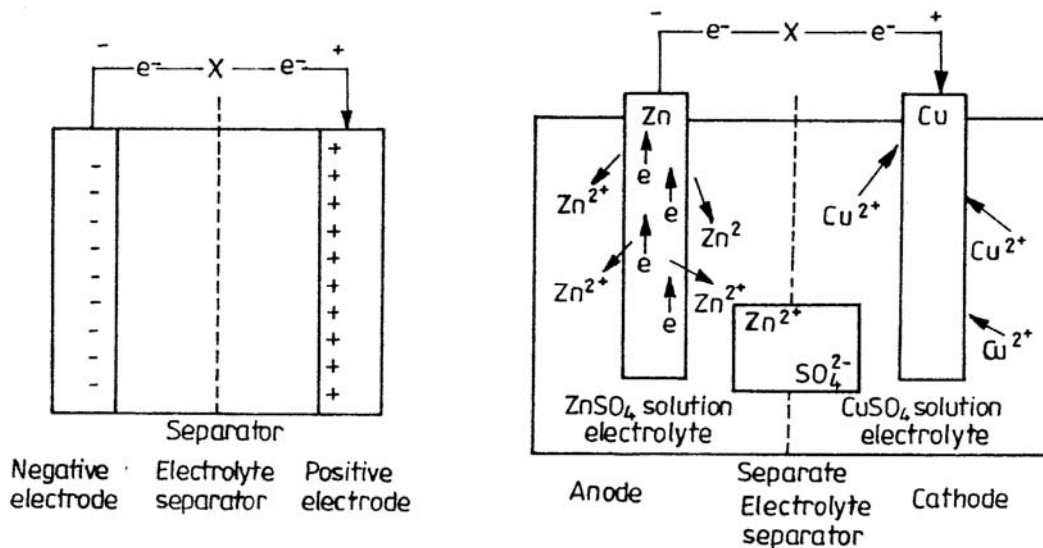


Fig. 3. Representation of electrochemical capacitor and battery (reproduced from ref. 3.)

Basic Principles of Supercapacitors

The basic principle of energy storage in a supercapacitor is based on creating a charge-separated state in an electrochemical double layer. In this case, energy storage is based on the separation of charges in the double layer across the electrode/electrolyte interface. The positive electrode is electron deficient whereas the negative electrode contains a surplus of electrons. The energy (W) stored in a capacitor as a function of the voltage applied (U) and the capacity (C) is given by the equation : $W = CU^2/2$.

Compared to conventional capacitors where a total capacitance of pF and mF is typical, the capacitance of and the energy density stored in the electrochemical double layer are high. In order to achieve a higher capacitance the electrode surface area is additionally increased by using porous electrodes with an extremely large internal effective surface. Combination of two such electrodes gives an electrochemical capacitor of rather high capacitance.

CLASSIFICATION OF ELECTROCHEMICAL CAPACITORS

Electrochemical capacitors may be distinguished by several criteria such as the electrode material utilized the electrolyte, or the cell design. With respect to electrode materials there are three main categories: carbon based, metal oxides and polymeric materials.

CARBON

Carbon in various modifications is the electrode material used most frequently for electrodes of electrochemical capacitors. Reasons for using carbon are manifold such as (i) low cost, (ii) high surface area, (iii) availability, and (iv) availability of established electrode production technologies. Carbons are available with a specific surface area of up to 2500 m²/g. There are researches going about to replace carbon nanotubes with ceramics for their superconducting properties.

Advantages over Batteries

Supercapacitors are well suited to replace batteries in many applications. This is because at the moment their scale is comparable to that of batteries, from small ones used in cellular phones to large ones that can be found in cars. Even though supercapacitors have a lower energy density compared to batteries, they avoid many of the battery's disadvantages.

Batteries have a limited number of charge/discharge cycles and take time to charge and discharge because the process involves chemical reactions with non-instantaneous rates. These chemical reactions have parasitic thermal release that causes the battery to heat up. Batteries have a limited life cycle with a degrading performance and acidic batteries are hazardous to the environment.

Supercapacitors can be charged and discharged almost unlimited number of times. They can discharge in a matter of milliseconds and are capable of producing enormous currents. Hence they are very useful in load leveling applications and fields where a sudden boost of power is needed in a fraction of a second. They do not release any thermal heat during discharge.

Supercapacitors have a very long lifetime, which reduces maintenance costs. They do not release any hazardous substances that can damage the environment. Their performance does not degrade with time. Supercapacitors are extremely safe for storage as they are easily discharged. They have low internal resistances, even if many of them are coupled together.

Even though they have a lower energy density, are bulkier and heavier than an equivalent battery, they have already replaced batteries in many applications due to their readiness in releasing power.

APPLICATIONS

Supercapacitors were initially used by the US military to start the engines of tanks and submarines. Most applications now a days are in the field of hybrid vehicles and handheld electronic devices.

Electrochemical capacitors are used as back-up memory for electronic devices like VCR circuits, CD players, cameras, computers, clocks, clock radios, telephones and other electronic equipments. Electrochemical capacitors also used in hybrid electric vehicles in combination with batteries as their power density is higher than batteries for load leveling. Electrochemical capacitors in combination with batteries occupy less space and are light, have excellent cold weather starting and increased battery life. Other uses of electrochemical capacitors include regenerative braking, unmanned monitoring units, uninterruptible power supplies (UPS), and high power lasers.

The supercapacitor has become available to the public. A commercial supercapacitor can hold 2500 farads, release 300 A of peak current with a peak voltage handling of about 400 V. The life-cycle of this supercapacitor is more than 1×10^6 charge/recharge cycles.

SUPERCONDUCTING MAGNETIC ENERGY STORAGE

Superconducting magnetic energy storage (SMES) system is a device for storing and instantaneously discharging large quantities of power. It stores energy in the magnetic field created by the flow of DC in a coil of superconducting material that has been cryogenically cooled. These systems have been in use for several years to improve industrial power quality and to provide a premium-quality service for individual customers vulnerable to voltage fluctuations. The SMES recharges within minutes and can repeat the charge/discharge sequence thousands of times without any degradation of the magnet. Recharge time can be accelerated to meet specific requirements, depending on system capacity.

How does it work?

A superconducting material enhances storage capacity. In low-temperature superconducting materials, electric currents encounter almost no resistance. The challenge is to maintain that characteristics without having to keep the systems quite so cold. However, the applications of superconductors have been limited by the conditions of low transition temperature, critical magnetic field and critical current density.

As an energy storage device, SMES is a relatively simple concept. It stores electric energy in the magnetic field generated by DC current flowing through a coiled wire. If the coil were wound using a conventional wire such as copper, the magnetic energy would be dissipated as heat due to the wire's resistance to the flow of current. However, if the wire is superconducting (no resistance), then energy can be stored in a "persistent" mode, virtually indefinitely, until required. Superconductors have zero resistance to DC electrical current at low temperatures so that ohmic heat dissipation is eliminated; hence the refrigerator is needed in the SMES to cool the coil. In AC applications, there are still electrical losses, but these can be minimized through appropriate wire architecture and device design. For both DC and AC applications, energy savings will be significant. The current carrying capacity of the wire is dependent on temperature and the local magnetic field. The optimal operating temperature for most of the devices will be 50-77 K.

The energy stored within the coil is given by $E = \frac{1}{2} LI^2$ where L is the inductance of the coil, and I is the current passing through it. The volumetric energy density is given by $U_D = B^2/2\mu_0$

SMES coils vary in size depending on the energy they store. The superconductor of choice for this application is a niobium-titanium alloy which needs to be kept at liquid helium temperature in order to superconduct. High-temperature superconductors, those that operate at liquid nitrogen temperature or above, are not as technically advanced at this point of time to be considered for a large-scale application such as this. Once SMES has established a foothold in the utility market based on conventional superconductors, high-temperature superconductors can be introduced to reduce capital and operating costs once their physical characteristics have improved, and the manufacturing processes are more mature.

Operation of an SMES System

The basic operation of a complete SMES system is very simple. The transmission voltage (from the AC network) is first stepped down from a few hundred kV to several hundred volts using a step-down transformer. This is then converted into DC which is fed into the superconducting coil. Hence when the power flows from the system to the coil, the DC voltage will charge up the superconducting coil and the energy is stored in the coil. The maximum energy stored depends on the design of the device. When the AC networks requires a power boost, say when there are sags, spikes, voltage and frequency instabilities, the coil discharges and acts as a source of energy. The DC voltage is converted back into AC voltage through the converter.

An SMES system includes a superconducting coil, a power conditioning system, a cryogenically cooled refrigerator and a cryostat/vacuum vessel. SMES are highly efficient at storing electricity (greater than 97% efficiency), and provide both real and reactive power. These facilities are used to provide grid stability in a distribution system and power quality at manufacturing plants requiring ultra-clean power, such as microchip fabrication facilities.

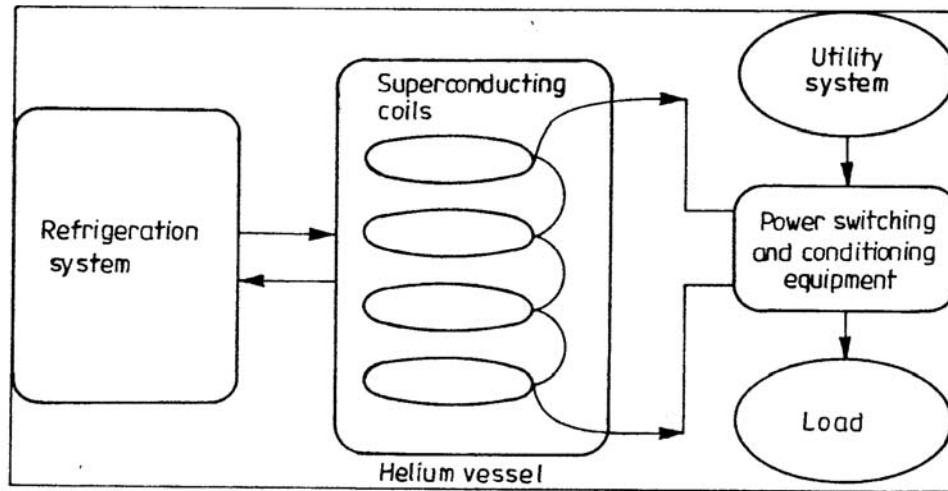


Fig. 4. Operation of superconducting magnetic energy storage system

How much energy does it store?

Energy is stored directly in a superconducting magnetic energy storage system. It is able to store energy with a loss of only 0.1% per hour (this is required for the cooling system), compared to a loss of about 1% per hour loss for flywheels. It is claimed that SMES is 97-98% efficient and it is better at providing reactive power on demand.

At this point SMES systems are able to store up to about 10 MW. Theoretically, a coil of around 150-500 m radius would be able to support a load of 5000 MWh, at 1000 MW; depending on the peak field and ratio of the coil's height and diameter.

Recent developments have tried to use silicone-based three-phase adjustable speed motor drives (ASDs), which bring down the scale of SMES to fit into lorry trailers. Storing energy in the range of 1-10 MWs, they are aimed at the power quality market.

Advantages of SMES

SMES systems are environmentally friendly because superconductivity does not produce a chemical reaction. In addition, there are no toxins produced in the process. SMES can be used in enhancing transmission line capacity and performance. In a SMES system, energy is stored within a magnet that is capable of releasing megawatts of power within a fraction of cycle to replace a sudden loss in line power. Since the SMES recharges within minutes and can repeat the charge and discharge sequence thousands of times without any degradation of the magnet.

Some SMES systems are designed to improve the power quality for critical loads and to provide carryover energy during voltage sags and momentary power outages. The system stores energy in a Superconducting coil immersed in liquid helium. It helps out overcome problems like sags, spikes, and voltage and frequency instabilities.

CHEMICAL ENERGY

Hydrogen Storage

Hydrogen contains more energy on a weight for weight basis than any other substance; it is also the lightest chemical element and therefore has a very low energy per unit volume. Hydrogen is a neutral energy carrier. This means that the environmental benefit of using hydrogen depends upon how the hydrogen is produced. Hydrogen can be produced from water and hydrocarbons in various methods by using renewable

energy sources like solar energy and wind energy. A renewable energy system using hydrogen as a carrier or for energy storage does not result in harmful pollutants being released to the natural environment. The most suitable method for storing hydrogen will depend on many factors including the volume to be stored, weight of the storage unit, storage time, space restrictions and the end use.

SOLID-STATE STORAGE OF HYDROGEN

Hydrogen can also be stored by the use of a reversible chemical reaction. This usually takes the form of the reaction of a metal with hydrogen to create a metal hydride. The reaction forms hydride at higher pressures and reverses to chemical 1 and hydrogen at lower pressures. These types of systems operate at room temperature and relatively low pressures. Storage is efficient in terms of volume but heavy due to the mass of metal hydride. Solid-state hydrogen storage can occur by one of the three generic routes:

Adsorption : (e.g. carbon and zeolite materials). Hydrogen molecule binds to the surface of the adsorbent in a weak reversible manner. The variation of attractive surface forces as a function of distance from the surface determine whether Vander Waals type physisorption of hydrogen occurs or whether the dissociation and chemisorption of atomic hydrogen takes place.

Absorption : (e.g. simple metal hydrides) Hydrogen molecules dissociate at the surface of the absorbent into hydrogen atoms. These atoms then diffuse into the solid to form a hydride; two hydrogen atoms recombine during the desorption process to form H_2 .

The host material initially dissolves some hydrogen as a solid solution (α -phase); as the hydrogen pressure and concentration of hydrogen in the host increases nucleation and growth of the hydride (β -phase) occurs. The thermodynamics of this can be explained by pressure composition isotherms. While the two phases, α and β , coexist the isotherms show a plateau, the length of which determines the amount of hydrogen that can be stored reversibly with small pressure variations. The two phase region ends at a critical point, T_C , after which the transition from α to β is continuous. The plateau pressure is strongly dependent on temperature and is related to changes in enthalpy and entropy.

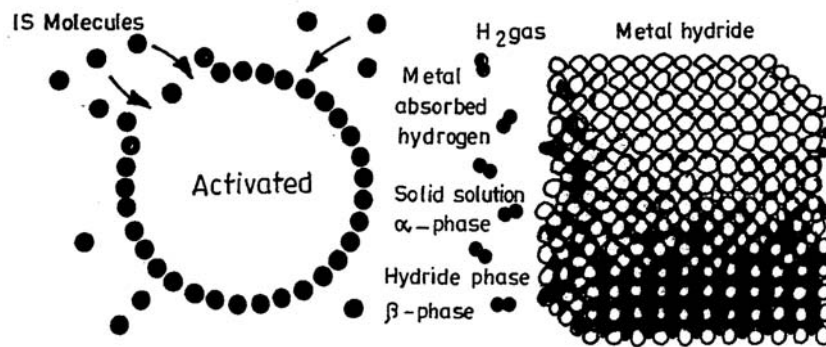


Fig. 5. Physisorption and chemisorption of hydrogen (reproduced from ref. 4.)

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Chemical Reaction : e.g., complex metal hydrides and chemical hydrides). Some of the lightest elements in the periodic table (e.g., Li, B, Na, Al) form stable ionic compounds with hydrogen. However, such compounds only desorb hydrogen at temperatures in the range 80 °C to 600 °C.

APPLICATIONS

A fuel cell combines hydrogen and oxygen to produce electricity, heat, and water. Fuel cells are often compared to batteries. Both convert the energy produced by a chemical reaction into usable electric power. However, the fuel cell will produce electricity as long as fuel (hydrogen) is supplied, never losing its charge.

In near future, hydrogen could also join electricity as an important energy carrier. An energy carrier moves and delivers energy in a usable form to consumers. Renewable energy sources like the sun and wind can not always provide energy all the time. But they could, for example, provide electric energy and hydrogen, which can be stored until it is needed. Hydrogen can also be transported (like electricity) to locations where it is needed.

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CHAPTER - 9

Carbon Materials

Carbon is the sixth element in the periodic table, it has six electrons and is listed at the top of column IV (group) consisting of silicon, germanium, tin and lead. The fourth group element has the general electronic configuration ns^2np^2 , where electrons of carbon give rise to the electronic configuration $1s^22s^22p^2$. The property of the element in the IV group varies in which carbon show nonmetallic behaviour, Si and Ge shows metalloid character, whereas tin and lead show metallic behaviour. They exhibit +4 oxidation state as most common oxidation state. In Carbon the $1s^2$ electrons are strongly bound core electrons and the $2s^22p^2$ contain the more weakly bound valence electrons. These valence electrons form $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals and it is these that are important in forming covalent bonds in carbon materials. Because the energy difference between the upper $2p$ energy levels and lower $2s$ level is small compared to the binding energy of the chemical bonds, these four states can mix with each other leading to an increased bonding character of the carbon atom with its neighbours. This mixing of $2s$ and $2p$ orbitals is called hybridization and the mixing of a single $2s$ level with one, two or three $2p$ states give rise to sp^n hybridization. The ability of carbon to form bond with itself is called catenation. Carbon has a strong tendency towards forming compounds with chains of C-C bonds (catenation) and/or double bonds. It is peculiar to certain elements alone and carbon has the ability to form long chain, whereas other elements like sulphur and silicon can form short chains.

Table 1. Classification scheme for carbon allotropes, molecular crystals and derived forms

sp^3	sp^2	sp^1
Diamond	Graphite	Carbyne
Cubic	Hexagonal	α - Carbyne
Hexagonal	Rhombohedral	β - Carbyne
		Chaoite
$sp^3 + sp^2 + sp^1$		sp^n (with $3 > n > 1$, $n \neq 2$)
Mixed forms of carbon	Intermediate forms of carbon	
	$3 > n > 2$	$2 > n > 1$
Amorphous carbon	Fullerene, C_x	Cyclo (N) carbons
Glassy carbon	$x = 60, 70, 84, \dots$	$N = 18, 24, 30, \dots$
Carbon black	(when $x = \infty$, $n = 2$)	(when $N = \infty$, $n = 1$)
Adamantine carbon	Carbon onions	
	Carbon nanotubes	

A phase diagram is the description of the stability domains of the different phases (gas, liquid, solid) of a pure species as a function of two intensive variables, such as the temperature, T and pressure, P. Though gaseous and liquid phases of any pure compound is unique, its solid phase may be polymorphic, "a polymorph is a solid crystalline phase of a given compound resulting from the possibility of at least two different arrangements of the molecules of that compound in the solid state", as with carbon. Carbons can exist in many forms as diamond, graphite, carbynes, activated carbons, fullerenes and carbon nanotubes and other cyclic forms. The mode of classification and their examples are given in the table 1. Besides the usual hybridization (sp^3 , sp^2 , sp^1), structures involving more than a single type of hybridization (mixed forms) and intermediate hybridization of type sp^n (with $3 > n > 1$, $n \neq 2$) are included. The former cover

mixed short-range order carbon species with more or less randomly distributed C atom, while the latter describe structure in which curvature introduces strains responsible for the mixture of different hybridization, for example the structure of fullerene C_{60} leads to attributing to the C atoms a hybridization intermediate between sp^2 and sp^3 i.e., $sp^{2.28}$. Carbon exists in different solid phases constitute allotropic forms, with each form desirable by a specific equation of state and differing by the spatial arrangement of its atoms. The allotropic forms of carbon are diamond, graphite and fullerene. The phase diagram of carbon is shown in Fig. 1. From this figure, one can select the values of parameters like pressure and temperature for the formation of different forms of carbon.

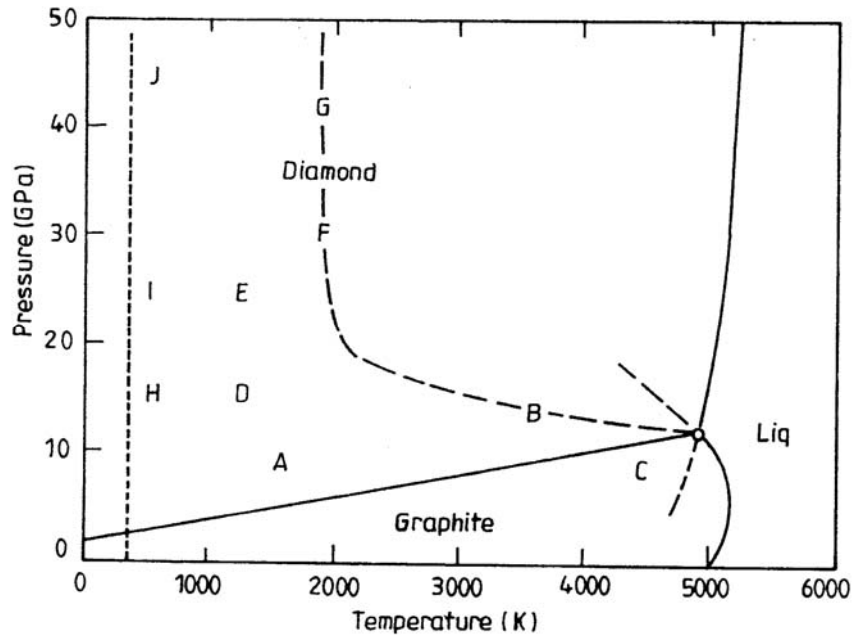


Fig. 1. The phase and transition diagram for carbon

DIAMOND

The diamond is sp^3 hybridization with cubic arrangement of crystal lattice, space group $Fd3m$, $a_c = b_c = c_c = 3.5597 \text{ \AA}$, with 8 atoms per unit cell as shown in Fig. 2. It is optically transparent and has greater thermal conductivity than that of copper at room temperature, which is explicable by the small mass of the C atoms, the symmetry of the crystal lattice, and the strong interatomic covalent bonds.

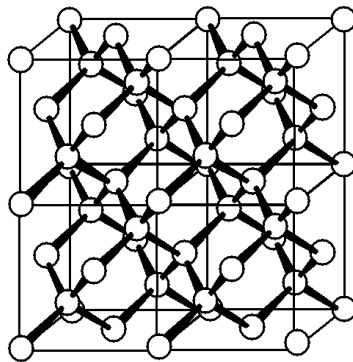


Fig. 2. Crystal structure of diamond; each carbon atom is bonded covalently to four neighbours forming a regular three dimensional pattern of atoms

CARBYNES

The existence of carbynes was questionable for long times because of the sample prepared are microscopic size and often associated with impurities. The stability is inferior to that of the diamond and meta stable with respect to hexagonal graphite. α - Carbyne ($-C\equiv C-C\equiv C-$)_n with poly-yne links of bond-lengths $\sim 1.20 \text{ \AA}$ (for $C\equiv C$) and $\sim 1.38 \text{ \AA}$ (for $C-C$) and parameters $a = 8.92 \text{ \AA}$; density: 2.68 g/cm^3 . β - Carbyne ($=C=C=C=C=$)_n with cumulene like, a resonant form of a carbyne, with single bond-length $\sim 1.28 \text{ \AA}$. and parameters : $a = 8.24 \text{ \AA}$; $c = 7.68 \text{ \AA}$; density 3.13 g/cm^3 . The conformation of chains as $-^{\ominus}C=C=C=C^{\oplus}- \leftrightarrow -C\equiv C-C\equiv C- \leftrightarrow -^{\oplus}C=C=C=C-$ and the C atoms in the chains must be even number. The presence of charges at the ends of the chains forces the single bonds to form an angle $\alpha_c = \pm 60^\circ$ (or $\pm 30^\circ$), so that the axes of successive chains are staggered laterally as shown in Fig. 3.

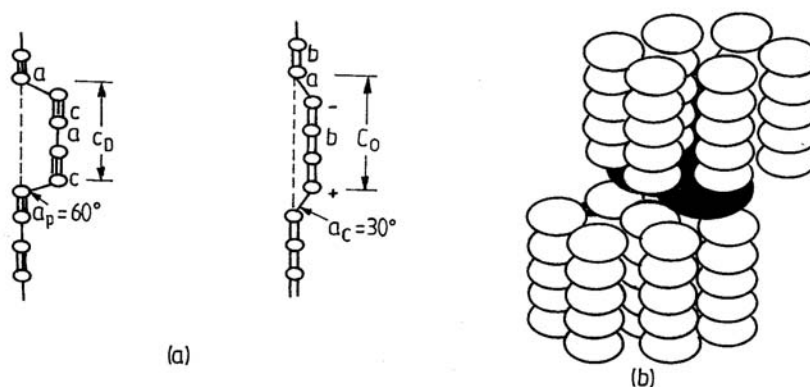


Fig. 3 (a) Carbyne chains, (b) stack of carbyne chains

GRAPHITE

Graphite is hexagonal crystal lattice, space group $P6_3/mmc$, with $a = b = 2.461 \text{ \AA}$, $c = 6.708 \text{ \AA}$, 4 atoms per unit cell. In graphite, two dimensional (2D) sheets of carbon are stacked along the c axis at 3.354 \AA from each other, with each atom in a layer symmetrically bonded to three other atoms at 1.421 \AA , thus forming a honeycomb of sp^2 hybridized carbon atoms. The relative position of two successive layers is determined by translation vectors leading to formation of different stacking of graphitic layers as shown in Fig. 4 as AAA type with no translation vector parallel to the layers; ABAB type, with translation vector $+\Delta$ and $-\Delta$; ABCA type with a single translation vector Δ .

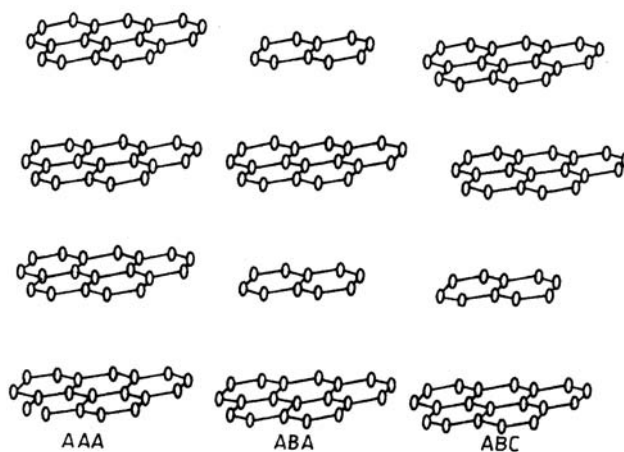


Fig. 4. Stacking of graphitic layers

Graphite is highly refractory and thermally exceptionally stable. The thermal conductivity along the layers is comparable to that of diamond. Graphites are used as lubricants due to its low resistance to shearing stresses perpendicular to the crystallographic c axis. The presence of electrons (one per C atom) confers a particular structure to the energy bands of solid. The valence and conduction bands slightly overlap (~ 0.04 eV) at the Fermi level, where the electron density is slight, giving to graphitic semi-metallic characteristics. Although the concentration of charge carriers is small, the electrical conductivity of graphite along the layers is high because of the exceptional mobility of the carriers. Another property is exceptional diamagnetism at room temperature and mostly highly diamagnetic substance after the superconductors. The intercalation reaction can preserve the structure and the hybridization of carbon layers, large number of intercalated compounds can be prepared with electronegative as well as electropositive species. Typical use of one type of intercalated compounds is in lithium ion batteries.

AMORPHOUS CARBONS

The carbon materials which are non crystalline in nature, issued from the organic matter and therefore containing hydrogen and, eventually, other heteroatoms such as oxygen and/or nitrogen, with no long range ordered carbon. These types of carbon materials show different varieties of pseudo-polymorphic carbons, which often have physical properties interesting for industrial applications. Various forms of amorphous carbon and their applications are given in the table 2.

Table 2. Various forms of amorphous carbon and their applications

Forms of Carbon	Application
Activated Carbon	Purification of water and air
Carbon black	To reinforce tires
Carbon fiber composites	Ultra light graphite sporting goods and air craft brakes
Carbon foams	Fire retardant foams

THE FULLERENES

The fullerene is a spheroidal or polyhedra shaped carbon molecule. It can be inscribed in a sphere and is composed of 20 triangular equilateral faces, with 12 apices, each at the junction of 5 triangles. The Fullerene was discovered in 1984 by Harry Kroto and Richard Smalley at Rice University. For many years, diamond and graphite were believed to be the only carbon allotropes. Kroto, Smalley and their colleagues were studying carbon clusters and came upon some heavier molecules that added up to exactly 60 carbon atoms. The discovered material was called a buckminsterfullerene. It was called so because of the resemblance to the polyhedra architectural structure of Buckminster Fuller. The carbon molecule very closely resembles the soccer ball shape. It has 20 hexagons and 12 pentagons; structural studies of C_{60} has shown to have face centered cubic (FCC) lattice as shown in the Fig 5. The lattice parameter is $a = 14.17 \pm 0.001$ Å, with a van der Waals space of 2.9 Å. Because of the high symmetry of the molecule, the ^{13}C NMR spectrum and the IR absorption spectrum are particularly simple. Doping the C_{60} crystals with a metal M changes the conductivity also yields a phase superconducting for temperature less than 18 K. The functionalisation of C_{60} is relatively well known like reduction, oxidation, alkylation, and metal complex formation. The characteristics of fullerene are so close to those of graphite and that the molecules are hollow which leads to form inclusion derivatives ($M_x @ C_{60}$). $M_x @ C_{60}$ behaves as superconductors. The possible metal doping in C_{60} is given in table. 3. The temperature (T_C) at which they behave as superconductors is also given. Heating C_{60} at high pressure and temperature leads to polymerization of the molecules by forming intermolecular bonds, as evidenced from a decrease in their distance from 2.9 Å in pristine C_{60} to 1.64 – 1.68 Å. The resulting three dimensional phases is found to be harder than diamond.

Fullerenes can be made in a variety of ways. There are also many different fullerene type species. 60, 70, 76, 84 and many other fullerene molecules can be formed. During formation of fullerenes, it is common for other carbon allotropes to form such as diamond, graphite, and carbon nanotubes. Several different methods are used to generate these unique molecules. These include the electric arc process, 1st generation combustion, 2nd generation combustion, and others.

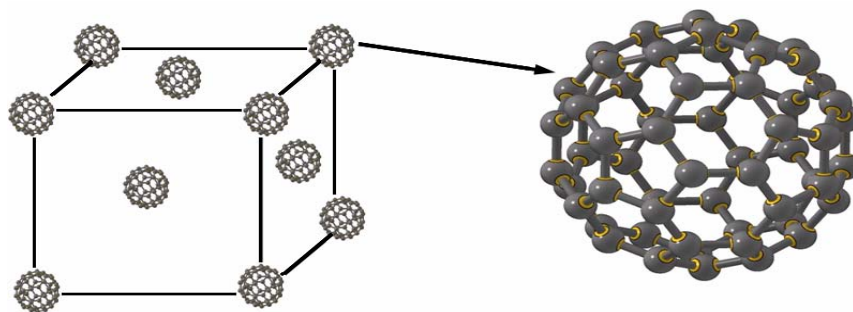


Fig. 5. FCC unit cell of the buckminster fullerene crystal. Each lattice point has a C_{60} molecule

Table 3. Alkali metal doped C_{60} ($M_x @ C_{60}$), and their Curie temperature

A_3C_{60} (A – metal)	T_c , K
K_3C_{60}	19.3
Rb_3C_{60}	29.6
<hr/>	
A_3XC_{60}	
Cs_2RbC_{60}	33
$K_3Ba_3C_{60}$	5.6
$Rb_3Ba_3C_{60}$	2.0
Li_4CsC_{60}	8.0
Li_3CsC_{60}	10.5

Electric Arc Synthesis

The process is carried out using a graphite rod in a low pressure chamber along with an inert gas and vaporizing the rod with electrical current. The by-products and fullerenes must then be separated with solvents. The carbon arc method developed at the University of Arizona was the first method used to make fullerenes. It is a very low production synthesis method and therefore expensive. This process creates a variety of different fullerenes as well as nanotube type molecules and endohedral fullerenes. The endohedral fullerenes have other molecules trapped inside their structure.

Combustion Synthesis

First Generation Combustion Synthesis Method involves a continuous low flow of hydrocarbon fuel is burned at low pressure in a “flat” flame. Solvents are used to separate fullerenes from other combustion by-products. Whereas in the Second Generation Combustion Synthesis Method a continuous high flow of hydrocarbon is burned at low pressure in a 3-dimensional chamber. Second generation combustion synthesis method has advanced that of the first generation process, enabling both high production and high purity of the material obtained. Nan carbon (a manufacturing concern) is now capable of producing > 95% purity fullerenes or fullerene mixtures. It can also tailor the production conditions to create materials optimized for specific customer requirements. Economical production of higher fullerenes, the rarer forms of carbon, is also possible.

Laser vaporization

A laser beam is focused on the graphite and extreme temperatures are created. The carbon breaks apart and reforms into fullerenes and other carbon molecules when blasted with inert gasses to cool it. When the graphite is impregnated with metal atoms, endohedral fullerenes form. Endohedral fullerenes are fullerenes filled with an atom of another element. They are also termed dopyballs. Impregnated fullerenes are an area

of current research. Doped fullerenes have a lot of potential in many different fields. These fullerenes have a large variance in properties due to what is impregnated inside the fullerene molecule. Nitrogen impregnated fullerene can be used for quantum computers and other molecules entrapped fullerenes can be used in photovoltaic cells. Interesting properties arise with such a versatile molecule. The C_{60} molecule is known to rotate very rapidly at room temperature while it is in the solid state. This presents a liquid like behavior that is very strange for a solid. The rehybridization that occurs during the formation of the molecule creates an enhanced electron affinity measured to be 2.65eV and has higher electronegativity than most hydrocarbons. It also exhibits conducting properties at higher temperatures and superconducting properties at 19 K. Fullerenes dissolved in non-polar solvents create unique colors like a red-wine color to deep purple for C_{60} and C_{70} molecules in benzene.

USES FOR FULLERENES

Quantum Computers (N doped fullerenes)

Properties of $N@C_{60}$ -The only Physical quantity of interest is the spin of the encapsulated atom. Repulsive interaction between the Fullerene cage and the encapsulated atom does not allow any charge transfer. The electrons of the encased atom are tightly bound than in the free atom. Nitrogen retains central site position inside the fullerene cage. The encapsulated Nitrogen atom can be considered as an independent atom, with all the properties of the free atom. The charge is completely screened, the Fullerene cage does not take part in the interaction process and it can be considered as a trap for the Nitrogen encased atom. This technology could be used to create nano storage devices and nano computers.

Antioxidants

Fullerenes are powerful antioxidants, reacting readily and at a high rate with free radicals, which are often the cause of cell damage. Fullerenes hold great promise in health and personal care applications where prevention of oxidative cell damage is desirable, as well as in non-physiological applications where oxidation and radical processes are destructive in nature. (Food spoilage, plastics deterioration, metal corrosion).

Biopharmaceuticals

Major pharmaceutical companies are exploring the use of fullerenes in controlling the neurological damage of such diseases as Alzheimer's disease and Lou Gehrig's disease (ALS), which are results of radical damage. Drugs for atherosclerosis, photodynamic therapy, and anti-viral agents are also in development. They can be used for recognition of HIVP.

Polymer Electronics and Bulk Polymers

Fullerenes are chemically reactive and can be added to polymer structures to create new copolymers with specific physical and mechanical properties. They can also be added to make composites. Much work has been done on the use of fullerenes as polymer additives to modify physical properties and performance characteristics. Currently, the record efficiency for a polymer solar cell is a fullerene/polymer blend, where the fullerene acts as the n-type semiconductor. Polymer transistors and photodetectors have also been developed using the n-type semiconducting properties of fullerenes.

It is viable now that the great diversity of the fullerene will lead to many great new ideas and inventions. This newly found molecule promises to serve many functions. The fullerenes are still in the very early ages of development, and much knowledge on the fullerene is needed to exploit their potential.

CARBON NANOTUBES

The discovery of fullerenes provided exciting new insight into carbon nanostructures and how architectures built from sp^2 carbon units based on simple geometrical principles can result in new symmetries and structures like carbon nanotubes. Carbon nanotubes were first discovered in 1991 by Sumio Iijima of the

NEC Corporation in Tsukuba, Japan. Wrapping planar graphitic sheet into cylinders results in the nanotube structure, where Single Walled Nanotube (SWNT) consists of singular graphene cylindrical walls with diameter ranging between 1 and 2 nm as shown in Fig. 6. Individual SWNTs have uniform diameter, show a strong tendency to pack together in larger bundles. The packing occurs in a regular triangular lattice structure with an intertube spacing in each of the bundles that corresponds to about 0.315 nm and a lattice parameter of 1.7 nm.

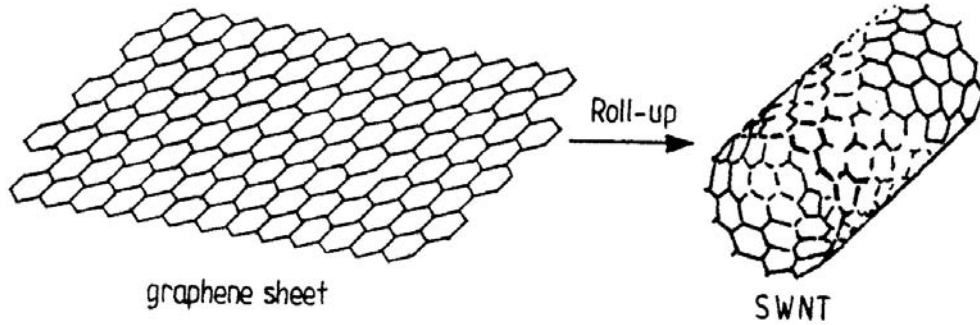


Fig. 6. The graphene sheet rolled to form cylindrical nanotube (SWNT)

Multi Walled Nanotube (MWNTs) has thicker walls, consisting of several coaxial graphene cylinders separated by a spacing (0.34 nm) that is close to the interlayer distance in graphite. The outer diameter of the MWNTs range between 2 and 25 nm and the inner hollows range from ~ 1 to 8 nm. In MWNTs there is no three dimensional ordering between the individual graphitic layers, suggesting that the interlayer structure is turbostratic. This results from the severe geometrical constraints of having too much of open edges when forming continuous cylindrical geometry and at the same time maintaining a constant interlayer spacing.

CLASSIFICATION OF CARBON NANOTUBES

The structure of the single wall carbon nanotube (SWCN) is determined by the orientation of the hexagonal ring of the carbon atoms in the honeycomb lattice relative to the axis of the nanotube. Some examples of the tubes are shown in Fig. 7 and it can be seen that the direction of the hexagonal ring can be taken as almost arbitrary without any distortion to the ring. However, there will be distortion due to the curvature of the tube. This means there are many possible structures for a carbon nanotubes even though the tube is always cylindrical in shape.

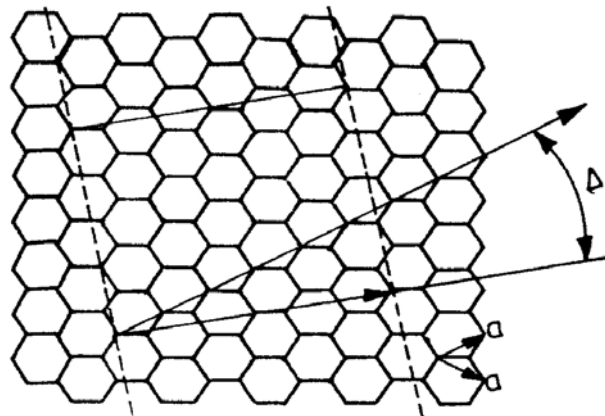


Fig. 7. Basic Structure of a sheet of graphene. Consider the carbon atoms to be placed on each point on the edge of the hexagon

The basic structure of a SWCN is specified by a single vector called the chiral vector C_h . In Fig. 7 this vector is defined as \vec{OA} and this is the section of the nanotube perpendicular to the nanotube axis, which when rolled up is the circumference of the tube. Fig. 7. shows the unrolled lattice of the nanotube, and in this case, the direction of the nanotube axis is given by the vector \vec{OB} . The lattice can then be rolled to form a cylinder by lining up the points so that O is on top of A and B is on top of B'. The chiral vector C_h is then determined by the real space lattice vectors a_1 and a_2 , which are defined and this leads to the following equation: $C_h = na_1 + ma_2 = (n, m)$

The main symmetry classification of a tube is defined as being either achiral or chiral. An achiral tube is defined as one where the mirror image of the tube is identical to the original one. A chiral tube is then defined as a tube where the mirror image cannot be superposed onto the original tube and they show spiral symmetry. There are two types of achiral tubes, which are named armchair and zigzag nanotubes. These two types can be seen in Fig. 8 where (a) is an armchair tube and (b) is a zigzag tube. These two tubes get their names from the shape of the cross-sectional ring at the edge of the nanotubes. An armchair nanotube is then defined as the case where $n = m$ in equation 1, a zigzag corresponds to the case where $m = 0$. All other chiral vectors corresponds to the production of a chiral nanotube but this is subject to the constraint that m is less than or equal to n .

This leads to the cases that all armchair nanotubes are metallic, and zigzag nanotubes are only metallic if n is a multiple of 3. Fig. 9 shows which carbon nanotubes are predicted to be metallic and which are semiconducting, denoted by the yellow and blue circles respectively. It can be seen from this diagram that approximately one third of carbon nanotubes are metallic while the other two thirds are semiconducting.

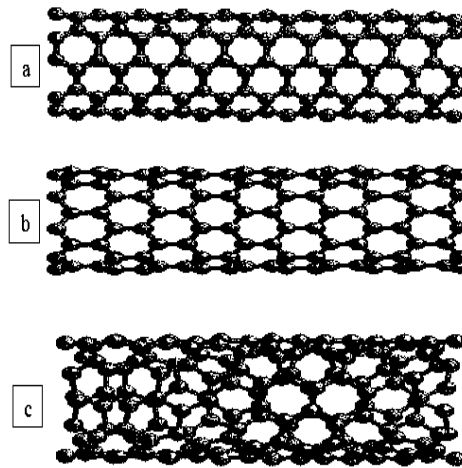


Fig. 8. Three different classification of nanotubes, (a) shows a (9,0) zigzag tube, (b) shows a (5,5) armchair tube and (c) shows a (6,4) chiral tube

One basic property of the semiconducting nanotube is the fact that the band gap in these types of tubes is inversely proportional to the radius. Thus, the larger nanotubes will have a smaller band gap than the nanotubes with a smaller diameter. This result is also independent of the chiral angle, so two tubes with similar diameters should have the same band gap, if they are both semiconductors.

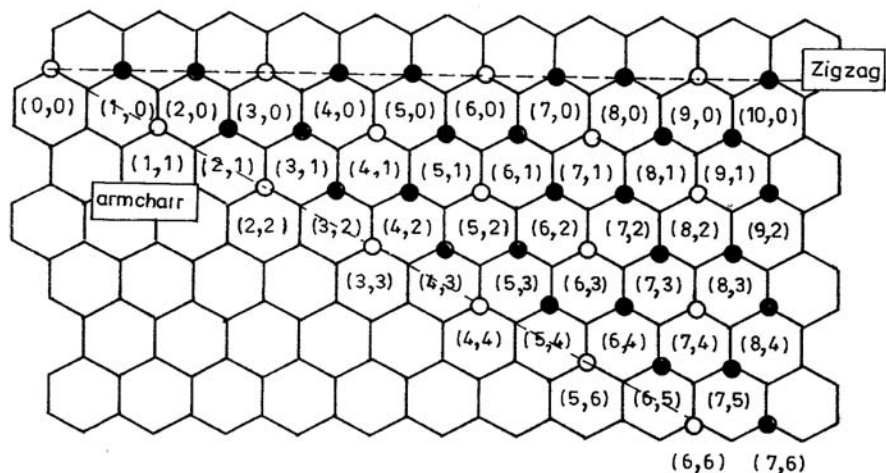


Fig. 9. The carbon nanotubes (n,m) that are metallic are denoted by circles and the semiconducting ones are denoted by spheres

Synthesis of Carbon Nanotubes

The carbon nanotubes were first noticed at the ends of the graphite electrodes used in an electric arc discharge employed in fullerene synthesis and the structures were examined by transmission electron microscopy (TEM). Decomposition of hydrocarbon gases by transition metal catalyst particles (Co, Fe, Ni) has been used to produce carbon nanofibres that are similar in dimensions to the nanotubes, but far away in structural perfection. SWNTs were first made by the electric arc through the introduction of catalyst species (Fe, Co) into the carbon plasma. Several metal catalysts have been tried, but good yield of carbon nanotubes has been obtained with Co, Ni and bimetallic systems such as Co-Ni, Co-Pt, and Ni-Y as catalysts. Another effective way to produce SWNTs is by using laser evaporation. It was shown that nanotubes could be obtained with good uniformity in size and structure (helicity). Depending on the temperature of the oven in which the nanotubes are grown, the diameter varied between 1 and 5 nm diameter; the higher the temperature (range between 800 to 1200 °C) the larger the nanotubes diameter. Other alternative strategies for the synthesis of nanotubes are through catalytic chemical vapor deposition (CVD) or using well defined porous inorganic membranes (such as alumina) as templates wherein a disordered form of carbon is deposited by CVD and graphitized further at higher temperature to yield nanotubes. The advantage of such template based methods is that the size of the particles and the pores, which determine the size of the nanotubes, can be controlled prior to the deposition of carbon. The length of the nanotubes formed can be controlled by adjusting the amount of carbon vapor feedstock supplied and the thickness of the membranes. By removing the templates after the nanotubes growth, freestanding arrays of highly graphitized nanotubes can be formed.

APPLICATIONS OF CARBON NANOTUBES

The numerous properties that carbon nanotubes possess could lead to many diverse applications for their use. One of the primary uses could be in electronic devices where their size could be an important fact in the drive towards smaller and smaller devices, which is reaching the nanometer scale. The nanotube may eventually be used as the interconnections between electronic components and as logic and storage devices. Another application is to use tubes as devices to store energy, where they could be used as batteries or fuel cells. One of the most promising applications in this area is the hydrogen fuel cell, which may be used as a source of portable energy in the future. The hydrogen fuel cell works by converting the hydrogen to water and releasing electrical energy in the process. The main problem with hydrogen is the fact that it is a flammable gas, which means it is difficult to store. There are some materials (Palladium for example) that absorb hydrogen and then release it again. However, it was discovered in 1997 that it was possible to store

various gases in single wall carbon nanotubes, hydrogen being one of these. This marks them out as one of the prime candidates for use in fuel cell technology.

Carbon nanotubes have a structure, which is almost perfect, the absence of virtually any defects leads to an enhancement in the strength of the material and these tubes rank among the strongest known materials. Nanotubes are exceptionally rigid with a Young's modulus in the terapascal range, this makes them almost an order of magnitude more rigid than steel. In fact, single wall carbon nanotubes are so strong and light that it would be possible to construct a wire that extended into space without it breaking under its own weight. These features indicate that single wall carbon nanotubes may well replace synthetic graphite fibers and revolutionize the materials industry. There are also many other applications where the carbon nanotube may be useful, from electronic transistors to field emission lamps for use in displays and there unique properties will mean that they will become important in many applications as research into them carries on.

Carbon nanotube based sensors and Targeted Drug Delivery

Medicines encapsulated in carbon nanotubes are well suited for targeted drug delivery. Functionalized carbon nanotubes with groups such as COOH, NH₂ and OH for binding biomolecules such as DNA, antibody-antigen, bioreceptors and proteins for developing nanoimplantable sensors and actuators. On this basis, one can design a targeted drug delivery system. Interfacing biomolecules with carbon nanotube will be of immense importance in development of highly sensitive and selective miniaturized biocompatible sensors and actuators with dimensions in micro and nano range. This will revolutionise in vivo early diagnosis and targeted drug delivery.

Molecular motors

In living systems various kinds of movements of vital organs and muscles take place through different systems of molecular motors, such as, myosin-actin, microtubules-kinesin, microtubules-dynein, microtubules-bacterial flagella motor. It is possible to extract motors from their native environment, prepare assemblies of them on a plane surface. For these motors to be useful in nanofabrication, it is essential that external control can be applied to the following properties: (a) translocation speed; (b) translocation direction; (c) activation and arrest. These characteristics can be controlled by altering the chemical and/or the physical environments of the motors.

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CHAPTER – 10

Reactions in Solid State

INTRODUCTION

The study of reactions involving solids is an important aspect of solid state chemistry from the point of view of understanding the influence of structure and imperfections on the chemical reactivity of solids. It is important to identify the factors governing solid state reactivity in order to be able to synthesize new solid materials with desired structure and properties. A solid state chemical reaction in the classical sense occurs when local transport of matter is observed in crystalline phases. This definition does not mean that gaseous or liquid phases may not take part in solid state reactions. However, it does mean that the reaction product occurs as a solid product. Solid state reactions differ from those in homogeneous fluid media in a fundamental respect; whereas reactions in the liquid or the gaseous state depend mainly on the intrinsic reactivity and concentration of the chemical species involved, solid state reactions depend to a large extent on the arrangement of the chemical constituents in crystals. The fact that the constituents are fixed in specific positions in crystals introduces a new dimension in the reactivity of solids, not present in other states of matter. In other words, chemical reactivity is determined more often by the crystal structure and defect structure of solids rather than by the intrinsic chemical reactivity of the constituents.

FEATURES OF SOLID STATE REACTIONS

- In solution the reactivity is mainly dependent on the electronic properties of the reactants. On the other hand, in crystals it depends on a balance between steric packing factors and electronic properties. There are cases of similar behaviour of different compounds in isostructural crystals and of different reactivity of the same compound in different crystal phases, only the phase that allows a favorable topochemistry being reactive.
- Solid state reactions are diffusion controlled reactions.
- Solid state reactions are generally initiated at the points of defects or near impurities, which are likely to provide pockets of free space for molecular motion. Sometimes it is possible to induce a reaction in a perfect crystal simply by touching it with a pin.
- Most of the solid state reactions are exothermic in nature.
- Solid state reactions are thermodynamically controlled.
- Atomic arrangement in the reactant crystal remains unaffected during the course of the reaction, except for changes in dimension in one or more directions i.e. topochemically controlled.
- The solid state unimolecular reactions are usually easier than processes that require an encounter of two or more chemical entities, unless the crystal geometry is such that reacting counterparts are favorably positioned side by side; thus, there are cases in which proper orientation of reacting group's speeds up the reaction in the crystal with respect to solution or the melt. When this is not the case, solid state reaction rates are slower than solution ones. Diffusion and/or mother-daughter separation processes are often the rate determining steps in solid state reactions, but in many cases the kinetics are biased by the inhomogeneity of the medium. Hence it is difficult to expect a simple dependence of reaction rate on reactant concentration.
- The intrinsic reactivity of a molecule is less important than the nature of the packing of the neighbouring molecules around the reactants (in the case of organic solid state reactions).
- In a crystal, the possible types of intermolecular contacts, space symmetries with relation to the nearest neighbours and directionality of approach of the relevant molecular moieties are strictly limited and well defined. This brings out dramatic differences between solid and solution state reactivities (in the case of organic solid state reactions).
- Because of structural and packing effects, interesting reaction products may be obtained only in the solid state and not in solution.
- Many reactions do not involve the movement of molecules but even then the reactions occur very fast. The molecules in the crystals are so designed as to engineer them to react in a particular fashion. This is a diffusionless reaction and this type of reaction comes under the category of crystal engineering.

KINETICS OF SOLID STATE REACTIONS

Since the solid state reactions may involve one or more of the elementary (rate-limiting) steps: (i) sorption phenomena (adsorption and desorption), (ii) reaction on the atomic scale (homogeneous or interface reaction), (iii) nucleation of a new phase (in the bulk or at the surface of the reacting solid), and (iv) transport phenomena (diffusion or migration), these reactions show complex rate behaviour that is not easily understood and cannot easily be fitted to a single kinetic equation. These reactions are mainly diffusion controlled and the kinetics proceeds through a definite model. General models for describing solid state reactions are given in table 1.

DIFFUSION MODEL

The rate, in the cases of most reactions between solid substances, is limited by diffusion of the reactant through the layer of the product. As the reaction proceeds in the solid state, a one dimensional diffusion process with constant diffusion constant is governed by equation:

$$D(\alpha) = \alpha^2 = k.t/x^2 \quad \text{----- (1)}$$

where 'D' is the diffusion constant, 'k' is the rate constant, 'x' is the thickness of the reacting layer at any time 't' and 'α' is the fraction of the total product formed.

NUCLEI-GROWTH MODEL

This model is concerned with the nucleation of the product at active sites and the rate at which the nucleated particles grow. Two common equations for the kinetics of reactions involving nucleation are discussed.

Prout-Tompkins equation : If the rate of the solid state reaction is assumed to be controlled by linearly growing nuclei that branch into chains then the following equation can be used.

$$\ln(\alpha/1-\alpha) = k.t \quad \text{----- (2)}$$

Avrami-Erofeyev equation : If the rate of a solid state reaction is assumed to be governed by random nuclei that grow in three dimensions and ingest other nuclei, then the following equation can be used. The value of 'n' varies and is assigned to be 1/4.

$$-\ln(1-\alpha)^n = k.t \quad \text{----- (3)}$$

'n' also take values of 1/3, 1/2, 2/3 and 1 for different reaction systems.

PHASE-BOUNDARY MODEL

If the solid state reaction is assumed to be controlled by the advancement of phase boundaries from outside of a crystal to inside, then a series of equations can be derived. If a reaction is assumed to react along one direction, then the rate is a function of time only and a zero order rate equation is applied :

$$1-\alpha = k.t \quad \text{----- (4)}$$

OTHER EQUATIONS

Power-law equation : It has no theoretical basis but it has been used to analyze solid state rate data, where $n = 1/4, 1/3, 1/2$ and 1.

$$\alpha^n = k.t$$

Equations based on the concept of reaction order : Since the concept of molecularity of a reaction is not well defined for solid state reactions, kinetic equations based on order are not widely used. Nevertheless, sometimes data are analyzed in terms of order of reactions. Equations (i), (ii), and (iii) for first, second and third order reactions respectively have been used.

$$1-\alpha = k.t \quad \text{----- (i)}$$

$$\ln \alpha = k.t \quad \text{----- (ii)}$$

$$1/(1-\alpha) = k.t \text{ ----- (iii)}$$

Table 1. Commonly employed models for describing Solid State Reactions

Name of the model	f(α)	G(α)
Random Nucleation Deceleratory first order	(1-α)	-ln(1-α)
Generalized n th order	(1-α) ⁿ	1/n(1-(1-α) ⁽ⁿ⁻¹⁾)
1D or 2D Avrami-Erofeyev	2(1-α)(-ln(1-α) ^{1/2})]	(-ln(1-α) ^{1/2})
2D or 3D Avrami-Erofeyev	3(1-α)(-ln(1-α) ^{2/3})	(-ln(1-α) ^{1/3})
3D Avrami-Erofeyev	4(1-α)(-ln(1-α) ^{3/4})	(-ln(1-α) ^{1/4})
Generalized Avrami-Erofeyev	n(1-α)(-ln(1-α) ^{n-1/n})	(-ln(1-α) ^{1/n})
Contracting area & Sharp interface controlled reaction	(1-α) ^{1/2}	2(1-(1-α)) ^{1/2}
Contracting volume & Sharp interface controlled reaction	(1-α) ^{1/3}	3(1-(1-α)) ^{1/3}
Generalized model by Sestak	(1-α) ⁿ (-ln(1-α)) ^p α ^m	---
Prout-Tompkins Model	(1-α) α	(ln α/(1-α))
One dimensional Diffusion	½ α	(α ²)
Two dimensional Diffusion	-ln(1-α)-1	(1-α)ln(1-α) + (α)
Three dimensional Diffusion (Jander model)	3(1-α) ^{2/3} / (2(1-(1-α) ^{1/3} -1) ²)	(1-(1-α) ^{1/3}) ²
Three dimensional diffusion (Ginstling-Brounshtein model)	3/2((1-α) ^{-1/3} -1)	(1-2(α)/3)-(1-α) ^{2/3})

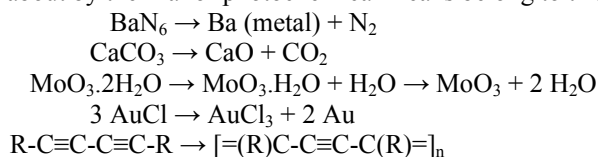
TYPES OF SOLID STATE REACTIONS

Solid state reactions are classified into two types : (A) Homogeneous and (B) Heterogeneous. The former involves reactions by a single compound whereas the latter involves reactions between two different compounds. So the reactions involving solids, distinction can be made between five different reaction types, namely processes in which

- (i) single solid yielding products, as in the decomposition and polymerization reactions;
- (ii) solid + solid giving products, as in the formation of complex oxides from simpler components;
- (iii) solid + gas yielding products, as in oxidation;
- (iv) solid + liquid resulting in products, as in intercalation; and
- (v) reactions at the surface of a solid, as in electrode reactions.

Reactions involving a Single Solid Phase

Decomposition of inorganic solids and dimerization as well as polymerization of organic molecules in the solid state brought about by thermal or photochemical means belong to this category of reactions.



Decomposition of salts such as metal carbonates, oxalates, azides and ammonium perchlorate have been studied for quite some time and the underlying mechanisms are fairly well established. The crucial step in decomposition reactions, as established from kinetic studies, is nucleation. Kinetic data plotted as fraction of the solid decomposed vs. time show typical sigmoid curves (Fig. 1.) consisting of at least three different periods : induction period (A), acceleration period (B) and decay period (C). These kinetic curves are interpreted in terms of a mechanism involving the initiation of the reaction at specific sites of the solid to give product nuclei (nucleation in region A), followed by their growth. Growth occurs by interfacial reaction at the product-reactant interface. As the reaction proceeds, the interface expands continuously, making the reaction accelerate up to the inflexion point B. Beyond this point, growing nuclei seem to overlap, leaving behind isolated chunks of unreacted material. The decreasing reaction rate in period C is likely to be due to the decrease in the interfacial area as the reaction goes towards completion. In the decay region C, the reaction frequently follows either the unimolecular law or the contracting cube law [eq. 2 or 3].

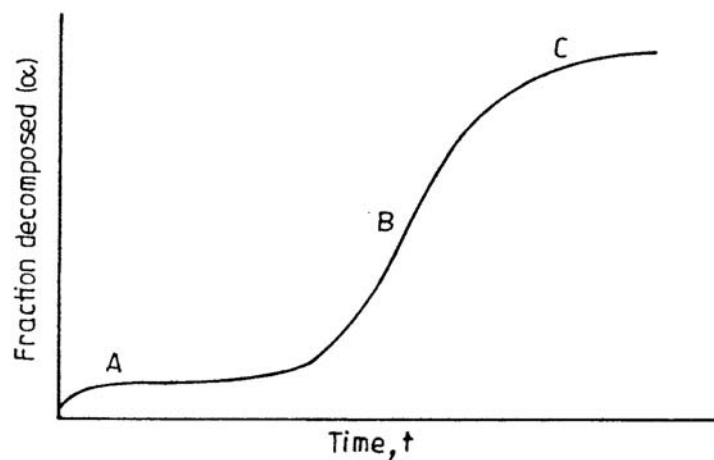


Fig. 1. Typical single solid decomposition curve showing fraction decomposed, α , as function of time, t

Formation and growth of nuclei have been observed in single crystals in several decomposition and dehydration reactions.

Solid-Solid Reactions

Two solids can react entirely within the solid phase, yielding solid products. Reactions of this type occurring between several inorganic solids such as metal oxides, halides, carbonates, sulphates and so on were studied some years ago by Hedvall. They fall into two categories : addition reactions (e.g., $\text{ZnO} + \text{Fe}_2\text{O}_3 \rightarrow \text{ZnFe}_2\text{O}_4$) and exchange reactions (e.g., $\text{ZnS} + \text{CdO} \rightarrow \text{CdS} + \text{ZnO}$). The general mechanism of solid-solid reactions consists of the initial formation of one or more solid products that spatially separate the reactants. Subsequent reaction requires mass transport through product layers. When at least one of the reactants is in the form of a single crystal and the other in a compressed pellet form, the kinetics of the

reaction follow a parabolic law analogous to the tarnishing of metals. Solid-solid reactions are as a rule exothermic, and the driving force of the reaction is the difference between the free energies of formation of the products and the reactants. A quantitative understanding of the mechanism of solid-solid reactions is possible only if reactions are studied under well-defined conditions, keeping the number of variables to a minimum. This requires single-crystal reactants and careful control of the chemical potential of the components. In addition, knowledge of point-defect equilibria in the product phase would be useful.

Addition Reactions

The simplest cases of solid-solid addition reactions are those between ionic oxides AO and B₂O₃, forming AB₂O₄ spinels. Since the product is a ternary oxide, experimental conditions are uniquely defined if, in addition to temperature and pressure, the activity of oxygen is fixed. The classical mechanism suggested by Wagner for this reaction involves counter diffusion of cations through the product layer. Since the reaction occurs between ionic solids, it is reasonable to expect that the fluxes are provided by ions; moreover the fluxes due to differently charged ions must be coupled during the reaction to maintain electrical neutrality. The Wagner mechanism of counter diffusion of cations for spinel formation is shown in fig. 2; other possible mechanisms are also indicated in this figure.

The various mechanisms may be grouped into two categories : (i) those involving ionic transport through the product layer only and (ii) those in which oxygen transport occurs through the gas phase in addition to cation transport through the product layer. The latter mechanism is possible only in cases where the reaction product exhibits electronic conduction and incorporates a transition-metal ion that can undergo oxidation-reduction.

In the formation of spinel oxides, the phase-boundary reaction at the AO/AB₂O₄ interface consists essentially of a homogeneous rearrangement of cations in the octahedral and tetrahedral sites of the cubic close-packed oxygen lattice, since the anion sublattice remains essentially the same in both the rock salt (AO) and spinel structures. Accordingly, it is found that in the reaction between single-crystalline MgO and polycrystalline Cr₂O₃, the product growing at the MgO/Cr₂O₃ phase boundary is also mono-crystalline. What is surprising is that, in a similar reaction between polycrystalline NiO and single-crystalline Al₂O₃ the product formed at the NiAl₂O₄/Al₂O₃ phase boundary is also mono-crystalline. The reaction would involve two steps at this phase boundary: a change of anion-layer sequence from the hcp of α-Al₂O₃ to the ccp of spinel followed by redistribution of cations. It has been suggested that a changeover of anion packing sequence occurs by a correlated motion involving dislocations rather than by diffusional motion.

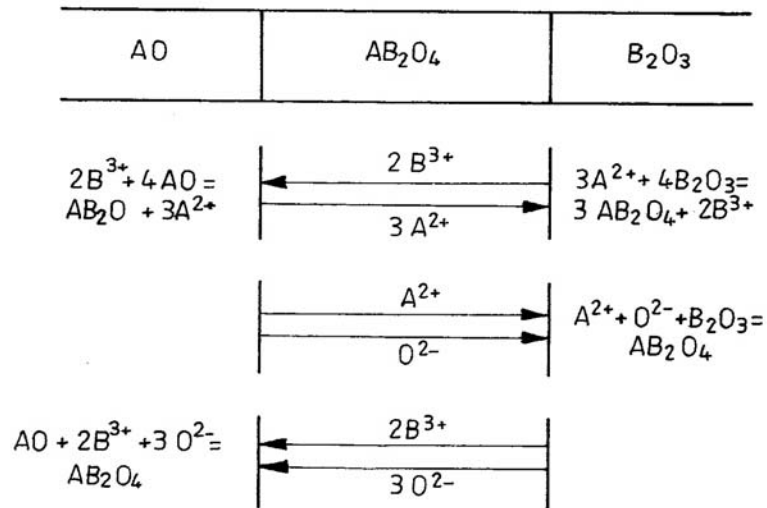
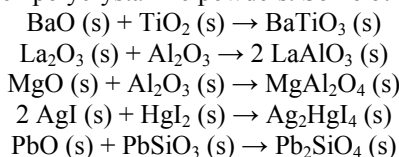


Fig. 2. Reaction mechanisms for the formation of AB₂O₄ spinel by solid-solid reaction between AO and B₂O₃

The kinetics of spinel growth generally follows a parabolic-rate law when the thickness of the product layer dx exceeds $1 \mu\text{m}$. The parabolic-rate law can be understood by assuming that a gradient in component activities (point-defects) exists across the product layer. The parabolic-rate constant has also been calculated with the knowledge of the self-diffusion coefficients of cations through the spinel and the Gibbs free energies of formation of the product. The calculation assumes certain reaction conditions to hold, but the agreement with experiment is quite good.

Inert markers have been used to obtain additional information regarding the mechanism of spinel formation. A thin platinum wire is placed at the boundary between the two reactants before the reaction starts. The location of the marker after the reaction has proceeded to a considerable extent is supposed to throw light on the mechanism of diffusion. While the interpretation of marker experiments is straightforward in metallic systems, giving the desired information, in ionic systems the interpretation is more complicated because the diffusion is restricted mainly to the cation sublattice and it is not clear to which sublattice the markers are attached. The use of natural markers such as pores in the reactants has supported the counter-diffusion of cations in oxide spinel formation reactions. A treatment of the kinetics of solid-solid reactions becomes more complicated when the product is partly soluble in the reactants and also when there is more than one product.

The foregoing treatment assumes that at least one of the reactants is a single crystal and the reactant/product geometry is well-defined. Many technologically important ceramic reactions, on the other hand, are usually carried out between polycrystalline powders. Some other examples are shown below.

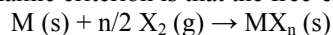


Exchange Reactions

Exchange or double reactions in which two solids react to give two different products are more complicated and less completely understood. Two limiting mechanisms have been proposed, one by Jost (1937) and the other by Wagner (1938). Both the mechanisms assume that cations are far more mobile than anions. The Jost mechanism assumes that the reactants AX and BY are separated by the products BX and AY forming adjacent coherent layers in between. Progress of the reaction requires transport of A and B ions through the product layers as is indeed the case in the reaction $\text{MS} + \text{M}'\text{O} \rightarrow \text{M}'\text{S} + \text{MO}$, where $\text{M} = \text{Pb}$ or Zn and $\text{M}' = \text{Cd}$, Wagner found that many exchange reactions between solids are quite fast and cannot be explained in terms of the Jost mechanism, which requires mobility of the cations through both the products. Wagner suggested a closed ionic-circuit mechanism in which ions are required to move through their own products. The mechanism also does not require the products to be formed as adjacent layers; instead they form a mosaic structure that facilitates simultaneous diffusion of cations through their products. Metal exchange reactions such as $\text{Cu} + \text{AgCl} \rightarrow \text{Ag} + \text{CuCl}$ and $2 \text{Cu} + \text{Ag}_2\text{S} \rightarrow 2 \text{Ag} + \text{Cu}_2\text{S}$ are believed to follow the Wagner mechanism.

Solid-Gas Reactions

The most widely studied solid-gas reaction is the tarnishing of metals by reactive gases like oxygen and halogens (Hauffe, 1976; Smeltzer & Young, 1975). Tarnishing is essentially an oxidation reaction giving rise to solid products such as metal oxides and halides that form layers on the metal surface. The tendency of a metal to become tarnished in a particular atmosphere is governed by both thermodynamic and kinetic factors. The thermodynamic criterion is that the free-energy change in the reaction



should be negative. This criterion is fulfilled in almost all the metal oxides, chalcogenides and halides, except those of the noble metals. There are certain metals, like aluminium, which resist tarnishing by oxygen and sulphur although the free energies of formation of the oxide and sulphide are negative. In order to understand such effects, we have to examine the kinetics and mechanism of solid-gas reactions.

The reaction of a metal with a gaseous reactant like oxygen consists of, first, a phase-boundary reaction forming a product layer on the metal surface. Further reaction depends on the nature of the product layer. If the layer is porous, it does not prevent access of the reacting gas to the metal and hence oxidation

proceeds unimpeded; the reaction follows a linear law (rate is constant in time), irrespective of the thickness of the product layer. If, on the other hand, a compact nonporous product is formed, the reacting gas has no direct access to the metal; further reaction can proceed only by transport of at least one of the reactants through the product. The mechanism of metal oxidation crucially depends, therefore, on whether the product layer is non-porous or porous. A useful criterion in this regard is that of Pilling & Bedworth (1923), who suggested that a porous, non protective product layer is formed when the ratio of the molar volume of the product to that of the reacting solid is less than unity. Oxidation of alkali and alkaline-earth metals belongs to this category.

High-temperature oxidations forming fairly thick ($> 1000 \text{ \AA}$) product layers exhibit parabolic growth kinetics

$$dx/dt = k/x; x^2 = k_p \cdot t + C$$

where 'x' is the thickness of the product layer at time 't' and ' k_p ' is the parabolic-rate constant. The parabolic-rate law is generally indicative of a mechanism involving rate-limiting diffusion of reactants through the product layer. When the oxidation occurs at fairly low temperatures, there is an initial rapid reaction followed by virtual cessation of the reaction forming thin-film products ($< 1000 \text{ \AA}$). In thin-film products, the electroneutrality condition is not fulfilled, owing to the appearance of space charges (Cabrera & Mott, 1948) and so diffusion across the product layer under the influence of a chemical concentration gradient is not the rate-limiting step. Thin-film product growth follows a variety of kinetic laws such as logarithmic, linear, cubic and fourth power.

The oxidation of transition metals at high temperatures giving thick product layers follows parabolic growth kinetics. The reaction takes place by diffusion of either oxygen or metal. Oxides of metals in groups IIIB-VIB (with the exception of monoxides) grow by preferential transport of oxygen, while oxides of other transition metals grow by predominant transfer of metal ions.

The parabolic-rate law for the growth of thick product layers on metals was first reported by Tammann (1920), and a theoretical interpretation in terms of ambipolar diffusion of reactants through the product layer was advanced later by Wagner (1936, 1975). Wagner's model can be described qualitatively as follows: when a metal is exposed to oxygen at high temperatures, a compact thick product layer is formed which separates metal and oxygen (Fig. 3). Diffusion of reactants under the influence of concentration gradients in the product layer becomes rate-limiting. In principle, diffusion of the metal from interface I to II and of oxygen in the opposite direction is possible, but, in practice, diffusion of one of the reactants (either metal or oxygen) predominates, depending on the defect structure of the metal oxide in question.

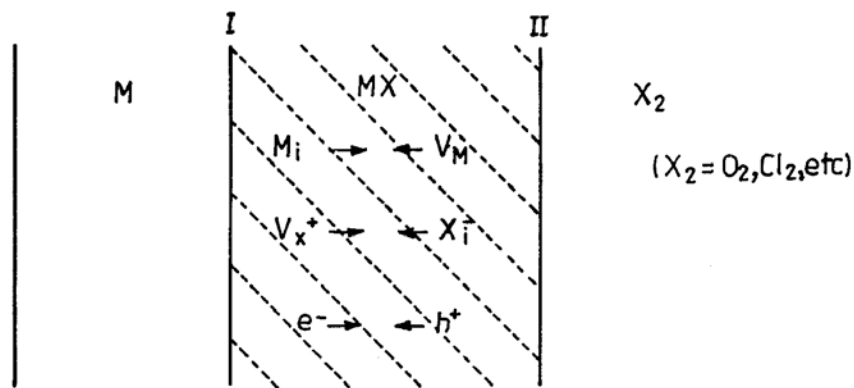


Fig. 3. Schematic representation of oxidation of a metal M by a gas X_2

Wagner's model assumes that the transported species are ions and electrons/holes instead of neutral atoms. There is a large body of data on the oxidation of metals that supports broad features of Wagner's model. Oxidation of copper to copper oxide, zinc to zinc oxide etc. is the examples whose kinetics has been interpreted in terms of the Wagner model.

Solid-Liquid Reactions

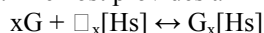
Solid-liquid reactions are much more complex than solid-gas reactions and include a variety of technically important processes such as corrosion and electrodeposition. When a solid reacts with a liquid, the products may form a layer on the solid surface or dissolve into the liquid phase. Where the product forms a layer covering the surface completely, the reaction is analogous to solid-gas reactions; if the reaction products are partly or wholly soluble in the liquid phase, the liquid has access to the reacting solid and chemical reaction at the interface therefore becomes important in determining the kinetics.

The simplest solid-liquid reaction is the dissolution of a solid in a liquid. The rate at which a solid dissolves in a liquid depends on the particular crystallographic plane (face) exposed. The effect of crystallographic planes on dissolution is clear from the observation that spherical single crystals acquire polyhedral shapes while dissolving. In the dissolution of zinc oxide in acids, the plane containing oxygens (0001) is attacked more rapidly than the one containing zinc atoms (000 $\bar{1}$).

Like thermal decompositions, dissolution of solids is influenced significantly by dislocations. For example, etch pits are formed at sites where dislocations emerge on the crystal surface. It is for this reason that etching is a useful technique to render dislocations visible and even to determine their density. Measurements of the rate of growth of etch pits in NiSO₄·6H₂O have been made use of by Thomas et al. (1971) to determine the lowering of activation energy for nucleation at dislocation sites. The correspondence between etch pits on one half of a freshly cleaved anthracene crystal and photodimerization reaction centres on the other half of the same crystal was shown by Thomas (1967).

Ion-exchange, acid-leaching and intercalation reactions are solid-liquid reactions. Ion-exchange reactions of several metal oxides have been discussed by Clearfield (1988). The exchange occurs mostly in aqueous solution or in molten salt media at relatively low temperatures and is accompanied by minimal reorganization of the structure of the parent solid. A typical example is the exchange of Li in LiAlO₂ with protons (Poeppelmeler & Kipp. 1988). This oxide crystallizes in three different structures, α , β and γ of which only the α -modification, which adopts a rock salt superstructure, undergoes facile exchange of Li⁺ with H⁺ in molten benzoic acid. The β - and γ -forms of LiAlO₂, where Li occurs in tetrahedral coordination, do not exhibit a similar ion-exchange. Unlike ion-exchange, acid-leaching of oxide materials may involve considerable reconstruction of the parent structure as in the case of chain silicates and tungstates like LiAlW₂O₈.

Intercalation refers to a solid state reaction involving reversible insertion of guest species G into a host structure [Hs]. The host provides an interconnected system of accessible unoccupied sites, □.



Certain solids possessing layered structures (e.g., graphite, silicates, metal dichalcogenides such as TiS₂, TaS₂) are capable of intercalating a wide variety of atoms, molecules and ions. The reason for this behaviour is due to the weaker van der Waals bonds between the layers.

Some examples are: Graphite + K (melt) → C₈K

Graphite + FeCl₃ → graphite/FeCl₃ intercalate

Graphite + Br₂ → C₈Br

$x\text{C}_4\text{H}_9\text{Li} + \text{TiS}_2 \rightarrow \text{Li}_x\text{TiS}_2 + x/2 \text{C}_8\text{H}_{18}$

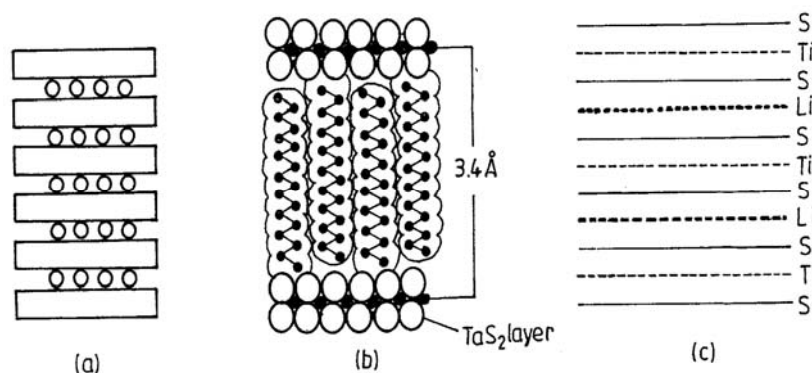


Fig. 4. Structures of (a) C₈K (b) TaS₂-n-alkylamine and (c) LiTiS₂

Reactions at the Surface of a Solid

Heterogeneous catalytic reactions and Electrocatalytic reactions belong to this category. A variety of solids: metals, alloys, metal oxides, clays, sulphides, nitrides, carbides and so on are used as catalysts. Catalysts may be single-phase substances and multiphase mixtures; they may be crystalline, microcrystalline or even amorphous. These reactions involve several steps : (i) mass transport of fluid reactants to the surface, (ii) chemisorption of reactants on the surface, (iii) diffusion and chemical reaction at the surface and (iv) desorption and diffusion of products from the surface. In most of the cases, step (iii), involving the formation of surface intermediates, is the key step. Some examples are given below.

Table 2. Some examples of heterogeneously catalysed reactions

Reaction	Solid catalyst
Cracking of hydrocarbons in presence of hydrogen	Zeolites
Hydrodesulphurization of petroleum	Co-Mo/alumina
Methanation of CO and H ₂	Ni/alumina
Ammonia synthesis	Fe, Al and Ca oxides with K ₂ O promoter
Fischer-Tropsch synthesis (hydrogenation of CO)	Fe and Co promoted with K ₂ O and ThO ₂
Oxidation of CO in automobile exhaust	Pt/alumina or Pd/alumina

Table 3. Some examples of electrocatalysed reactions

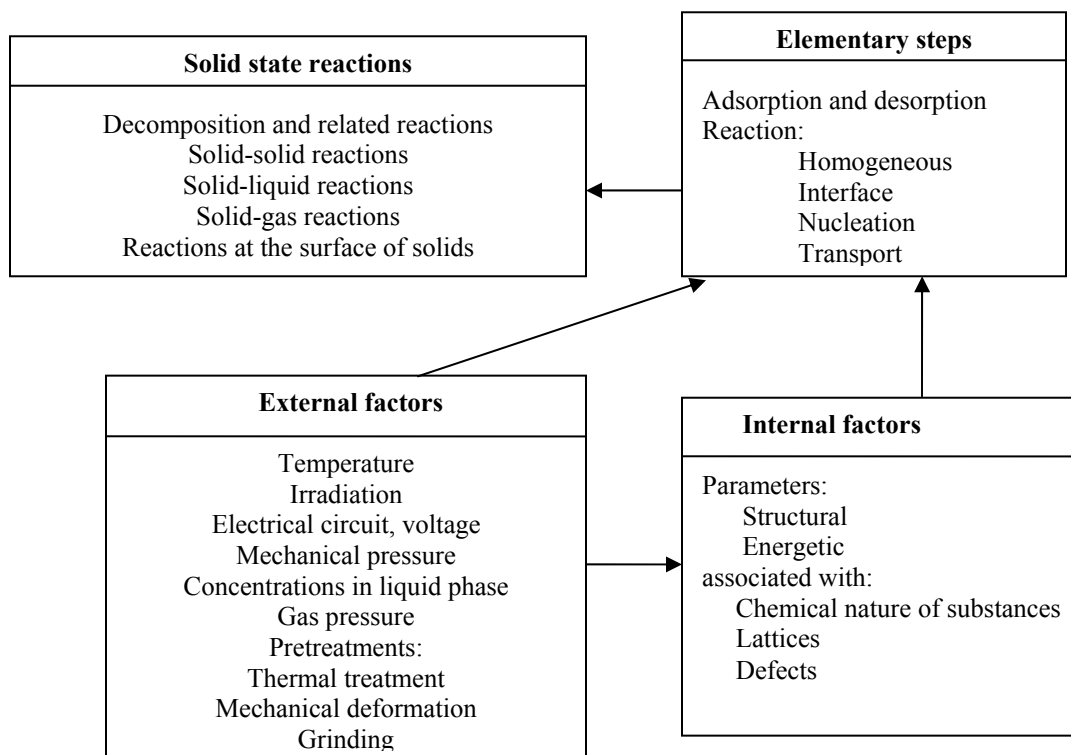
Reaction	Solid catalyst
H ₂ oxidation and H ₂ reduction	Pt, some metal carbides
Methanol oxidation	Pt, Pt-M (M = Ru, Co, Fe etc), metal oxides (NiO, SrRuO ₃ , Co ₃ O ₄ , La ₂ CuO ₄ , La-Sr-Cu-O), WC
CO oxidation	Pt, Pt alloys
Oxygen reduction	Pt, Pt alloys (Pt-Co, Pt-Fe), WC, metal oxides (LaCoO ₃ , NiFe ₂ O ₄ , Pb ₂ Ru ₂ O ₇), metal chalcogenides (Mo ₂ Ru ₅ S ₅ , Ru _x Se _y)

Factors influencing the solid state reactions

Several factors affect the solid state reactions and the overall reactivity is determined by the factors controlling the rate-determining step. These factors will be termed here 'internal' since they are inherent to the reacting system considered. They are essentially the structural and energetic factors associated with the chemical nature of the reaction partners and products, with the lattices involved (lattice spacings, symmetry, surface area), and with the defects present therein (interstitials, vacancies, impurities, electrons, holes, dislocations). These internal factors vary by the action of what we will call 'external factors' like temperature, irradiation, voltage, gas pressure, particle size, mechanical treatment, foreign additives etc. The general scheme showing the relationship between overall reactions, elementary steps, and internal and external factors which can influence the reactivity are shown in Scheme 1.

Thermal decompositions are sensitive to the nature of pretreatment given to solids. Perhaps the earliest observation in this-respect is that of Michael Faraday who noticed that the efflorescence of sodium carbonate was promoted by scratching the crystal with a pin. Modern interpretation of this observation is that dislocations produced by scratching provide sites for the reaction. Enhanced reactivity at dislocations has been demonstrated in several decomposition reactions (Thomas & Williams, 1971; Parasnis, 1970). Preirradiation of solids with neutrons, protons, or with UV -, X- or γ -radiation decreases the induction period and increases the rate of the decomposition without affecting the activation energy significantly. This observation has been taken to indicate that preirradiation increases the number of nuclei-forming sites, while retaining essentially the same mechanism. Although it is recognized that dislocations enhance the reactivity in several solid state processes, there is as yet no clear understanding of the exact role of dislocations. In general, enhanced reactivity at dislocations can arise from two factors. The core energy and the elastic strain energy associated with dislocations can aid in the nucleation process, bringing down the activation energy significantly. The abnormal stereochemistry of atoms or molecules at dislocations may also facilitate the attainment of a transition state that would otherwise be difficult to achieve in a perfect solid: In addition, there are factors such as trapping of electrons, holes and excitons in the neighbourhood

of dislocations that may enhance the reactivity of thermally and photochemically stimulated decomposition of solids.



Scheme 1. Various factors influencing the solid state reactions

Several factors affect solid-solid reactions. Of these, particle size, gas atmosphere and foreign additives are of importance. Increase of reactivity with decreasing particle size is well known in heterogeneous catalysis; small particle size also favors solid-solid reactions. Gas atmosphere can have significant effects on reactivity if the gas is also a component exchangeable between solid phases; the formation of a spinel such as ZnFe_2O_4 is favored in the presence of air (rather than nitrogen). Doping with foreign additives has been found to affect reaction rates. The reaction $\text{ZnO} + \text{CuSO}_4 \rightarrow \text{ZnSO}_4 + \text{CuO}$ is favoured by doping ZnO with Li_2O . Since the reaction $\text{Ge} + 2 \text{MoO}_3 \rightarrow \text{GeO}_2 + 2 \text{MoO}_2$ involves electron transfer from Ge to MoO_3 , n-type Ge is more reactive. Certain reactions are favoured if they are carried out at the phase transition temperature of one of the reactants (Hedvall effect); formation of CoAl_2O_4 is easier at the γ - α transition of Al_2O_3 . Boldyrev (1979) has examined the factors affecting the total process rate, the reaction at a specific location (and in a required direction), and the reaction mechanism in solid state reactions. The method of preparation (prehistory) affects topochemical reactivity; the effect of mechanical treatment of solids is to introduce different types of defects, which in turn affect the total process rate. Similarly other reactions e.g., solid-gas, solid-liquid and reactions on solid surfaces also influenced structural and energetic factors. The ultimate aim is to control solid state reactivity not only in time but also in space.

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CHAPTER - 11

Catalysis by Solids

The role of solids as catalysts is inexplicable owing to the complexity of their function, multiplicity of applications, diverse principles involved in such processes. Catalysis and Industry are inseparable in such a way that almost all industrial processes involve the concept of catalysis in one way or the other. Conventionally, there were a great number mineral acids such as H_2SO_4 , HCl , and HNO_3 that have been used in various acid catalyzed processes. But, they pose severe threat to human habitation. They are environmentally unfriendly. The present trend in industry is to replace all the conventional mineral acids with possible superior solid acids which will be environmentally acceptable, efficient in their performance, highly active and selective. Now we have to pose the question: What does solid state has to do with superior performance and peculiar properties? How to design these solid state catalysts ? What are the principles involved? What are their properties? How to understand the effect of structural features on the performance of the material? Before taking up these interesting questions, let us have a glance at the fundamental aspects of catalysis.

The role of a catalyst in bringing about a reaction is a stimulating one. Catalysis in some form or other is involved in more than 90% of the processes in the petroleum, petrochemical and fertilizer industries. Catalytic processes are widely employed in the manufacture of bulk as well as fine chemicals. Industrial catalysts are required to have a substantial working life and have to retain their effectiveness. Solid state catalysts are appealing in these respects.

The term Catalysis (Greek, kata = wholly, lein = to loosen) was coined by Berzelius. He realized that there are substances which increase the rate of a reaction without themselves being consumed. He believed that the function of such a substance was to loosen the bonds which hold the atoms in the reacting molecules together.

Catalytic processes have been used by mankind for some thousands of years. The process of fermentation, known since primitive times is involved in the conversion of fruit juice into wine, and of malt into beer, and in the making of vinegar, bread and cheese. The complex chemical reactions that occur during fermentation depend upon catalytically active enzymes produced by micro-organisms.

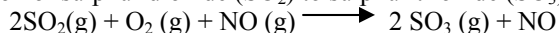
A catalyst is a substance which alters the velocity of a chemical reaction, although at the end of the reaction the catalyst is still present and has not undergone any permanent chemical change. The physical state of the catalyst may, however, change.

A catalyst may be gaseous, liquid or solid. The general phenomenon of the action of catalysts is known as Catalysis.

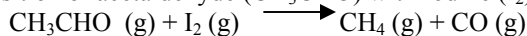
Since classification brings in order and systematics in any branch of study, in general, catalysis can be classified in to two main categories : Homogeneous catalysis, if the reactants (substrates) and the catalysts were to be in same phase and the catalyst will be evenly distributed throughout and Heterogeneous catalysis, if the reactants and the catalyst were to be in different phase. The demarcation between homogeneous and heterogeneous catalysis is, however, not always clear.

(1) Examples of homogeneous catalysis in gas phase

- (a) Oxidation of sulphur dioxide (SO_2) to sulphur trioxide (SO_3) with nitric oxide (NO) as catalyst.

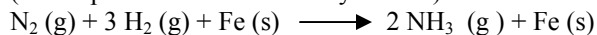


- (b) decomposition of acetaldehyde (CH_3CHO) with Iodine (I_2) as catalyst

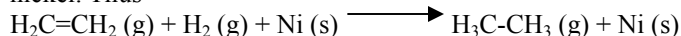


(2) Examples of Heterogeneous catalysis

- (a) Combination of nitrogen and hydrogen to form ammonia in the presence of finely divided iron (Haber process for Ammonia synthesis)



- (b) Hydrogenation reactions of unsaturated organic compounds are catalysed by finely divided nickel. Thus



CHARACTERISTICS OF CATALYTIC REACTIONS

1. A catalyst remains unchanged in mass and chemical composition at the end of the reaction (it may undergo a physical change).
2. A small quantity of catalyst is generally needed to produce almost unlimited reactions. (on the other hand there are catalysts which need to be present in relatively large amount to be effective. Thus in Friedel-Crafts reaction anhydrous Aluminium chloride functions as a catalyst effectively when present in the extent of 30 % to the mass of benzene.
3. A catalyst is more effective when finely-divided.
4. A catalyst is specific in its action.



5. A catalyst does not affect the final position of equilibrium, although it shortens the time required to establish the equilibrium.

It implies that in a reversible reaction the catalyst accelerates the forward and the reverse reaction equally. Thus the ratio of the rates of two opposing reaction i.e., the equilibrium constant remains unchanged.

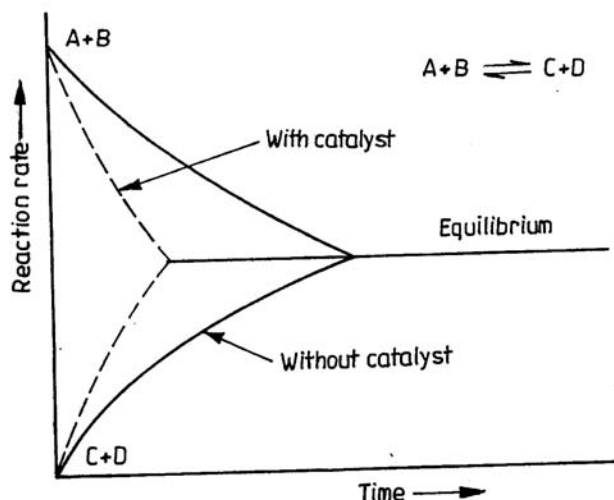


Fig. 1. Effect of a catalyst on the time required for the equilibrium to be established

The effect of a catalyst on the time required for equilibrium to be established for the reaction $A + B \leftrightarrow C + D$ is illustrated in fig. 1. To start with the concentration of A and B are at the maximum and hence the rate of the forward reaction is maximum. As the time passes, the rate of the reaction decreases till the equilibrium is established. For the reverse reaction, the initial concentration of C and D are zero, and the rate of reaction is lowest. As the time passes, the rate of reaction increases, till the equilibrium is established.

SOME IMPORTANT TERMS IN CATALYSIS

Activity : It is the ability of catalysts to accelerate chemical reactions; the degree of accelerations can be as high as 10^{10} times in certain reactions. A good example of catalytic activity is that of the reaction of H_2 and O_2 in the presence of Pt to form water with explosive violence.

Selectivity : Many chemical reactions of interest lead to the formation of several different, but all thermodynamically feasible, products. It is often of greater interest to produce one of the products 'selectively' rather than increasing the over all rate. This leads to selectivity in catalysis. A selective catalyst will facilitate the formation of one product molecule while inhibiting the production of other different molecules, even though thermodynamically the formation of all the products is feasible.

Turn over rate : The speed of a catalyzed reaction is often described in terms of Turn over rate : it reveals how many reactant molecules are converted on an active site or a unit catalytic surface area per second at a given temperature, pressure and concentration of reactant and product.

Active site : The catalytic action occurs at specific sites on solid surface often called active sites.

Specific rate : Specific rate provides a figure of merit to compare the activity of different catalysts for the same reaction under similar experimental conditions. It is important to note that only a part of the catalyst surface is active during the reaction, but this fraction is usually unknown. The specific rate provides a lower limit of the catalysts activity.

Turn over number : By multiplying the specific rate by the reaction time used in a given study, the turnover number (TN) (no. of the product molecules per catalyst surface site) can be obtained. The TN must be greater than unity to assure that the reaction is catalytic. If the turn over number is less than unity, we may be dealing with a stoichiometric reaction where the solid surface may be acting as a reactant rather than a catalyst.

Reaction probability : The number of product molecules formed per number of reactant molecules incident on the catalytic surface.

Catalyst deactivation : A catalyst may loose its activity by any of the following path ways namely : (i) direct poisoning (chemical effect), (ii) Fouling, coking, carbon deposition (chemical or mechanical), (iii) Thermal damage (Thermal), (iv) Loss of catalytic phase (chemical), (iv)Attrition (Mechanical effect).

Poisoning : It can be simply a physical act of blocking of active site in some way or the other. The possibilities are : (i) Blocking of the site, (ii) preferential adsorption of poison, (iii) Electronic structure of the catalyst is altered, (iv) Restructure of the catalyst (v) Physically block two adsorbed species, (V) Surface migration or diffusion of the species can be blocked.

Table 1. Selective Poisoning

Catalyst	Active species	Reaction	Poison	Mode
Zeolites	Acid	Cracking	Basic molecules Heavy metals like V, Cr	Neutralization of acidity Blocking of sites/Destruction of phase
Transition metals	Metal centers	Hydrogenation/ Dehydrogenation	S, P, As, Sb, Pb, Hg	Chemisorption
Ni, Pt	Metal centers	Reforming	H ₂ S, As	Chemisorption
Ag	Metal site	Ethylene oxidation	Acetylene	Coke formation
V-oxide	Oxide	Partial oxidation	Arsenic	As gets incorporated into the lattice; mixed oxide phase will be formed
Co-Mo-Al ₂ O ₃	MoS ₂	Hydrodesulphurization (we remove sulphur and add Hydrogen	Asphaltins	Coke deposition; fouling

STEPS INVOLVED IN HETEROGENEOUS REACTIONS

The over all catalytic reaction may be divided into several steps, which are significant from the point of view of understanding the mechanism of a catalytic reaction. Dividing the reaction into such elementary

steps helps in finding out which one could be the rate determining step in the over all catalytic reaction.

These steps are :

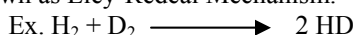
- Diffusion of reactants to the surface (surface diffusion)
- Adsorption of reactants at the surface
- Chemical reaction on the surface (molecular rearrangements at active surface sites)
- Desorption of the products from the surface
- Diffusion of products away from the surface

These are consecutive steps and the slowest step therefore determines the rate of the reaction. Steps (a) and (e) are usually rapid. Since rate of diffusion proportional to $T^{1/2}$ where T is the temperature of the process. Therefore, a slow increase in the rate with temperature will indicate the diffusion controlled reaction. Steps (b) and (d) are generally more rapid than step (c). In most reactions, therefore, step (c) i.e., the surface reaction is rate limiting. However, many cases are known where steps (b) and (d) are rate limiting.

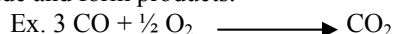
CATALYTIC MECHANISM

Two types of mechanisms are generally envisaged.

- Eley Redeal Mechanism (E-R) : A surface reaction need not involve two surface species. If a gas-phase molecule strikes an adsorbed molecule there is a possibility that the collision leads to reaction and that the product escapes directly into the gas phase. This mechanism is known as Eley-Redeal Mechanism.



- Langmuir Hinshelwood Mechanism : Both reactants are adsorbed on the surface where they collide and form products.



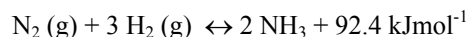
The whole range of heterogeneous catalysts used in various reactions can be divided into different types based on the nature of the catalytic sites, on which the reaction takes place. Dehydration, alkylation, isomerisation, and cracking, for example, essentially require acid sites and hence, alumina, silica-alumina, zeolites and such acidic oxides are used in these reactions. On the other hand, supported metal catalysts are essentially suited for hydrogenation and dehydrogenation reactions involving hydrogen. These could be termed as mono-functional catalysts. By judicious combination of the acid and metal functions, bifunctional catalysts can be prepared, which are industrially important. A general classification of heterogeneous catalysts is presented in table 2.

Table 2. General classification of heterogeneous catalysts

Class of catalyst	Examples	Applications
Metals (supported, mono, bi, multi), alloys	Pt, Pd, Rh, Ni, Fe, Co, Cu, Ag on Al_2O_3 , Activated carbon	Hydrogenation Dehydrogenation
Metal oxides (amorphous and crystalline) and mixed metal oxides	MgO, CuO, $\text{SiO}_2\text{-Al}_2\text{O}_3$, Zeolites, AlPOs, SAPOs, Perovskites, spinels, fluorites	Alkylation, cracking, isomerization, disproportionation, hydration, dehydration, ammoxidation
Metal sulfides	CoMo, Ni-Mo, Ni-W on Al_2O_3 , SiO_2	Hydrodesulfurization Hydrogenation
Metal salts Ion exchange resins	$\text{Zr}_3(\text{PO})_4$, ZnS, LaPO_4 Nafion-H, Amberlyst-15	Etherfication Dehydration Hydration Esterification
Heteropoly acids	$\text{H}_3\text{PW}_{12}\text{O}_{40}$ $\text{H}_4\text{SiW}_{12}\text{O}_{40}$	Acid catalysed reactions

SYNTHESIS OF AMMONIA

In 1909 Fritz Haber established the conditions under which nitrogen and hydrogen would combine to give ammonia.



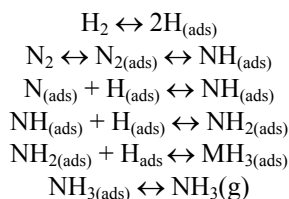
Catalyst : Promoted Iron catalyst

Industrial (unreduced) iron catalysts consists of Fe_3O_4 and typically about 1 % Al_2O_3 and 1 % K_2O to which sometimes small amounts of other oxides such as CaO , SiO_2 and MgO are added. Al_2O_3 can enter the magnetite lattice up to a concentration of a few percent. K is concentrated between the magnetite domains. The addition of Al_2O_3 causes a pronounced increase of the surface area of the catalyst while K_2O has no such effect. Al_2O_3 is a structural promoter which prevents sintering while potassium acts as an electronic promoter entering directly the surface chemistry. The promoters cover a large fraction of the iron surface, even if their normal bulk concentration is only of the order of 1 % . One of the effects of the promoters consists in the prevention of sulfur deposition. A promoter is a substance which when added to a catalyst increases the catalytic activity to a notable extent although the promoter alone does not have any marked catalytic action on the reaction under study. A promoter is often a metal oxide not reducible by hydrogen.

At high pressure (20 atm) study on the kinetics of ammonia synthesis on well defined Fe single crystal surfaces was performed at 773 K. The activity varied in the order (111) > (100) > (110) by more than two order of magnitude. This indicate that the reaction is highly structure sensitive. Fe (111) plane exhibits highest activity.

Mechanism

The steps involved in this reaction are as follows :



As evident from the above mechanism N_2 is dissociatively chemisorbed on the surface of the catalyst. Dissociative chemisorption of nitrogen is the rate limiting step (as long as the temperature is not too low i.e. $T \geq 500 \text{ K}$).

Uses of Ammonia

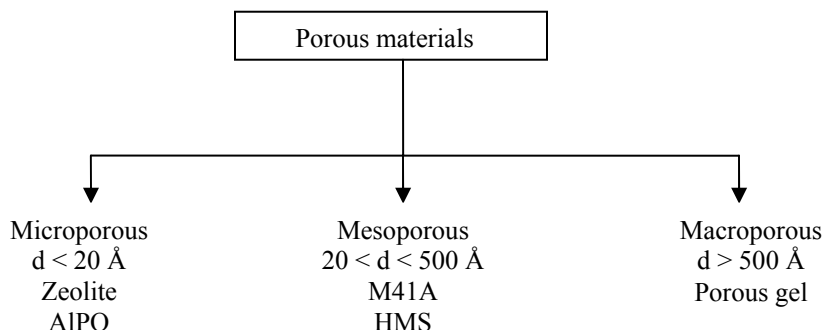
Ammonia finds diverse applications not only in the agricultural sector but also in pharmaceutical sector. Ammonia synthesis has changed the scenario of food production all over the world by bringing about green revolution. Some typical applications of ammonia have been listed in Table 3.

Table 3. Uses of ammonia

Industry	Use
Fertilizer	Ammonium sulphate , ammonium phosphate, Urea
Chemical	Nitric acid, Hydrogen cyanide, Hydrazine
Explosive	Ammonium nitrate
Fibers and plastics	Nylon
Refrigeration	For making ice, Air conditioning units
Pharmaceuticals	Manufacture of drugs such as sulfonamide
Pulp and paper	Ammonium hydrogen sulfite
Cleaning	Cleaning agent such as in cloudy ammonia

Having seen the typical function of metals as catalysts, now we shall move on to metal oxides, in particular Zeolites, a class of solid acids, which function efficiently and effectively in bringing about various catalytic transformations .

POROUS SOLIDS : Based on the pore diameter, porous materials can mainly of three types as shown below.



ZEOLITES

Zeolites are special. They form fascinating class of minerals. They are widely used in ion-exchange application, offer unique properties as sorbents and molecular sieves, and they play a dominant role in heterogeneous catalysis. The properties of zeolites derive directly from the particular characteristics of their crystal structures and the broad field of solid state chemistry provides few other examples where the interplay between local structure and the bulk macroscopic properties can be so directly observed.

The term zeolite was coined in 1756 by the Swedish mineralogist A. F. Cronstedt who observed that the mineral Stilbite frothed and gave off steam when heated in a blowpipe flame. The name comes from the Greek and it means boiling stone.

A number of reactions that are catalyzed by acids and bases in solution are also catalysed by solids having acidic and basic properties. The most important catalysts belonging to this class are aluminosilicates. The surface hydroxyl groups of the oxides of a single element, for example, silica or alumina have poor acidic behaviour and are of little importance as catalysts. Binary oxides in which the two elements are in two different oxidation states have acidic properties and make good catalysts.

In the aluminosilicates, Si^{4+} and Al^{3+} are present in tetrahedral environment of shared oxide ions. The presence of trivalent aluminium introduces an extra negative charge in the frame work of every Al^{3+} . This is compensated by cations and if the cation is a proton, the aluminosilicate acquires Bronsted acidity, if the aluminium atom is linked to three oxygen atoms that may arise due to breaking of Al-O bond during dehydration by heating, the Al with a lone pair of electrons will become a Lewis acid site. The Lewis acid site may interact with the neighbouring silanol group forming Bronsted acid centre.

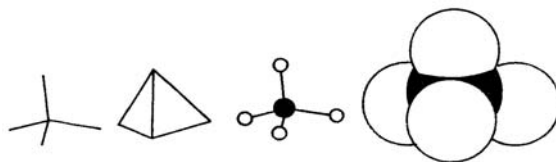


Fig. 2. A TO_4 tetrahedron, the primary building block of all zeolite structures

Aluminosilicates can be amorphous as well as crystalline. Amorphous aluminosilicates have been extensively used in industries but they are now replaced by crystalline aluminosilicates, the zeolites. Zeolites are crystalline solids with 3-dimensional frame work containing micropores of uniform size and are formed by corner sharing of SiO_4^{4-} and AlO_4^{5-} tetrahedral. Due to the excess negative charge on the aluminium tetrahedron, neutrality is achieved by incorporating cations (inorganic/organic) outside the

framework. When protons (H^+) are used as cations, the materials act as Bronsted acids. The ionic nature of the bond between these counter cations and the zeolite framework allows the exchange of cations by others without altering the crystalline structure of the solid.

The basic or the primary building unit of zeolites is the TO_4 tetrahedra (T = tetrahedral species, Si, Al, etc.) (Fig. 2.), each apical oxygen atom of which is shared with an adjacent tetrahedron.

Secondary Building Units (SBUs) : The primary building units condense to form various polymeric units known as secondary building units. A secondary building unit is basically a selected grouping of the above mentioned tetrahedral. There are nine such building units. All the known zeolitic structures can be visualized by different combinations of the nine secondary building units. The secondary building units consists of 4, 6 and 8 membered rings, 4-4, 6-6 and 8-8 double rings and 4-1, 5-1, and 4-4-1 branched rings as shown in fig. 3.

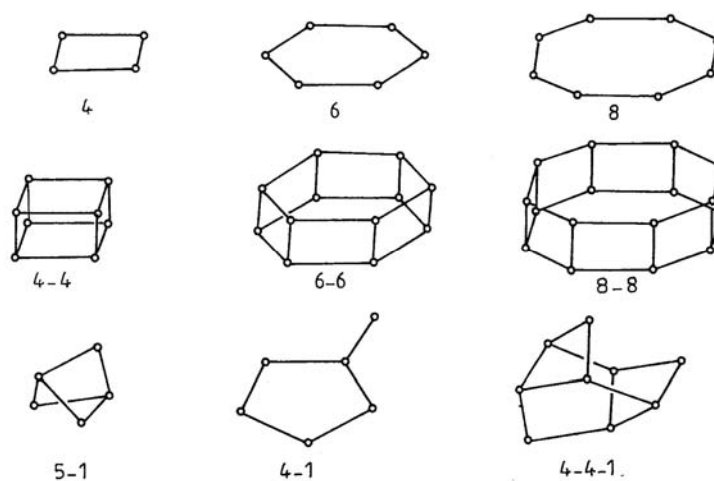


Fig. 3. Secondary Building Units

Zeolites are, by definition, distinguished in having more open structures that will reversibly sorb and desorb water (or larger molecules), and that contain large non-framework cations that can readily be exchanged. The building up of zeolite structures can be understood as shown in fig. 4.

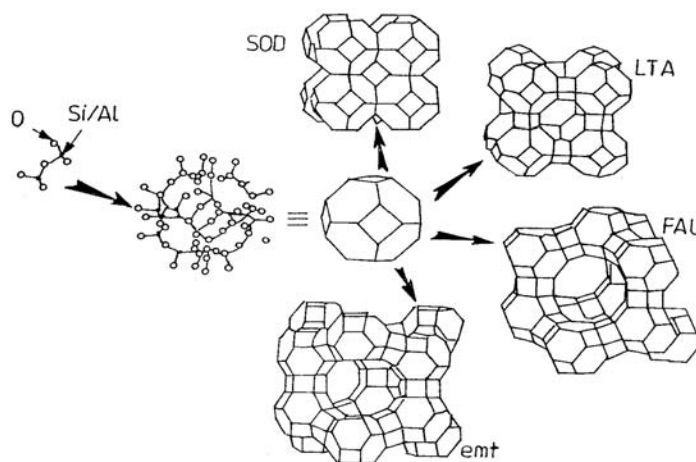


Fig. 4. The figurative construction of four different zeolite frameworks that contain sodalite or β -cages (truncated octahedral).

In fig. 4. it can be seen that a pair of TO_4 tetrahedra sharing one vertex is linked into a single sodalite cage. In a less cluttered representation, the oxygen atoms are omitted and the cage is drawn as straight lines connecting the tetrahedral (T) sites (with hidden lines removed). The sodalite cage unit is found in the SOD, LTA, and FAU frameworks. The emt frame work is a hexagonal variant of FAU. The mineral faujasite and synthetic zeolites X, Y, CSZ-3, and SAPO-37 adopt the FAU framework. The framework code defines the topology, the extended manner in which the TO_4 tetrahedra are interconnected in three dimensions. The structural details, such as the bond lengths and angles for the framework components and the distribution of non-framework species, depend on the composition and conditions

Nomenclature : Initially, there was no systematic nomenclature developed for molecular sieves. Breck used Arabic alphabets, e.g., Zeolites A, B, X, Y and L. Mobil Oil and Union Carbide initiated the use of Greek alphabets alpha, beta and omega. Later on, Mobil Oil adopted a ZSM (Zeolites synthesized by Mobil) series with Arabic numerals as suffices such as ZSM-5, ZSM-11 etc. The zeolites having structures related to mineral zeolites were assigned the name of minerals e.g., synthetic mordenite, chabazite, erionite, offretite, etc. However, in order to systematize the nomenclature, International Zeolite Association along with IUPAC developed a three letter code for each zeolite structure type like MFI (ZSM-5), MEL (ZSM-11), BEA (Beta), FAU etc.

Classification : Zeolites or molecular sieves are classified on the basis of either pore opening size or chemical composition (Si/Al ratio)

(1) Pore Opening Size : All zeolites are classified by the number of T atoms, where T = Si or Al, that define the pore opening. Zeolites containing these pore openings are also referred to as small pore (8 member ring), medium pore (10-member ring), large pore (12 member ring), and ultra-large pore (14-or more member ring). Some examples on the basis of pore size classification is given below in table 4.

Table 4. Classification of the zeolites on the basis of their pore opening ring size

Zeolite type	Pore opening	Example
Small pore	8-membered ring	MTN, NU-1
Medium pore	10-membered ring	MFI, MEL
Large pore	12-membered ring	FAU, MTW, BEA, NCL-1
Extra large pore	14-membered ring	UTD-1

(1) Chemical composition : Zeolites are also classified on the basis of chemical composition as shown in table 5.

Table 5. Classification of the zeolites on the basis of their Si/Al molar ratio

Type	Si/Al Ratio	Example
Low silica	1.5	LTA, FAU, LTL
High silica	5-500	MFI, BEA, NCL-1
All silica	∞	Si-MFI, Si-UTD-1

The catalytic properties of zeolites depend on (i) the pore diameter and (ii) the number and the strength of acid sites. Medium pore (ZSM-5, pore dia $\approx 5.5 \text{ \AA}$) and large pore (X, Y mordenite, pore dia $\approx 7 \text{ \AA}$) zeolites are widely used as catalysts in chemical industries and in petroleum refining. The acidity and the acid strength of a zeolite can be modified by changing the sample treatment or preparation method, by exchanging the cations or by modifying the Si/Al ratio.

The unique shape selectivity exhibited by zeolites has been responsible for the development of several important industrial processes during the last decade. By virtue of their structure and chemical characteristics, zeolite catalyst offer a number of advantages during use. These are high activity, low coke formation, resistance to poisoning and high regeneration stability. In addition to the above advantages, the shape selective nature of some medium pore and small pore zeolites could be advantageously utilized to improve reactant and product selectivity.

MOLECULAR SIEVING

Zeolites can act as molecular sieves. The sieving action is as shown below in Figure 4 and is governed by the pore size of the zeolite as well as the dimensions of the molecule involved in the reaction.

Molecular sieving is a good example of how structure on an atomic scale can determine macroscopic properties, and how a detailed knowledge of structure can enable prediction of performance. A wider range of separations exploit the differing affinities for differing molecules that can all enter into the zeolite. Several factors determine the equilibrium composition of the sorbed phase within a zeolite in contact with a gas or liquid mixture. When the affinities between the zeolite and the various molecules present differ significantly, the compositions of sorbed and contacting phases will be different and the zeolite can be used to effect separations

SHAPE SELECTIVITY : There are three types of shape selectivities.

(i) Reactant selectivity : This occurs when some of the molecules in a reactant mixture are too large to diffuse into the zeolite pores. This is illustrated by the selective cracking of linear alkanes in preference to branched alkanes on small and medium pore zeolites.

(ii) Product selectivity : If a reaction produces several products, some large and some small, the smaller molecules can readily diffuse out through the narrow pore openings and can be obtained in preference to the larger ones. A good example is the elective isomerization of the xylems into a product mixture rich in p-xylem.

(iii) Restricted transition state selectivity : When certain reactions are prevented because the corresponding transition state would require more space than available in the pores. Reactions requiring smaller transition states proceed without hindrance. A good example is the selective summarization of 2-phenyl prop anal to phenyl acetone rather than to propiophenone over an iron pentasil zeolite because the reactions are more selective since the undesirable competing reactions can be avoided. The discovery of ZSM-5 has given a major impetus to organic synthesis because of its unique shape selectivity.

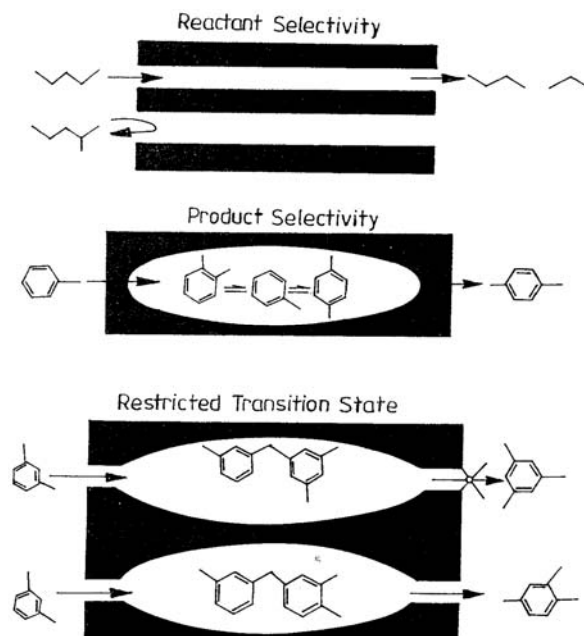


Fig. 5. Schematic of the types of shape selectivity exhibited by Zeolite catalysts

The unique shape selectivity exhibited by these zeolitic catalysts has been pictorially represented in fig. 5.

ZEOLITES AS ION EXCHANGERS

Zeolites by definition, have a capacity for partial or complete exchange of their non-framework cation complement by treatment with an appropriate salt solution or molten salt. The character of the ion-exchange equilibrium between a zeolite and a contacting solution or salt depends on several factors, including the character of the cations in question and the possible coordination environments for non-framework species provided by the zeolite structure.

Several commercial applications of zeolites exploit their ion exchange characteristics. Most, such as radio active waste water treatment, water purification, and agricultural, horticultural and medical uses rely on natural mineral zeolites such as clinoptilolite (HEU) or mordenite (MOR) which are relatively inexpensive. Synthetic zeolite A (LTA) has been widely used as a partial replacement for sodium tripolyphosphate (STPP) in low phosphate detergents. Zeolite A performs as a filler and exchanges Ca^{2+} and Mg^{2+} cations out of the washing water. Subsequently, under neutral or mildly acidic conditions in the environment, the zeolite dissolves to form relatively benign silicate and aluminate species.

Zeolites have been explored as industrial catalysts in petrochemical and fine chemical industries. In most of these cases, the catalytic activity is due to their acidic nature. They are used in a host of acid catalyzed reactions such as alkylation and acylation. The active sites in zeolites are mainly Bronsted acid sites and to some extent the Lewis acid sites. Among various zeolites, faujasite, mordenite and ZSM-5 type zeolites are widely used as catalysts. The faujasite type zeolite, namely zeolite-Y has been mainly used for the fluid catalytic cracking and hydrocracking reactions. Mordenite is used in isomerization of light alkenes for octane enhancement of gasoline. ZSM-5 is used widely for the production of fine chemicals. A large variety of organic reactions such as isomerization, rearrangement, alkylation and acylation have been studied and in all these cases, ZSM-5 has been exploited as a potential catalyst.

Aluminophosphate

Microporous aluminophosphates form another class of microporous solids, which has received considerable attention. The structures of these materials are to some extent similar to those of zeolites. They possess high thermal stability as well as high sorption capacities. Aluminosilicates and aluminophosphates form two different classes of microporous solids. Catalytic activity in these materials can be generated in a similar way as in Zeolites.

Today's environment concerns demand the need for alternate catalytic processes for the production of fine chemicals in an environmentally friendly manner. For the production of fine chemicals, at present hazardous chemicals like sulphuric acid, phosphoric acid have been employed. The problem associated with these chemicals is handling in addition to the environmental pollution. By using transition metal ion incorporated molecular sieves, it has been made possible to overcome these problems to a certain extent.

Need for mesoporous Zeolites

Even though, zeolites, having pore dimensions of 5 to 7 Å, served the purpose for most of the industrial reactions by providing high surface area, the pore dimensions are not sufficient enough to accommodate broad spectrum of larger molecules. The performance of the zeolitic systems is limited by diffusional constraints associated with smaller pores. To a certain extent, it is possible to overcome this problem with aluminophosphates, microporous crystalline materials with pore dimensions up to 13 Å. However, these materials suffer from limited thermal stability as well as negligible catalytic activity due to framework neutrality. Moreover, there is a need for present day catalytic studies dealing with processing of hydrocarbons with high molecular weights. These factors led to the discovery of mesoporous solids.

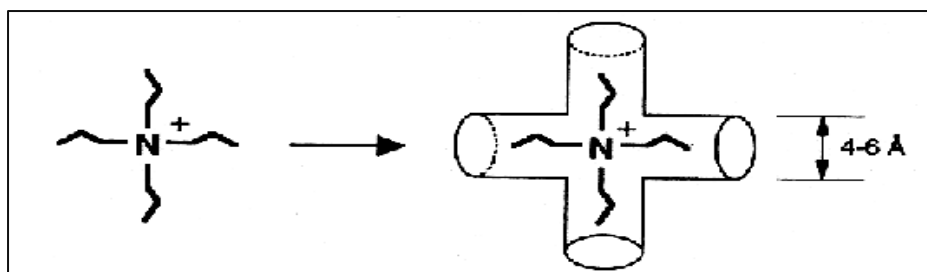
MESOPOROUS SOLIDS

Materials with super large pores possessing catalytic properties are attractive candidates as catalysts for non-shape selective conversion of large molecules, especially for the cracking of heavier petroleum feed stock. The large void volumes of such materials make them potential adsorbents with high adsorption capacity. The large pore can also act as host for various guest species so that the alteration of redox properties can also be achieved.

With the first successful report on the mesoporous materials (M41S) by Mobil researchers, with well defined pore sizes of 20-500 Å, the pore-size constraint (15 Å) of microporous zeolites was broken. The high surface area ($> 1000 \text{ m}^2/\text{g}$) and the precise tuning of the pores are among the desirable properties of these materials. Mainly, these materials ushered in a new synthetic approach where, instead of a single molecule as templating agents as in the case of zeolites, self-assembly of molecular aggregates or supra-molecular assemblies are employed as templating agent.

The basic difference in the synthesis of microporous and mesoporous molecular sieves is shown pictorially in fig. 6.

Microporous materials :



Mesoporous materials :

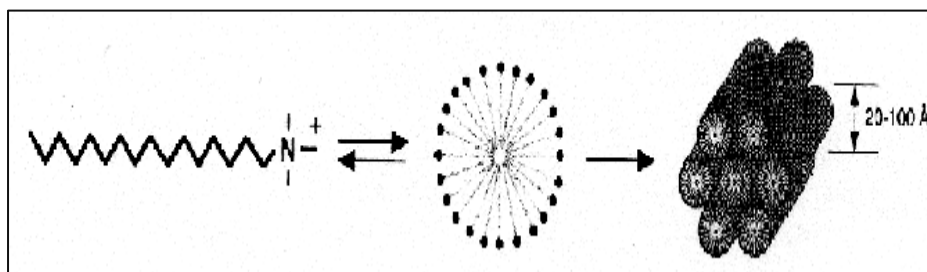


Fig. 6. Formation of microporous and mesoporous molecular sieves using small (top) and long (bottom) alkyl chain length quaternary directing agents

M41S series of mesoporous materials consists of uni-dimensional hexagonal MCM-41, three-dimensional cubic MCM-48 and lamellar MCM-50 which are represented in fig. 7. MCM-41 is the most investigated member of M41S series, which has a honeycomb structure as a result of hexagonal packing of uni-dimensional cylindrical pores. It has high surface area ($> 1000 \text{ m}^2/\text{g}$) and large pore dimensions, which can be tuned in the range of 20-100 Å. MCM-48, the second member of this series which comprises of three-dimensional inter-twined channels that do not intersect can represent the channel system of MCM-48. MCM-50 has a lamellar structure in the synthesized form.

MCM-41 IN CATALYSIS

It is generally observed that the acidity of these mesoporous solids are to an order less in acid strength, than zeolites, with these materials, it is possible to overcome the existing pore size constraints of microporous solids. The generation of acid and redox properties in general can be achieved by modification of the mesoporous solid.

Modification of MCM-41: Modifications in MCM materials can be achieved in a variety of ways. They are: (i) Generation of basic properties by ion exchange with IA group salt solutions, (ii) Alteration of acidic properties by incorporation of group 3+ cations, (iii) Incorporation of transition elements to generate redox properties, (iv) Immobilization of metal complexes inside the cavities, (v) Functionalization to generate chiral catalysts.

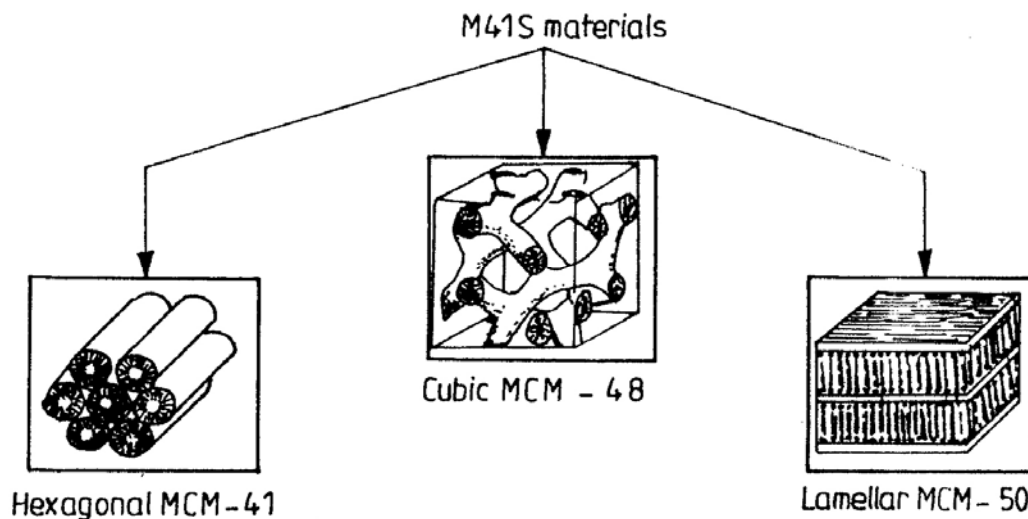


Fig. 7. M41S representation

METAL OXYGEN CLUSTER COMPOUNDS

Heteropoly compounds form the large fundamental class of metal oxygen cluster compounds. Acid form of heteropoly compounds are called heteropoly acids (HPAs). They are mainly used in the fields as diverse as analytical chemistry, medicine or magneto chemistry apart from acid and oxidation catalysis. HPAs are more active catalysts for various reactions in solution and in solid state than conventional inorganic and organic acids and they are used as industrial catalysts for several liquid phase and vapour phase reactions. Important characteristics accounting for the high catalytic activities are the acid strength, softness (large size and small charge) of the heteropoly anion, catalyst concentration and nature of the solvent.

STRUCTURAL ASPECTS OF HETEROPOLY COMPOUNDS

These heteropoly compounds are defined at the molecular level and they exhibit unique geometrical and architectural features that play a role in determining the acidity of these compounds. Based on the structure heteropoly compounds can be classified into a variety of types as shown in table 6.

Table 6. Types of Heteropoly compounds

Types	Molecular formula	Building units	Type of sharing	Central groups
Keg gin	$X^{n+}M_{12}O_{40}^{(8-n)-}$	M_3O_{13}	Edge	XO_4
Dawson	$X^{2n+}M_{18}O_{62}^{(16-2n)-}$	M_3O_{13}	Edge	XO_4
Anderson	$X^{n+}M_6O_{24}^{(12-n)-}$	M_2O_{10}	Edge	XO_6
Waugh	$X^{n+}M_9O_{32}^{(10-n)-}$	M_3O_{13}	Edge	XO_6
Silverton	$X^{n+}M_{12}O_{42}^{(12-n)-}$	M_2O_9	Face	XO_{12}

In the above formulae, X is the hetero atom which can be either P^{5+} or Si^{4+} . Apart from these two more than 65 elements except inert gases can function exceptionally well as heteratoms. M, represents the addenda or peripheral atom which can be any one of these metals like Mo, W, Nb, Ta, V and Os in their highest oxidation states.

The structures of various polyanions are shown in fig. 8 . The most widely investigated heteropoly compound is the so called Keggin anion which is composed of a central XO_4 tetrahedron surrounded by 12 edge and corner sharing MO_6 octahedra. The octahedra are arranged in four M_3O_{13} groups. Three octahedra forms each M_3O_{13} group sharing edges and having common oxygen atom, which is also shared by the central tetrahedron. Removal of three adjacent corner linked octahedral from Keggin anion gives lacunary species, fusion of such two $PW_9O_{34}^{9-}$ units generates the well-known Dawson anion figure 8(b). Anderson anion comprises of six MO_6 octahedra which share an edge with each other and with the central XO_6 octahedra . Waugh type polyanion can be formally derived from Anderson by removing three alternate MO_6 octahedra and placing two M_3O_{13} moieties one above and the other below the plane of central XO_6 octahedra. Silverton anion is formed by sharing MO_6 face with another MO_6 giving rise to M_2O_9 building unit, each octahedron sharing a face with the central XO_{12} icosohedron .

Many potential applications have been proposed for these compounds such as hydration of olefins, methanol conversion to hydrocarbons, oxyhydration of propene to acetone, synthesis of MTBE (Methyl t-butyl Ether) and others. Most of the reactions proceed not only on the acidic form of these compounds but also on neutral salts, even if the reaction is an acid catalyzed one. A remarkable characteristic of heteropoly compounds is their ability to absorb polar substances such as alcohols, ether and nitrogen-containing bases. Catalytic reactions also take place in the solid lattice known as 'pseudo-liquid phase catalysis'. Based on this concept, a kind of "molecular sieving effect" may be expected. This is not due to molecular size effect, as found for zeolites, but to polarity of these compounds suggesting many potential applications of these compounds. The use of heteropolyacids as catalysts for fine organic synthesis process is developing. Synthesis of antioxidants, medicinal preparations, vitamins and biologically active substances have been reported and some are already applied in practice. These catalysts are very important for industries related to fine chemicals, as flavours, pharmaceutical and food products , among others.

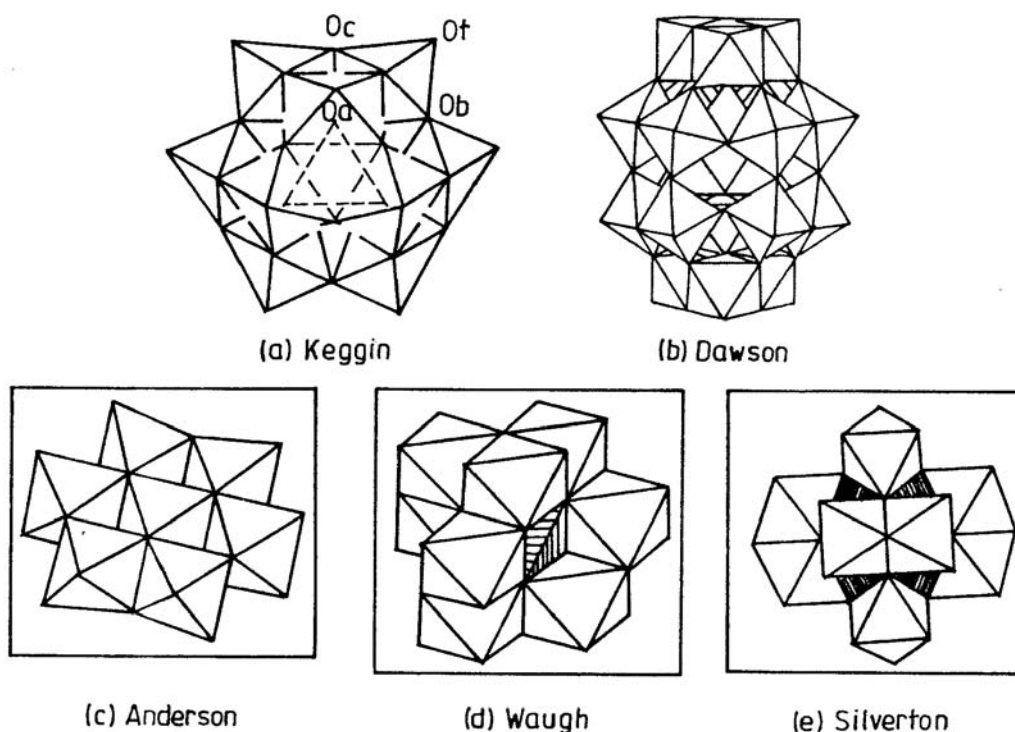


Fig. 8. Structures of various polyanions

The discussion on structure-property relationships, principles involved in the design of the catalysts, mechanistic path ways that are operative on the catalytic systems, unusual activities and appreciable selectivities goes on endlessly since the domain of Catalysis is immense.

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CHAPTER - 12

Materials in Day to Day Life

There are a variety of materials that one comes across in one's day-to-day life. These materials span the whole gamut of material science. It may not be possible to deal with all the materials that one uses in one's day-to-day life in this presentation, and hence only a limited usage of single materials that are essential for day-to-day life is considered.

Pigments

Inorganic materials have been used for many centuries for decoration. Initially naturally occurring ores were used, such as iron oxides. These were collected as yellow ochre and red ochre and used by the early people to color paintings and even their bodies. Although the colors obtained from plants (berries and barks) were used, the colored earths or ores were far more durable and resistant to fading.

Inorganic colors are mostly used as pigments rather than as dyes. Pigment can be defined as a solid particle dispersed into a medium (usually a liquid) without significant solution formation or other interaction. Pigments are different from dyes, since the latter are essentially soluble in the medium in which they are used. Pigments can scatter light because of particulate nature while dyes cannot.

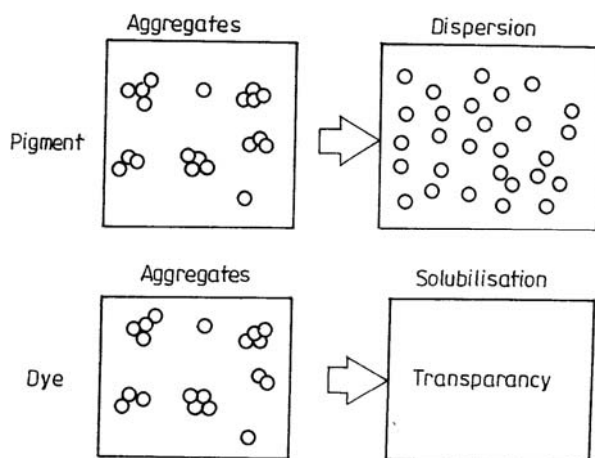


Fig. 1. Pictorial differentiation of a pigment and a dye

Pigments are used widely for decoration, in inks, paints, varnishes and wood-stains and also in plastics, tableware, pottery and glass items (e.g., plates and cups), sanitaryware (e.g., baths, toilets and wash-basins), ceramic tiles, cement products and cosmetics.

The important properties required for the pigments are colour, color strength, particle size distribution, stability to heat, light (lightfastness), Humidity (weather fastness), interaction with the medium, chemical stability and durability depending on the application.

Few of the pigments of the basic colors viz., red, yellow and blue along with black and white, which are used more frequently are described in the following paragraphs.

Iron oxides

Natural iron oxides are used as pigments since prehistoric times. The main colors are yellow ochre ($\text{FeO}\cdot\text{OH}$ or $\text{Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$) and red ochre ($\gamma\text{-Fe}_2\text{O}_3$, can be prepared from yellow ochre by controlled dehydration).

Synthetic iron oxides also dominate in the pigment industry for their controlled pigment properties. These iron oxide ores are generally of relatively low cost and very less toxic. Also iron oxides tend to dissolve in molten glass and thus are of limited use for ceramic decorations.

Titanium Dioxide (Titania, TiO₂)

Titanium dioxide is most brilliant white pigment currently in use with outstanding chemical stability. Not until the early 20th century the development of titanium dioxide as a pigment was started. It is used widely for pigmenting articles white and also in blending with other pigments to give pale colors and increased opacity. It has almost replaced the previously used white pigments such as basic lead sulfate, zinc oxide, antimony oxide and tin oxide, because of its superior optical properties as well as toxic nature. Even though both anatase and rutile phases are used as pigments, rutile has greater pigmentary opacities, because of the more compactness and higher refractive index, for similar particle size compared to anatase.

Cobalt Aluminate Blue (Cobalt(II) oxide-aluminum oxide, CoO · Al₂O₃)

Cobalt has been used to colour glazes and glasses since about 2000 BC, and in the 18th century, it was combined with alumina to obtain better colours. This is also called as 'Thenards' blues in honour of the chemist who pioneered the study of cobalt chemistry in the early 19th century. Incorporation of chrome in cobalt aluminate results in blue-green or turquoise pigment.

Cobalt aluminate pigments are chemically inert, with good resistance to heat and weathering, but are expensive. The greater stability of this pigment, replaced the organic phthalocyanine pigments in certain applications like ceramic enamels and coil coatings.

Charcoal black (Carbon, C)

Charcoal black is a common grayish black used as a black pigment since very earliest times. The burnt wood was the source of this pigment. Another black pigment of frequent use is the Bone black, which contains residual quantities of calcium phosphate and calcium carbonate with carbon.

Medicinal Applications

Living organisms are complex, self-contained, highly organized chemical reactors, where molecules are continually synthesized and broken down. A casual glance would suggest that the majority of the chemistry taking place in this reactor is mostly organic chemistry, as the elements C, H, N, O, P and S account for 99.3% of the atoms in a human body. The remaining 0.7 % are inorganic elements and play a vital role in the biochemistry and physiology of biological systems both as structural and functional components.

The ability of metals to coordinate with a variety of ligands makes them important components of many enzyme-catalyzed reactions where they are able to form, or stabilize, intermediates in the reactions. Metals with a catalytic role are often bound in strained or distorted coordination geometries in the enzyme. Few of the examples of the role of metals or metal ions in physiological system are calcium in bone, metal ions in the helical structural integrity of proteins, physiological signaling function of sodium and potassium ions and haem (iron porphrin) in the detoxification of foreign chemicals.

Inorganic compounds are first used as medicines in the early days of civilization, starting from the use of copper to sterilize water, mercurous chloride as a diuretic, antimony for syphilis and gold compounds for treating tuberculosis and arthritis.

PLATINUM ANTICANCER DRUGS

A major event in the history of inorganic medicinal chemistry was the discovery of the anti-tumor properties of platinum compounds by Barnett Rosenberg. The anti-tumor activity of platinum compounds was accidentally discovered by Rosenberg and coworkers in the 1960s. They observed that under the influence of an electromagnetic field generated using platinum electrodes, E.coli bacteria grew as long filaments, many times longer than normal cells. Investigation showed the effect to be due to low

concentration of platinum compounds formed in the culture medium. This evidenced the greater inhibition of cell division than cell growth and suggested that the compound would have anti-tumor properties; which was subsequently confirmed by the National Cancer Institute, USA.



Fig. 2. Filamentous growth of E. coli

Platinum (II) has a d^8 electron configuration and forms primary four-coordinate, square planar complexes. Systematic study of the series of compounds $[\text{PtCl}_x(\text{NH}_3)_y]$ ($x = 1$, to 4, $y = 4-x$) has indicated that the neutral *cis* complex is the most active one. A broader study of the two isomers of compounds $[\text{PtCl}_2\text{L}_2]$ ($\text{L} = \text{amine}$) confirmed anti-tumor activity for many *cis* compounds but no activity for the *trans* forms. The amine ligands in such complexes are inert to substitution while the chloride ligands can both be displaced, suggesting a requirement for a pair of *cis* leaving groups for activity. Examination of a wider range of neutral ligands L , e.g., sulfur- and phosphorus- based ligands also revealed a marked drop in activity. For the amine ligands the general order of activity is primary $>$ secondary \gg tertiary, a series which is believed to relate to the hydrogen bonding ability of these ligands.

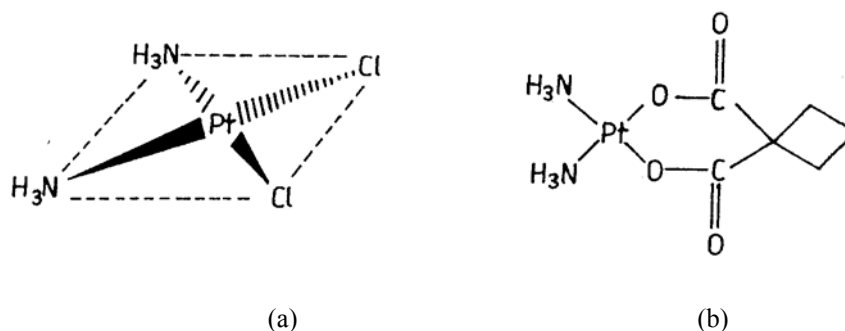
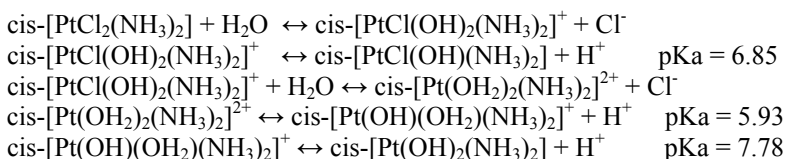


Fig. 3 (a) Cisplatin, (b) Carboplatin

In aqueous solution cisplatin undergoes hydrolysis and subsequent deprotonation reactions.



In blood the high chloride level (0.1 M) maintains $\text{cis-}[\text{PtCl}_2(\text{NH}_3)_2]$ as the major species; but inside the cell (with only 0.004 M Cl^-) $\text{cis-}[\text{PtCl}(\text{H}_2\text{O})(\text{NH}_3)_2]^+$, $\text{cis-}[\text{Pt}(\text{OH})_2(\text{NH}_3)_2]^{2+}$ and their hydroxo- forms

predominate. Substitution occurs more readily for the water ligands than for chloride or hydroxide and so the aqua complexes are the most likely reaction intermediates. As the pK_a values for these compounds are close to 7, a significant proportion of the platinum from cisplatin will be present as these reactive species. The ease of substitution of anionic groups in platinum(II) complexes has been determined using the series of compounds $[PtX(dien)]^+$ ($X =$ anionic ligand). Readily substituted ligands include nitrate, sulfate and water; while complexes containing ligands such as thiocyanate, nitrite and cyanide are unreactive. Halide complexes have intermediate reactivity.

Mechanism of Action

The original observation in *E. coli* bacteria that cisplatin inhibited cell division more strongly than cell growth suggested that the mechanism of action involved reaction with DNA rather than with other cellular macromolecules such as RNA (ribonucleic acid) or proteins. Determination of the intracellular disposition of platinum in relation to the relative concentration and molecular weights of DNA, RNA and proteins also suggested that DNA was the most likely site of action. Analysis of platinated DNA has shown that platinum is concentrated in guanine(G)-cytosine(C) rich regions. The kinetically preferred sites of reaction between cisplatin and nucleic acid bases were found predominantly to guanine.

There are four possible binding types of cisplatin to DNA; Chelation to a single base (G), an intrastrand crosslink, an interstrand cross link and a DNA- protein cross link. Of these there is no evidence for the first. Of the other possibilities the 1,2-intra-strand cross link (i.e., binding to neighboring bases on the same DNA strand) has been viewed as the most important, as this cannot be formed by the trans isomer.

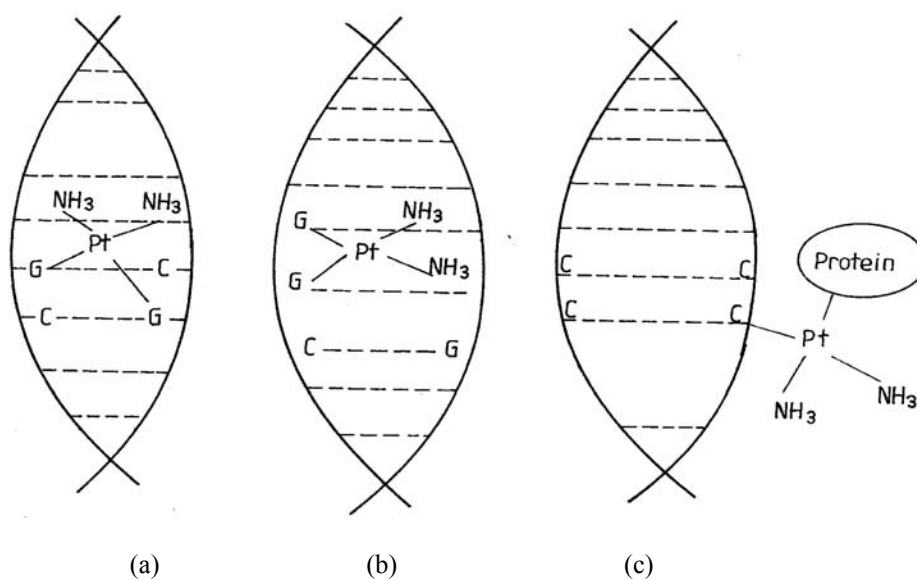


Fig. 4. Binding mode of cisplatin to Guanine unit of DNA (a) inter strand, (b) intra strand, (c) DNA-Protein cross link

In general, for suitability as drugs with intravenous infusion as the route of administration, candidate compounds should be stable in solution and have sufficient aqueous solubility for formulation. These criteria act against compounds containing weakly bound ligands such as sulfate (poor stability) and against many of the simple amine chloro complexes (low solubility). The substituted malonate ligands are potential candidates for their stability and solubility.

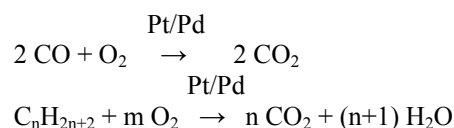
Carboplatin (cyclobutane dicarboxylate) (Fig. 3(b)) is found to be a cisplatin analogue with less or no kidney toxicity, which enabled outpatient treatment in many cases. Still greater convenience for the patient could be achieved with an orally administered drug. Efforts are still continuing in the search for new compounds for wider clinical applications.

AUTOMOBILE CATALYSTS

Air pollution, when looked into the history, is not a new problem; indeed the ancient atmosphere of earth was extremely poisonous to life. In more recent times many people have died from natural air pollution incidents, especially in the wake of volcanic eruption. In the recent past man made pollution affected a large numbers of people after the case of smog of Victorian London, which was responsible for the deaths of thousands of people. Major irritants in smog were smoke and sulfur dioxide (and sulfurous or sulfuric acid resulting from its dissolution in mist droplets and soot particles). The next severe public nuisance of smog occurred in Los Angeles in the 1950s, and resulted in the death of few thousand people.

Smog is a mixture of carbon monoxide, hydrocarbons, oxides of nitrogen and the toxic products of homogeneous and heterogeneous photochemical reactions in the atmosphere. Carbon monoxide results from the partial combustion of hydrocarbon fuel in the internal combustion engine. The unburnt hydrocarbon is let to the environment along with the mixture of oxides of nitrogen (NO and NO₂). As a result of the Los Angel smog incident, the Californian authorities took the courageous and inventive step of forcing improvements by legislation, requiring significant reductions in the three major gaseous emissions- hydrocarbons, carbon monoxide and oxides of nitrogen. The successful technology was emerged to convert these toxic compounds to harmless end products using precious metal catalysts.

In the beginning, only two of these three pollutants i.e., carbon monoxide and unburnt hydrocarbon were aimed to be removed by oxidation.



These reactions were relatively easy to catalyze and many noble metal or oxide catalysts could perform the job. The first automotive catalysts introduced were called as “two-way” catalysts, as they performed these two oxidation reactions.

The role of nitrogen oxide in the formation of photochemical smog, has necessitated its treatment. But catalytic removal of these nitrogen oxides represented a much more difficult challenge. Oxidation to NO₂/N₂O₄ occurs slowly in the gas phase, and is clearly undesirable. The most effective means of NO_x treatment was to reduce it to N₂. This reaction is also catalyzed by Pt/Pd or rhodium, with rhodium as the most effective one. With the inclusion of reduction of nitrogen oxides, the automotive catalyst facilitated three reactions, and so called as “three-way” catalyst.

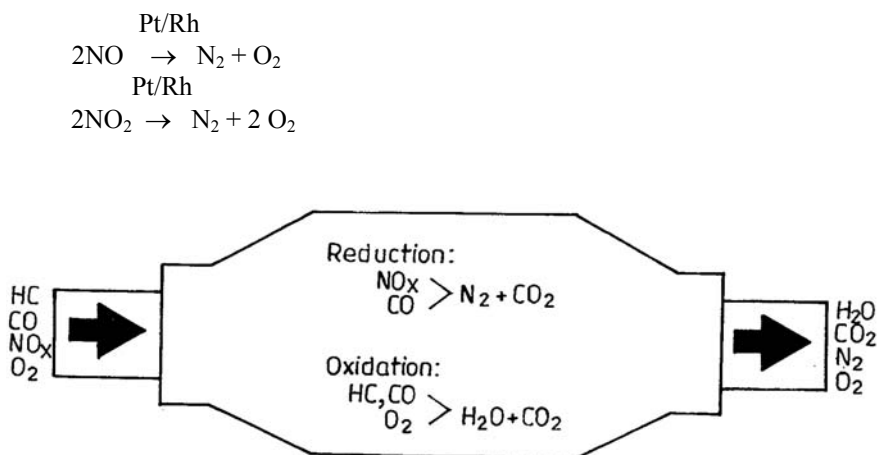


Fig. 5 Three-way Catalytic convertor

Previously the metal catalysts were pelletized, but they caused severe pressure build up problems. An alternate to pelletized catalysts was achieved with the use of ceramic monolith of honeycomb structure as

the catalyst support. The monolith structure is formed by extrusion of cordierite, a mineral with the composition $\text{Al}_3\text{Mg}_2(\text{Si}_5\text{Al})\text{O}_{18}$ and a subsequent firing of the extrudate at 1600-1700 K. The monolith in a typical family car is about 10 cm by 15 cm. The exhaust gases traverse it longitudinally. The catalyst particles were introduced on the monolith by 'dip and drain' technique followed by calcination, which resulted in supporting of 1-3 g of precious metals.

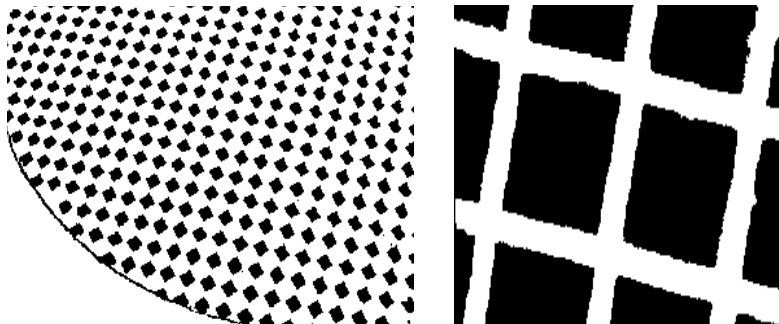


Fig. 6. Honeycomb structure of Ceramic monolith

SOAPS AND DETERGENTS

Soap

Soap is an excellent cleanser because of its ability to act as an emulsifying agent. An emulsifier is capable of dispersing one liquid into another immiscible liquid. This means that while oil (which attracts dirt) doesn't naturally mix with water, soap can suspend oil/dirt in such a way that it can be removed.

Soaps are sodium or potassium salts of fatty acid (**Surfactants**), produced from the hydrolysis of animal or vegetable fats in a chemical reaction called **Saponification**. Each soap molecule has a long hydrocarbon chain, sometimes called its 'tail', with a carboxylate 'head'. In water, the sodium or potassium ions float free, leaving a negatively-charged head.

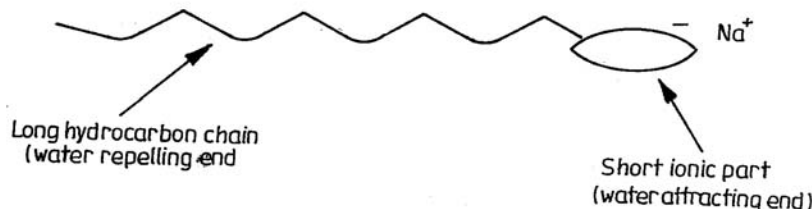


Fig. 7. Soap molecule

The organic part of a natural soap is a negatively-charged, polar molecule. Its hydrophilic (water-loving) carboxylate group ($-\text{CO}_2^-$) interacts with water molecules via ion-dipole interactions and hydrogen bonding. The hydrophobic (water-fearing) part of a soap molecule, its long, nonpolar hydrocarbon chain, does not interact with water molecules. The hydrocarbon chains are attracted to each other by dispersion forces and cluster together, forming structures called **micelles**. In these micelles, the carboxylate groups form a negatively-charged spherical surface, with the hydrocarbon chains inside the sphere. Because they are negatively charged, soap micelles repel each other and remain dispersed in water.

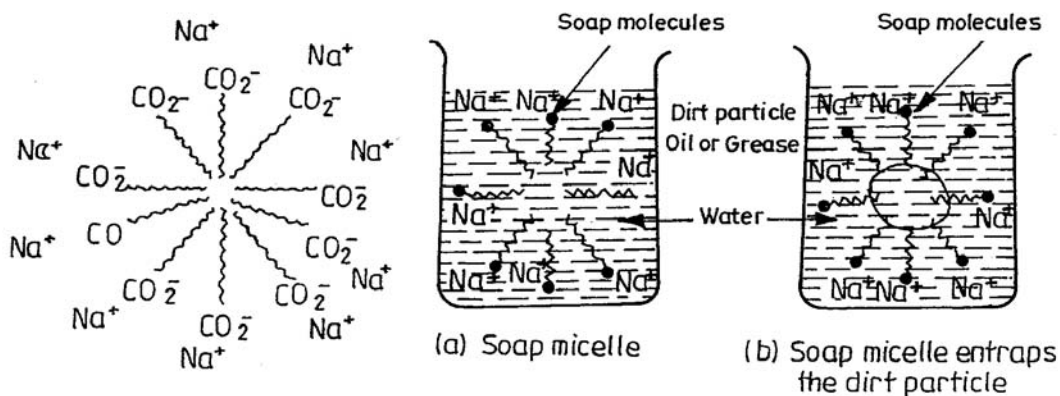


Fig. 8. Diagram of soap micelle

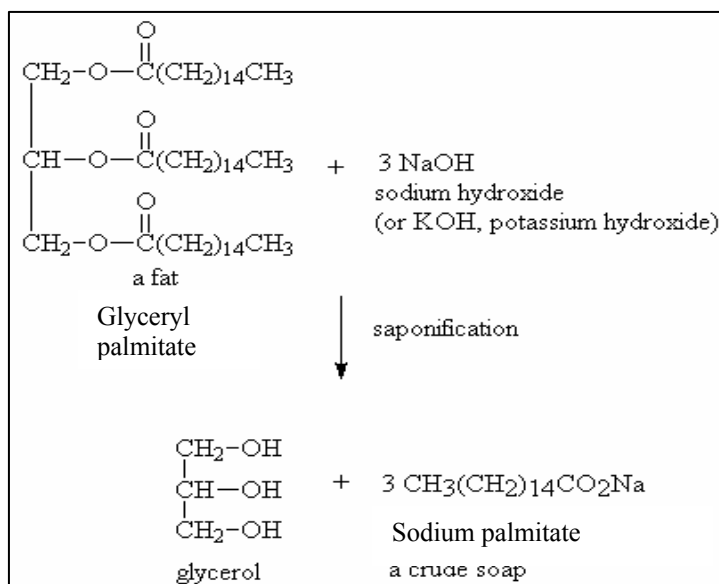


Fig.9. Saponification reaction

Grease and oil are nonpolar and insoluble in water. When soap and soiling oils are mixed, the nonpolar hydrocarbon portion of the micelles break up the nonpolar oil molecules. A different type of micelle then forms, with nonpolar soiling molecules in the center. Thus, grease and oil and the 'dirt' attached to them are caught inside the micelle. The similar charges around the micelles repel each other and avoid coalescence or redeposition of the dirt on the cloth and facilitates the rinsing off of the dirt.

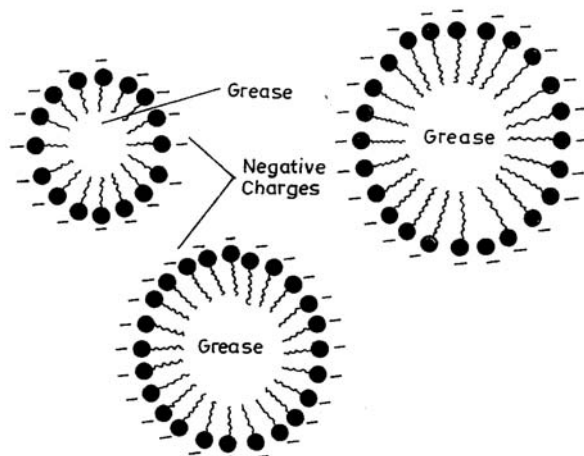
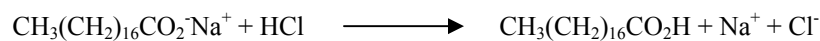
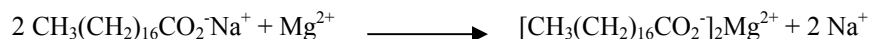


Fig. 10. Charge repulsion of the micelles

Although soaps are excellent cleansers, they do have disadvantages. As salts of weak acids, they are converted by mineral acids into free fatty acids:



These fatty acids are less soluble than the sodium or potassium salts and form a precipitate or soap scum. Because of this, soaps are ineffective in acidic water. Also, soaps form insoluble salts in hard water, such as water containing magnesium, calcium, or iron.



These insoluble salts form bathtub rings, leave films that reduce hair luster, and gray/roughen textiles after repeated washings.

Detergents

Detergents are the synthetic analogues of soaps. The sodium salts of fatty acids (Surfactants) are derived from the products of petroleum industry. These surfactants may be classified into anionic, cationic, nonionic or amphoteric depending on the nature of the hydrophilic part.

Anionic surfactants ionize in solution, carry a negative charge, have excellent cleaning properties. Linear alkylbenzene sulfonate, alcohol ethoxysulfates and alkyl sulfates are the most common anionic surfactants. They are used in laundry and as hand dishwashing detergents, household cleaners and personal cleansing products.

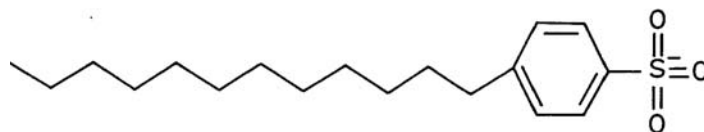


Fig. 11. Anionic surfactant (Alkyl benzene sulfonate)

Nonionic surfactants do not ionize in solution and thus have no electrical charge. They are resistant to hardness of water and clean well on most soils. The most widely used are alcohol ethoxylates typically used in laundry and automatic dishwasher detergents and rinse aids.

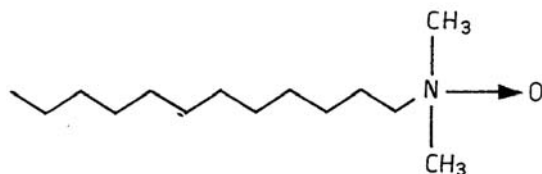


Fig. 12. Non ionic surfactant (Lauryldimethylamine oxide (LDAO))

Cationic surfactants ionize in solution and have a positive charge. Quaternary ammonium compounds are the principal cationic surfactants. They are used in fabric softeners and in fabric-softening laundrydetergents.

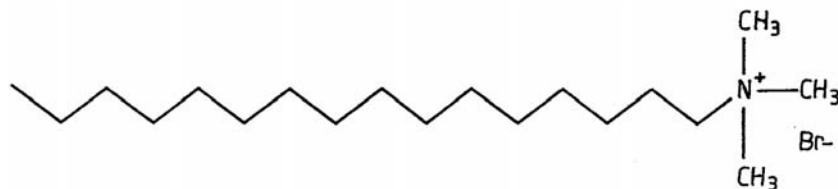


Fig. 13. Cationic surfactant (Cetyltrimethylammoniumbromide (CTAB))

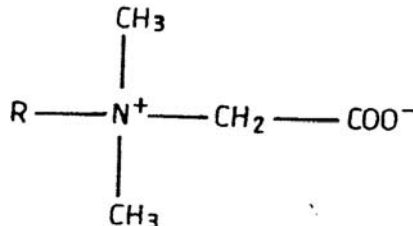


Fig. 14. Amphoteric surfactant (Alkyl betaine)

Amphoteric surfactants have the ability to be anionic (negatively charged), cationic (positively charged) or nonionic (no charge) in solution, depending on the pH (acidity or alkalinity) of the water. Imidazolines and betaines are the major amphoteric surfactants. They are used in personal cleansing and household cleaning products for their mildness and stability.

Synthetic detergents, however, may be soluble in both acidic and alkaline solutions and do not form insoluble precipitates in hard water. The comparison of the properties of detergents with soap is given in Table 1.

Detergents are not simple surfactants but a composite of different materials with varying functions. The composition of a typical detergent is given below.

- surfactant (detergent) (8-18%)
 - a builder (20-45%) e.g. phosphates or zeolites
 - a bleach (15-30%) e.g. sodium perborate
 - a fluorescer - 'whiter than white' (0.1%) e.g. Titanium dioxide
 - a filler (5-45%) e.g. sodium sulphate
- along with 4-20% water and may contain up to 0.75% enzyme.

Table 1. Comparison of the properties of soap and detergent

Soap	Detergent
Soaps cannot be used in hard water	Synthetic detergents can be used in hard water
Soap is made from vegetable oil or edible oils	Synthetic detergents made from byproducts of petroleum industry (to conserve edible oil)
Soaps cannot be used in acidic medium (otherwise precipitate the fatty acids)	Synthetic detergents can be used in any medium including acidic
Soaps have weak cleansing action	Synthetic detergents have strong cleansing action
Soaps are not very soluble in water	Synthetic detergents are highly soluble
Soaps are biodegradable and do not cause pollution	Synthetic detergents are not biodegradable and cause water pollution

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