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

PG & RESEARCH DEPARTMENT OF CHEMISTRY

STUDY MATERIAL

II-M.SC CHEMISTRY

SEMESTER – IV

RECENT TRENDS IN CHEMISTRY

BY

A. RAKINI

ASSISTANT PROFESSOR OF CHEMISTRY

UNIT – I: Nano Chemistry

Nano chemistry & fundamentals – Introduction – electronic structure –transport properties – mechanical properties – physical properties – applications – Nano tubes of other materials.

Nano Science: Self assembled mono layers – Introduction – mono layers on gold – growth process – phase transitions – pattering mono layers – mixed mono layer – SAME and applications

UNIT – II: Material Science

Crystal-crystal lattice-crystal defects-fullerene super conductors-High temperature materials-bio materials-thermo electronic materials- nano phase materials-smart material –NLO materials-conducting polymers.

UNIT – III: Supra Molecular Chemistry

Supra Molecular Chemistry – Concepts and Languages of supramolecular Chemistry – Supramolecular Reactivity and Catalysis. Catalysis by Reactive Macrocyclic Cation Receptor Molecules. Catalysis by Reactive Anion Receptor Molecules. Catalysis with Cyclophanes. Type Receptors. Supramolecular Metallocatalysis. Cocatalysis: Catalysis of Synthetic reactions. Biomolecular and Abiotic catalysis.Supramolecular Chemistry in solution: Cyclodextrin, Micelles, Dendrimmers, Gelators.Classification and typical reactions- Applications.

UNIT –IV: Green Chemistry

Green Chemistry – Photo Chemical Principles – Photo oxidation – photo degradation – Removal of hazardous chemicals from water – cleaner production concept – Implementation -Government rule.

UNIT – V: Chem-Informatics

Chem-Informatics: Introduction – Evaluation – History and uses – molecular modeling using computer –Basic idea - chemical information data base design and their management – data base concepts – structural languages chemical data base design Chemical information sources – chemical information researches formula searching.

****

UNIT – I: Nano Chemistry

Nano chemistry is the combination of chemistry and nano science. Nano chemistry is associated with synthesis of building blocks which are dependent on size, surface, shape and defect properties. Nano chemistry is being used in chemical, materials and physical, science as well as engineering, biological and medical applications. Nano chemistry and other nanoscience fields have the same core concepts but the usages of those concepts are different.

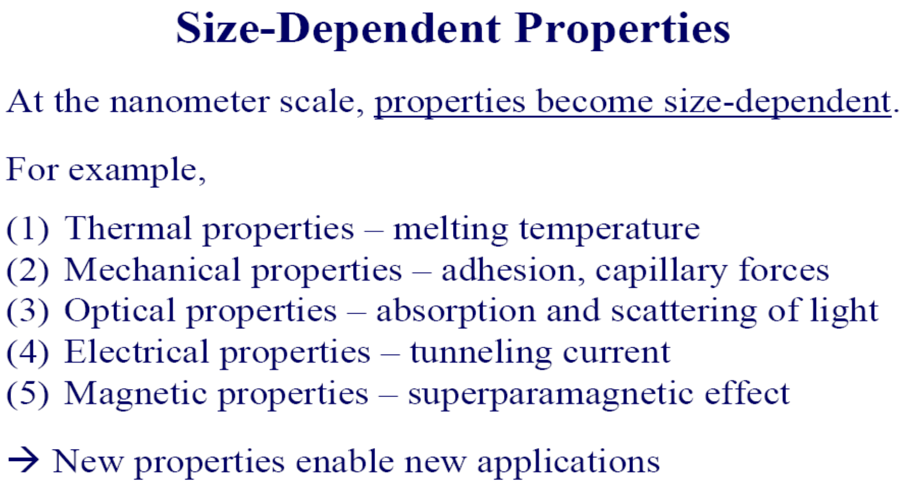
The nano prefix was given to nano chemistry when scientists observed the odd changes on materials when they were in nanometer-scale size. Several chemical modification on nanometer scaled structures, approves effects of being size dependent.

Nano chemistry can be characterized by concepts of size, shape, self-assembly, defects and bio-nano; So the synthesis of any new nano-construct is associated with all these concepts. Nano-construct synthesis is dependent on how the surface, size and shape will lead to self-assembly of the building blocks into the functional structures; they probably have functional defects and might be useful for electronic, photonic, medical or bioanalytical problems.

Silica, gold, polydimethylsiloxane, cadmium selenide, iron oxide and carbon are materials that show the transformative power of nano chemistry. Nano chemistry can make the most effective contrast agent of MRI out of iron oxide (rust) which has the ability of detecting cancers and even killing them at their initial stages. Silica (glass) can be used to bend or stop light in its tracks. Developing countries also use silicone to make the circuits for the fluids to attain developed world's pathogen detection abilities. Carbon has been used in different shapes and forms and it will become a better choice for electronic materials.

Overall, nano chemistry is not related to the atomic structure of compounds. Rather, it is about different ways to transform materials into solutions to solve problems. Chemistry mainly deals with degrees of freedom of atoms in the periodic table however nanochemistry brought other degrees of freedom that controls material's behaviors.

Nanochemical methods can be used to create carbon nanomaterials such as carbon nanotubes (CNT), graphene and fullerenes which have gained attention in recent years due to their remarkable mechanical and electrical properties.



Size-Dependent Properties

At the nanometer scale, properties become size-dependent.

For example,

(1) Thermal properties – melting temperature
(2) Mechanical properties – adhesion, capillary forces
(3) Optical properties – absorption and scattering of light
(4) Electrical properties – tunneling current
(5) Magnetic properties – superparamagnetic effect

→ New properties enable new applications

APPLICATIONS

Medicine

One highly researched application of nano chemistry is medicine. A simple skin-care product using the technology of nano chemistry is sunscreen. Sunscreen contains nanoparticles of zinc oxide and titanium dioxide. These nano chemicals protect the skin against harmful UV light by absorbing or reflecting the light and prevent the skin from retaining full damage by photoexcitation of electrons in the nanoparticle. Effectively, the excitation of the particle blocks skin cells from DNA damage.

Drug delivery

Emerging methods of drug delivery involving nanotechnological methods can be advantageous by improving increased bodily response, specific targeting, and efficient, non-toxic metabolism. Many nanotechnological methods and materials can be functionalized for drug delivery. Ideal materials employ a controlled-activation nanomaterial to carry a drug cargo into the body. Mesoporous silica nanoparticles (MSN) have been increasing in research popularity due to its large surface area and flexibility for various individual modifications while demonstrating high resolution performance under imaging techniques. Activation methods greatly vary across nanoscale drug delivery molecules, but the most commonly used activation method uses specific wavelengths of light to release the cargo. Nanovalve-controlled cargo release uses low intensity light and plasmonic heating to release the cargo in a variation of MSN containing gold molecules. The two-photon activated photo-transducer (2-NPT) uses near IR wavelengths of light to induce breaking of a disulfide bond to release the cargo. Recently, nanodiamonds have demonstrated potential in drug delivery due to non-toxicity, spontaneous absorption through the skin, and ability to enter the blood-brain barrier.

Tissue engineering

Because cells are very sensitive to nanotopographical features, optimization of surfaces in tissue engineering has pushed the frontiers towards implantation. Under the appropriate conditions, a carefully crafted 3-dimensional scaffold is used to direct cell seeds towards artificial organ growth. The 3-D scaffold incorporates various nanoscale factors that control the environment for optimal and appropriate functionality. The scaffold is an analog of the *in vivo* extracellular matrix *in vitro*, allowing for successful artificial organ growth by providing the necessary, complex biological factors *in vitro*. Additional advantages include the possibility of cell expression manipulation, adhesion, and drug delivery.

Wounds

For abrasions and wounds, nano chemistry has demonstrated applications in improving the healing process. Electrospinning is a polymerization method used biologically in tissue engineering, but can be functionalized for wound dressing as well as drug delivery. This produces nanofibers which encourage cell proliferation, antibacterial properties, and controlled environment. These properties have been created in macroscale; however, nanoscale versions may show improved efficiency due to nanotopographical features. Targeted interfaces between nanofibers and wounds have higher surface area interactions and are advantageously *in vivo*.

There is evidence certain nanoparticles of silver are useful to inhibit some viruses and bacteria.

New developments in nanochemistry provide a variety of nanostructure materials with significant properties that are highly controllable. Some of the application of these nanostructure materials include SAMs and lithography, use of nanowires in sensors, and nanoenzymes.

Electrics

Nanowire compositions

Scientists have also devised a large number of nanowire compositions with controlled length, diameter, doping, and surface structure by using vapor and solution phase strategies. These oriented single crystals are being used in semiconductor nanowire devices such as diodes, transistors, logic circuits, lasers and sensors. Since nanowires have one dimensional structure meaning large surface to volume ratio, the diffusion resistance decreases. In addition, their efficiency in electron transport which is due to the quantum confinement effect, make their electrical properties be influenced by minor perturbation. Therefore, use of these nanowires in nanosensor elements increases the sensitivity in electrode response. As mentioned above, one dimensionality and chemical flexibility of the semiconductor nanowires make them applicable in nano lasers. Peidong Yang and his co-workers have done some research on room-temperature ultraviolet nanowire nano lasers in which the significant properties of these nano lasers have been mentioned. They have concluded that using short wavelength nanolasers have applications in different fields such as optical computing, information storage, and microanalysis.

Catalysis

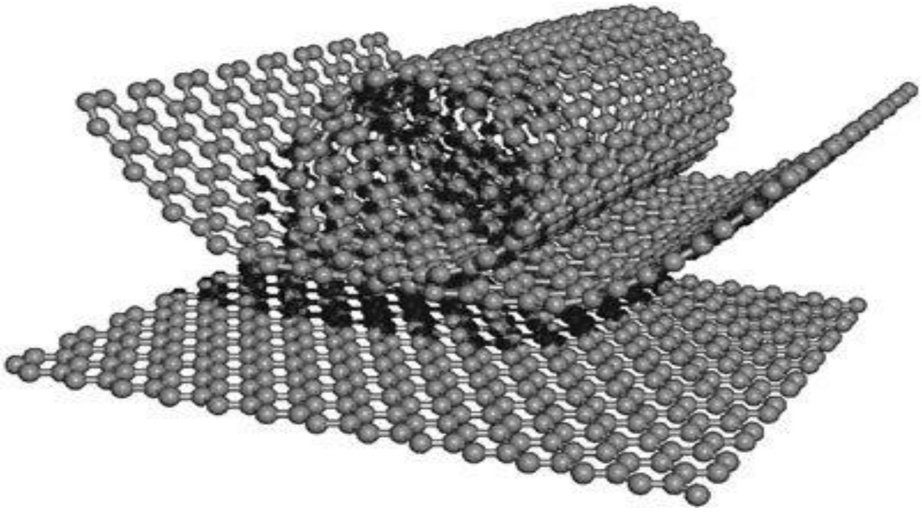
Nanoenzymes (or Nanozymes)

Nanostructure materials mainly used in nanoparticle-based enzymes have drawn attraction due to the specific properties they show. Very small size of these nanoenzymes (or nanozymes) (1–100 nm) have provided them unique optical, magnetic, electronic, and catalytic properties. Moreover, the control of surface functionality of nano particles and predictable nanostructure of these small sized enzymes have made them to create a complex structure on their surface which in turn meet the needs of specific application

What are carbon nanotubes?

Carbon nanotubes (CNTs) are cylindrical molecules that consist of rolled-up sheets of single-layer carbon atoms (graphene). They can be single-walled (SWCNT) with a diameter of less than 1 nanometer (nm) or multi-walled (MWCNT), consisting of several concentrically interlinked nanotubes, with diameters reaching more than 100 nm. Their length can reach several micrometers or even millimeters.

Like their building block graphene, CNTs are chemically bonded with sp2 bonds, an extremely strong form of molecular interaction. This feature combined with carbon nanotubes' natural inclination to rope together via van der Waals forces, provide the opportunity to develop ultra-high strength, low-weight materials that possess highly conductive electrical and thermal properties. This makes them highly attractive for numerous applications.

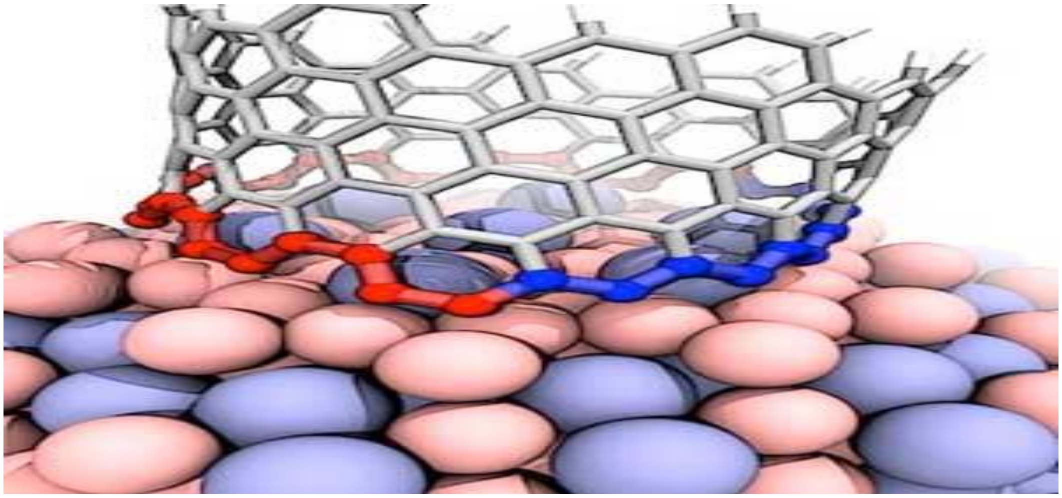


Schematic of how graphene could roll up to form a carbon nanotube.

The rolling-up direction (rolling-up or *chiral* vector) of the graphene layers determines the electrical properties of the nanotubes. Chirality describes the angle of the nanotube's hexagonal carbon-atom lattice.

Armchair nanotubes – so called because of the armchair-like shape of their edges – have identical chiral indices and are highly desired for their perfect conductivity. They are unlike *zigzag* nanotubes, which may be semiconductors. Turning a graphene sheet a mere 30 degrees will change the nanotube it forms from armchair to zigzag or vice versa.

While MWCNTs are always conducting and achieve at least the same level of conductivity as metals, SWCNTs' conductivity depends on their chiral vector: they can behave like a metal and be electrically conducting; display the properties of a semi-conductor; or be non-conducting. For example, a slight change in the pitch of the helicity can transform the tube from a metal into a large-gap semiconductor.



This illustration shows the interface between a growing carbon nanotube and a cobalt-tungsten catalyst. The atomic arrangement of the catalyst forces the nanotube to quickly transition from zigzag (blue) to armchair (red), which ultimately grows a nanotube.

Carbon nanotube uses and applications

CNTs are well-suited for virtually any application requiring high strength, durability, electrical conductivity, thermal conductivity and lightweight properties compared to conventional materials.

Currently, CNTs are mainly used as additives to synthetics. CNTs are commercially available as a powder, i.e. in a highly tangled-up and agglomerated form. For CNTs to unfold their particular properties they need to be untangled and spread evenly in the substrate.

Another requirement is that CNTs need to be chemically bonded with the substrate, e.g. a plastic material. For that purpose, CNTs are functionalized, i.e. their surface is chemically adapted for optimal incorporation into different materials and for the specific application in question.

Carbon nanotubes can also be spun into fibers, which not only promise interesting possibilities for specialty textiles but may also help realize a particularly utopian project – the space elevator.

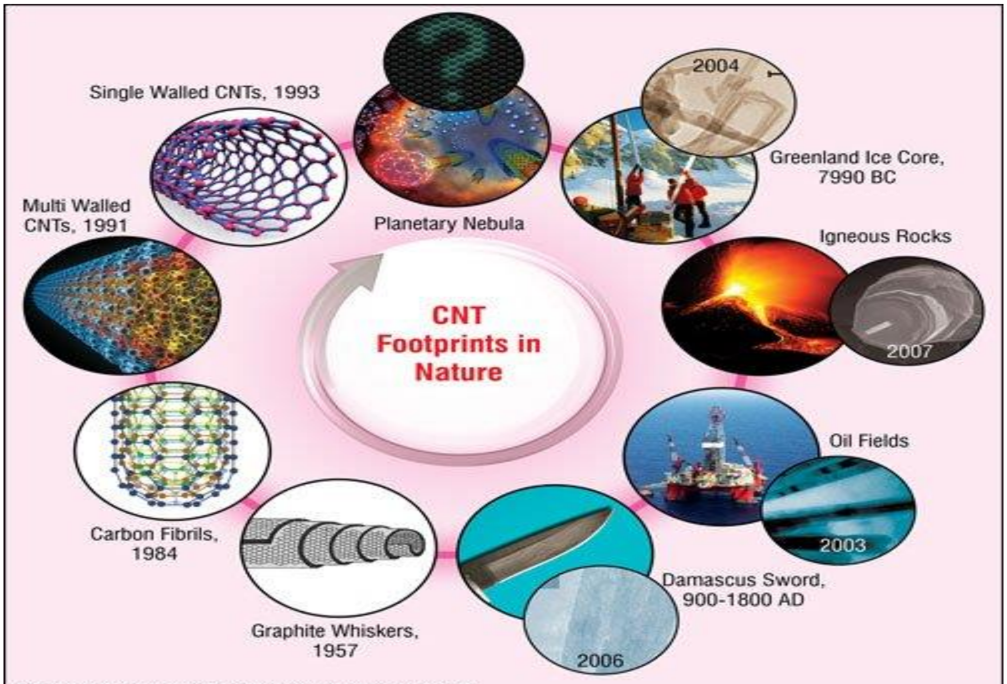
Materials

Carbon nanotube enabled nanocomposites have received much attention as a highly attractive alternative to conventional composite materials due to their mechanical, electrical, thermal, barrier and chemical properties such as electrical conductivity, increased tensile strength, improved heat deflection temperature, or flame retardancy.

These materials promise to offer increased wear resistance and breaking strength, antistatic properties as well as weight reduction. For instance, it has been estimated that advanced CNT composites could reduce the weight of aircraft and spacecraft by up to 30%.

These composite materials already find use in

- sporting goods (bicycle frames, tennis rackets, hockey sticks, golf clubs and balls, skis, kayaks; sports arrows)
- yachting (masts, hulls and other parts of sailboats)
- textiles (antistatic and electrically conducting textiles ('smart textiles'); bullet-proof vests, water-resistant and flame-retardant textiles)
- automotive, aeronautics and space (light-weight, high-strength structural composites)
- industrial engineering (e.g. coating of wind-turbine rotor blades, industrial robot arms)
- electrostatic charge protection (for instance, researchers have a developed electrically conducting and flexible CNT film specifically for space applications) and radiation shielding with CNT-based nanofoams and aerogels.



CNT footprints in nature and their respective year of discovery (inset)

Sensors

The group of Cees Dekker paved the way for the development of CNT-based electrochemical nanosensors by demonstrating the possibilities of SWCNTs as quantum wires and their effectiveness in the development of field-effect transistors.

Many studies have shown that although CNTs are robust and inert structures, their electrical properties are extremely sensitive to the effects of charge transfer and chemical doping by various molecules.

Most sensors based on CNTs are field effect transistors (FET) – although CNT are robust and inert structures, their electrical properties are extremely sensitive to the effects of charge transfer and chemical doping by various molecules. CNTs-FETs have been widely used to detect gases such as greenhouse gases in environmental applications.

The functionalization of CNTs is important for making them selective to the target analyte. Different types of sensors are based based on molecular recognition interactions between functionalism CNT and target analytes.

Nano Science:

Nanotechnology, also shortened to nanotech, is the use of matter on an atomic, molecular, and supramolecular scale for industrial purposes. The earliest, widespread description of nanotechnology referred to the particular technological goal of precisely manipulating atoms and molecules for fabrication of macroscale products, also now referred to as molecular nanotechnology.[1][2] A more generalized description of nanotechnology was subsequently established by the National Nanotechnology Initiative, which defined nanotechnology as the manipulation of matter with at least one dimension sized from 1 to 100 nanometers. This definition reflects the fact that quantum mechanical effects are important at this quantum-realm scale, and so the definition shifted from a particular technological goal to a research category inclusive of all types of research and technologies that deal with the special properties of matter which occur below the given size threshold. It is therefore common to see the plural form "nanotechnologies" as well as "nanoscale technologies" to refer to the broad range of research and applications whose common trait is size.

Nanotechnology as defined by size is naturally broad, including fields of science as diverse as surface science, organic chemistry, molecular biology, semiconductor physics, energy storage, engineering, microfabrication, and molecular engineering. The associated research and applications are equally diverse, ranging from extensions of conventional device physics to completely new approaches based upon molecular self-assembly, from developing new materials with dimensions on the nanoscale to direct control of matter on the atomic scale.

Self-Assembled Monolayer

Self-assembled monolayers (**SAM**) of organic molecules are molecular assemblies formed spontaneously on surfaces by adsorption and are organized into more or less large ordered domains. In some cases molecules that form the monolayer do not interact strongly with the substrate. This is the case for instance of the two-dimensional supramolecular networks of e.g. perylene tetracarboxylic dianhydride (PTCDA) on gold or of e.g. porphyrins on highly oriented pyrolitic graphite (HOPG). In other cases the molecules possess a head group that has a strong affinity to the substrate and anchors the molecule to it.[1] Such a SAM consisting of a head group, tail and functional end group is depicted in Figure 1. Common head groups include thiols, silanes, phosphonates, etc.

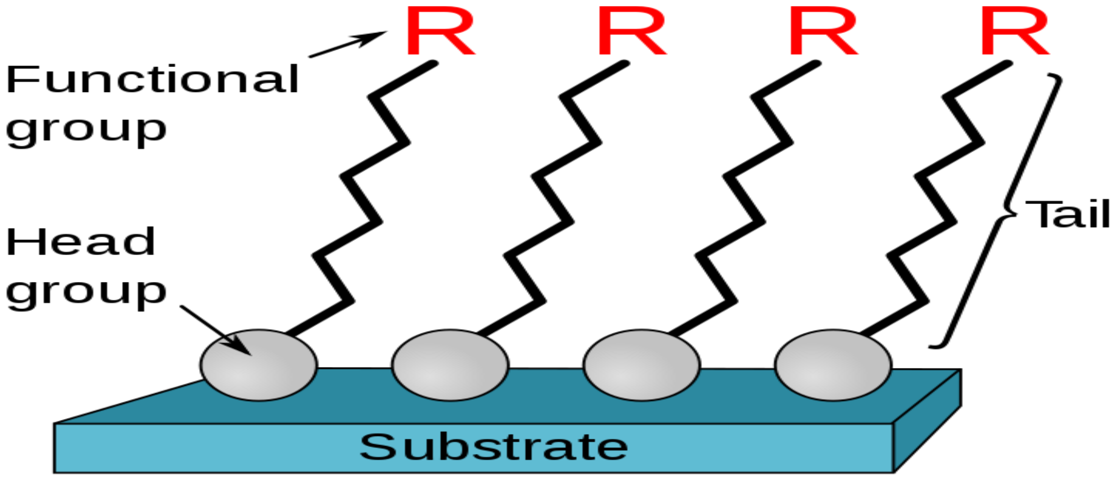


Figure 1. Representation of a SAM structure

SAMs are created by the chemisorption of "head groups" onto a substrate from either the vapor or liquid phase followed by a slow organization of "tail groups". Initially, at small molecular density on the surface, adsorbate molecules form either a disordered mass of molecules or form an ordered two-dimensional "lying down phase" and at higher molecular coverage, over a period of minutes to hours, begin to form three-dimensional crystalline or semicrystalline structures on the substrate surface.[9] The "head groups" assemble together on the substrate, while the tail groups assemble far from the substrate. Areas of close-packed molecules nucleate and grow until the surface of the substrate is covered in a single monolayer.

Adsorbate molecules adsorb readily because they lower the surface free-energy of the substrate and are stable due to the strong chemisorption of the "head groups." These bonds create monolayers that are more stable than the physisorbed bonds of Langmuir–Blodgett films. A Trichlorosilane based "head group", for example in a FDTS molecule, reacts with a hydroxyl group on a substrate, and forms very stable, covalent bond [R-Si-O-substrate] with an energy of 452 kJ/mol. Thiol-metal bonds are on the order of 100 kJ/mol, making them fairly stable in a variety of temperatures, solvents, and potentials. The monolayer packs tightly due to van der Waals interactions,[1][11] thereby reducing its own free energy. The adsorption can be described by the Langmuir adsorption isotherm if lateral interactions are neglected. If they cannot be neglected, the adsorption is better described by the Frumkin isotherm

Preparation

Metal substrates for use in SAMs can be produced through physical vapor deposition techniques, electrodeposition or electroless deposition.[1] Thiol or selenium SAMs produced by adsorption from solution are typically made by immersing a substrate into a dilute solution of alkane thiol in ethanol, though many different solvents can be used besides use of pure liquids. While SAMs are often allowed to form over 12 to 72 hours at room temperature, SAMs of alkane thiolates form within minutes. Special attention is essential in some cases, such as that of dithiol SAMs to avoid problems due to oxidation or photoinduced processes, which can affect terminal groups and lead to disorder and multilayer formation. In this case appropriate choice of solvents, their degassing by inert gasses and preparation in the absence of light is crucial[21][22] and allows formation of "standing up" SAMs with free –SH groups. Self-assembled monolayers can also be adsorbed from the vapor phase. In some cases when obtaining an ordered assembly is difficult or when different density phases need to be obtained substitutional self-assembly is used. Here one first forms the SAM of a given type of molecules, which give rise to ordered assembly and then a second assembly phase is performed (e.g. by immersion into a different solution). This method has also been used to give information on relative binding strengths of SAMs with different head groups and more generally on self-assembly characteristics

Kinetics

There is evidence that SAM formation occurs in two steps: an initial fast step of adsorption and a second slower step of monolayer organization. Adsorption occurs at the liquid–liquid, liquid–vapor, and liquid-solid interfaces. The transport of molecules to the surface occurs due to a combination of diffusion and convective transport. According to the Langmuir or Avrami kinetic model the rate of deposition onto the surface is proportional to the free space of the surface.

Where **θ** is the proportional amount of area deposited and **k** is the rate constant. Although this model is robust it is only used for approximations because it fails to take into account intermediate processes. Dual polarisation interferometry being a real time technique with ~10 Hz resolution can measure the kinetics of monolayer self-assembly directly.

Once the molecules are at the surface the self-organization occurs in three phases:

1. A low-density phase with random dispersion of molecules on the surface.

2. An intermediate-density phase with conformational disordered molecules or molecules lying flat on the surface.

3. A high-density phase with close-packed order and molecules standing normal to the substrate's surface.

The phase transitions in which a SAM forms depends on the temperature of the environment relative to the triple point temperature, the temperature in which the tip of the low-density phase intersects with the intermediate-phase region. At temperatures below the triple point the growth goes from phase 1 to phase 2 where many islands form with the final SAM structure, but are surrounded by random molecules. Similar to nucleation in metals, as these islands grow larger they intersect forming boundaries until they end up in phase 3, as seen below.

At temperatures above the triple point the growth is more complex and can take two paths. In the first path the heads of the SAM organize to their near final locations with the tail groups loosely formed on top. Then as they transit to phase 3, the tail groups become ordered and straighten out. In the second path the molecules start in a lying down position along the surface. These then form into islands of ordered SAMs, where they grow into phase 3, as seen below.

The nature in which the tail groups organize themselves into a straight ordered monolayer is dependent on the inter-molecular attraction, or van der Waals forces, between the tail groups. To minimize the free energy of the organic layer the molecules adopt conformations that allow high degree of Van der Waals forces with some hydrogen bonding. The small size of the SAM molecules are important here because Van der Waals forces arise from the dipoles of molecules and are thus much weaker than the surrounding surface forces at larger scales. The assembly process begins with a small group of molecules, usually two, getting close enough that the Van der Waals forces overcome the surrounding force. The forces between the molecules orient them so they are in their straight, optimal, configuration. Then as other molecules come close by they interact with these already organized molecules in the same fashion and become a part of the conformed group. When this occurs across a large area the molecules support each other into forming their SAM shape seen in Figure 1. The orientation of the molecules can be described with two parameters: α and β. α is the angle of tilt of the backbone from the surface normal. In typical applications α varies from 0 to 60 degrees depending on the substrate and type of SAM molecule. β is the angle of rotation along the long axis of tee molecule. β is usually between 30 and 40 degrees. In some cases existence of kinetic traps hindering the final ordered orientation has been pointed out. Thus in case of dithiols formation of a "lying down" phase was considered an impediment to formation of "standing up" phase, however various recent studies indicate this is not the case.

Applications

Thin-film SAMs

SAMs are an inexpensive and versatile surface coating for applications including control of wetting and adhesion, chemical resistance, bio compatibility, sensitization, and molecular recognition for sensors and nano fabrication. Areas of application for SAMs include biology, electrochemistry and electronics, nanoelectromechanical systems (NEMS) and microelectromechanical systems (MEMS), and everyday household goods. SAMs can serve as models for studying membrane properties of cells and organelles and cell attachment on surfaces. SAMs can also be used to modify the surface properties of electrodes for electrochemistry, general electronics, and various NEMS and MEMS. For example, the properties of SAMs can be used to control electron transfer in electrochemistry. They can serve to protect metals from harsh chemicals and etchants. SAMs can also reduce sticking of NEMS and MEMS components in humid environments. In the same way, SAMs can alter the properties of glass. A common household product, Rain-X, utilizes SAMs to create a hydrophobic monolayer on car windshields to keep them clear of rain. Another application is an anti-adhesion coating on nanoimprint lithography (NIL) tools and stamps. One can also coat injection molding tools for polymer replication with a Perfluordecyltrichlorosilane SAM.

Thin film SAMs can also be placed on nanostructures. In this way they functionalize the nanostructure. This is advantageous because the nanostructure can now selectively attach itself to other molecules or SAMs. This technique is useful in biosensors or other MEMS devices that need to separate one type of molecule from its environment. One example is the use of magnetic nanoparticles to remove a fungus from a blood stream. The nanoparticle is coated with a SAM that binds to the fungus. As the contaminated blood is filtered through a MEMS device the magnetic nanoparticles are inserted into the blood where they bind to the fungus and are then magnetically driven out of the blood stream into a nearby laminar waste stream.

Patterned SAMs

SAMs are also useful in depositing nanostructures, because each adsorbate molecule can be tailored to attract two different materials. Current techniques utilize the head to attract to a surface, like a plate of gold. The terminal group is then modified to attract a specific material like a particular nanoparticle, wire, ribbon, or other nanostructure. In this way, wherever the SAM is patterned to a surface there will be nanostructures attached to the tail groups. One example is the use of two types of SAMs to align single wall carbon nanotubes, SWNTs. Dip pen nanolithography was used to pattern a 16-mercaptohexadecanoic acid (MHA)SAM and the rest of the surface was passivated with 1-octadecanethiol (ODT) SAM. The polar solvent that is carrying the SWNTs is attracted to the hydrophilic MHA; as the solvent evaporates, the SWNTs are close enough to the MHA SAM to attach to it due to Van der Waals forces. The nanotubes thus line up with the MHA-ODT boundary. Using this technique Chad Mirkin, Schatz and their co-workers were able to make complex two-dimensional shapes, a representation of a shape created is shown to the right. Another application of patterned SAMs is the functionalization of biosensors. The tail groups can be modified so they have an affinity for cells, proteins, or molecules. The SAM can then be placed onto a biosensor so that binding of these molecules can be detected. The ability to pattern these SAMs allows them to be placed in configurations that increase sensitivity and do not damage or interfere with other components of the biosensor.

Many of the SAM properties, such as thickness, are determined in the first few minutes. However, it may take hours for defects to be eliminated via annealing and for final SAM properties to be determined. The exact kinetics of SAM formation depends on the adsorbate, solvent and substrate properties. In general, however, the kinetics are dependent on both preparations conditions and material properties of the solvent, adsorbate and substrate. Specifically, kinetics for adsorption from a liquid solution are dependent on:

- Temperature – room-temperature preparation improves kinetics and reduces defects.
- Concentration of adsorbate in the solution – low concentrations require longer immersion times and often create highly crystalline domains.
- Purity of the adsorbate – impurities can affect the final physical properties of the SAM
- Dirt or contamination on the substrate – imperfections can cause defects in the SAM

The final structure of the SAM is also dependent on the chain length and the structure of both the adsorbate and the substrate. Steric hindrance and metal substrate properties, for example, can affect the packing density of the film, while chain length affects SAM thickness. Longer chain length also increases the thermodynamic stability.

UNIT – II (MATERIAL SCIENCE)

CRYSTAL

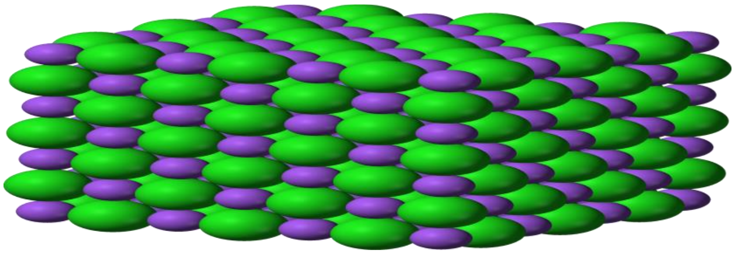
A **crystal** or **crystalline solid** is a solid material whose constituents (such as atoms, molecules, or ions) are arranged in a highly ordered microscopic structure, forming a crystal lattice that extends in all directions. In addition, macroscopic single crystals are usually identifiable by their geometrical shape, consisting of flat faces with specific, characteristic orientations. The scientific study of crystals and crystal formation is known as crystallography. The process of crystal formation via mechanisms of crystal growth is called crystallization or solidification

Crystal structure

he scientific definition of a "crystal" is based on the microscopic arrangement of atoms inside it, called the crystal structure. A crystal is a solid where the atoms form a periodic arrangement. (Quasicrystals are an exception, see below).

Not all solids are crystals. For example, when liquid water starts freezing, the phase change begins with small ice crystals that grow until they fuse, forming a *polycrystalline* structure. In the final block of ice, each of the small crystals (called "crystallites" or "grains") is a true crystal with a periodic arrangement of atoms, but the whole polycrystal does *not* have a periodic arrangement of atoms, because the periodic pattern is broken at the grain boundaries. Most macroscopic inorganic solids are polycrystalline, including almost all metals, ceramics, ice, rocks, etc. Solids that are neither crystalline nor polycrystalline, such as glass, are called *amorphous solids*, also called glassy, vitreous, or noncrystalline. These have no periodic order, even microscopically. There are distinct differences between crystalline solids and amorphous solids: most notably, the process of forming a glass does not release the latent heat of fusion, but forming a crystal does.

A crystal structure (an arrangement of atoms in a crystal) is characterized by its *unit cell*, a small imaginary box containing one or more atoms in a specific spatial arrangement. The unit cells are stacked in three-dimensional space to form the crystal.



Microscopic structure of a halite crystal. (Purple is sodium ion, green is chlorine ion). There is cubic symmetry in the atoms' arrangement

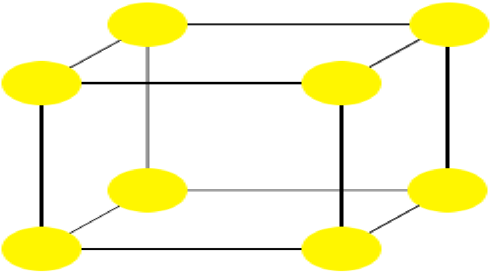
CRYSTAL LATTICE

The **crystal lattice** is the symmetrical three-dimensional structural arrangements of atoms, ions or molecules (constituent particle) inside a **crystalline** solid as points. It can be defined as the geometrical arrangement of the atoms, ions or molecules of the **crystalline** solid as points in space.

What is a Lattice?

A lattice is an ordered array of points describing the arrangement of particles that form a crystal.

The unit cell of a crystal is defined by the lattice points. The unit cell is the smallest part of a crystal that repeated regularly through translation in three dimensions creates the whole crystal.



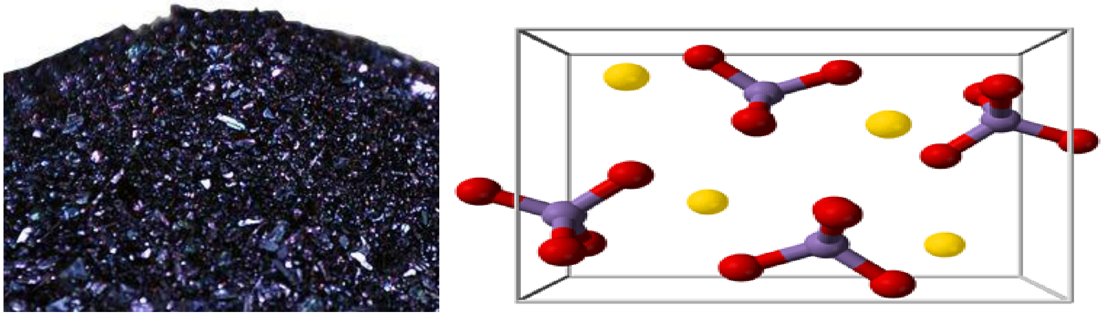
For example, the image shown here is the unit cell of a primitive cubic structure.

In the structure drawn, all of the particles (yellow) are the same. In this particular case, the lattice points defining the unit cell coincide with the centers of the crystal's particles. This need not always be the case.

The Ionic Lattice

If a crystal is formed of ions, the compound can be described as an ionic lattice.

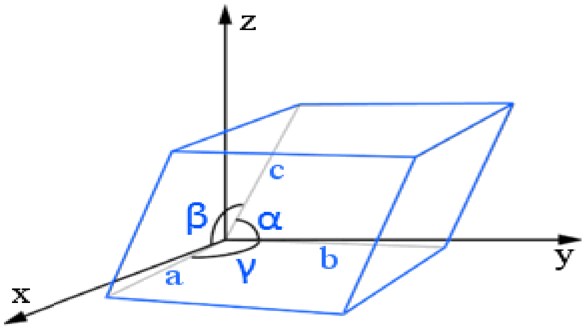
Well-known examples of ionic lattices are sodium chloride, potassium permanganate, borax (sodium borate) and copper(II) sulfate.



a) Potassium permanganate crystals. Image by Ben Mills.

b) Potassium permanganate's unit cell. Image by Ben Mills.

Lattice Constants



The lattice constants (or lattice parameters) are the lengths and the angles between of the edges of the unit cell.

In this parallelepiped lattice diagram, the lattice constants are a, b, and c (lengths) and α, β, and γ (angles).

CRYSTAL DEFECTES

Point defects

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

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

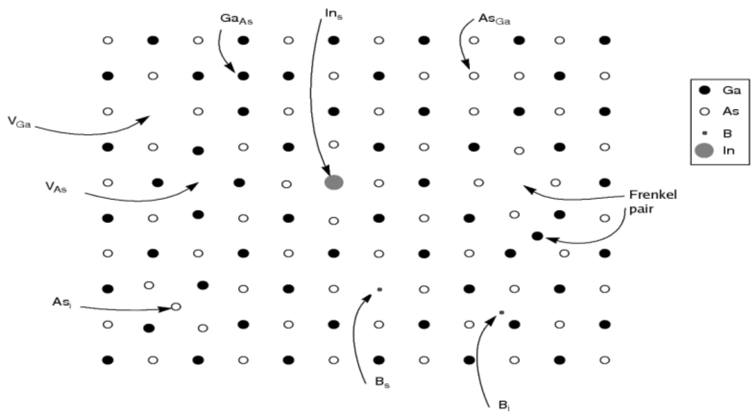
- Interstitial defects are atoms that occupy a site in the crystal structure at which there is usually not an atom. They are generally high energy configurations. Small atoms (mostly impurities) in some crystals can occupy interstices without high energy, such as hydrogen in palladium.

- A nearby pair of a vacancy and an interstitial is often called a Frenkel defect or Frenkel pair. This is caused when an ion moves into an interstitial site and creates a vacancy.

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

- **Antisite defects** occur in an ordered alloy or compound when atoms of different type exchange positions. For example, some alloys have a regular structure in which every other atom is a different species; for illustration assume that type A atoms sit on the corners of a cubic lattice, and type B atoms sit in the center of the cubes. If one cube has an A atom at its center, the atom is on a site usually occupied by a B atom, and is thus an antisite defect. This is neither a vacancy nor an interstitial, nor an impurity.

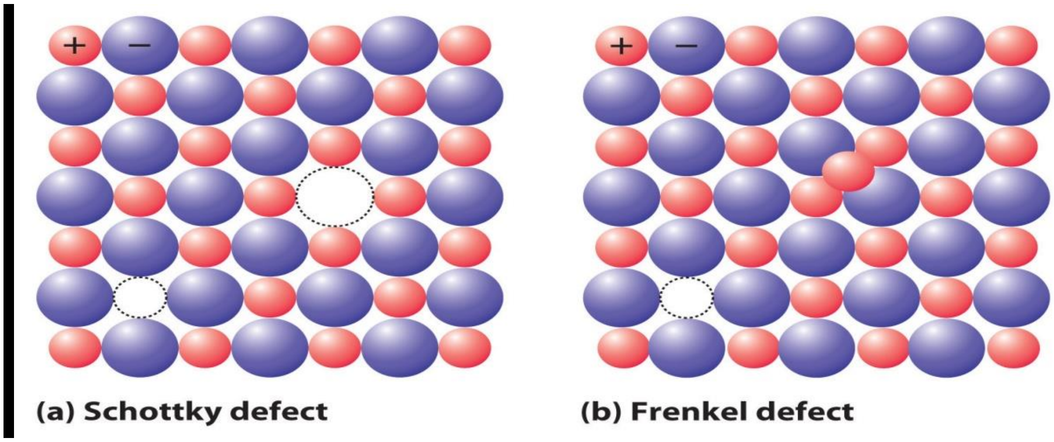
- Topological defects are regions in a crystal where the normal chemical bonding environment is topologically different from the surroundings. For instance, in a perfect sheet of graphite (graphene) all atoms are in rings containing six atoms. If the sheet contains regions where the number of atoms in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



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

- Also amorphous solids may contain defects. These are naturally somewhat hard to define, but sometimes their nature can be quite easily understood. For instance, in ideally bonded amorphous silica all Si atoms have 4 bonds to O atoms and all O atoms have 2 bonds to Si atom. Thus e.g. an O atom with only one Si bond (a dangling bond) can be considered a defect in silica.[8] Moreover, defects can also be defined in amorphous solids based on empty or densely packed local atomic neighbourhoods, and the properties of such 'defects' can be shown to be similar to normal vacancies and interstitials in crystals.
- Complexes can form between different kinds of point defects. For example, if a vacancy encounters an impurity, the two may bind together if the impurity is too large for the lattice. Interstitials can form 'split interstitial' or 'dumbbell' structures where two atoms effectively share an atomic site, resulting in neither atom actually occupying the site

The Two Most Common Defects in Ionic Solids



(a) A Schottky defect in KCl shows the missing cation/anion pair. (b) A Frenkel defect in AgI shows a misplaced Ag^+ cation.

- Occasionally one of the ions in an ionic lattice is simply in the wrong position. An example of this phenomenon, called a Frenkel defect, is a cation that occupies a tetrahedral hole rather than an octahedral hole in the anion lattice (part (b) in Figure 12.18 "The Two Most Common Defects in Ionic Solids"). Frenkel defects are most common in salts that have a large anion and a relatively small cation. To preserve electrical neutrality, one of the normal cation sites, usually octahedral, must be vacant.
- Frenkel defects are particularly common in the silver halides AgCl, AgBr, and AgI, which combine a rather small cation (Ag^+, ionic radius = 115 pm) with large, polarizable anions. Certain more complex salts with a second cation in addition to Ag^+ and Br^- or I^- have so many Ag^+ ions in tetrahedral holes that they are good electrical conductors in the solid state; hence they are called solid electrolytes. (As you learned in Chapter 4 "Reactions in Aqueous Solution", most ionic compounds do not conduct electricity in the solid state, although they do conduct electricity when molten or dissolved in a solvent that separates the ions, allowing them to migrate in response to an applied electric field.) In response to an applied voltage, the cations in solid electrolytes can diffuse rapidly through the lattice via

octahedral holes, creating Frenkel defects as the cations migrate. Sodium–sulfur batteries use a solid Al_2O_3 electrolyte with small amounts of solid Na_2O. Because the electrolyte cannot leak, it cannot cause corrosion, which gives a battery that uses a solid electrolyte a significant advantage over one with a liquid electrolyte.

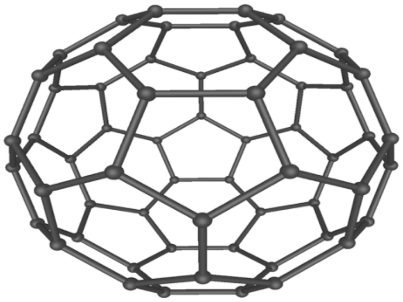
Fullerene

A **fullerene** is an allotrope of carbon whose molecule consists of carbon atoms connected by single and double bonds so as to form a closed or partially closed mesh, with fused rings of five to seven atoms. The molecule may be a hollow sphere, ellipsoid, tube, or many other shapes and sizes. Graphene (isolated atomic layers of graphite), which is a flat mesh of regular hexagonal rings, can be seen as an extreme member of the family.

Fullerenes with a closed mesh topology are informally denoted by their empirical formula C_n, often written C*n*, where *n* is the number of carbon atoms. However, for some values of *n* there may be more than one isomer.

The family is named after buckminsterfullerene (C_{60}), the most famous member, which in turn is named after Buckminster Fuller. The closed fullerenes, especially C_{60}, are also informally called **buckyballs** for their resemblance to the standard ball of association football ("soccer"). Nested closed fullerenes have been named **bucky onions**. Cylindrical fullerenes are also called carbon nanotubes or **buckytubes**. The bulk solid form of pure or mixed fullerenes is called **fullerite**.

Fullerenes had been predicted for some time, but only after their accidental synthesis in 1985 were they detected in nature [1][2] and outer space.[3][4] The discovery of fullerenes greatly expanded the number of known allotropes of carbon, which had previously been limited to graphite, diamond, and amorphous carbon such as soot and charcoal. They have been the subject of intense research, both for their chemistry and for their technological applications, especially in materials science, electronics, and nanotechnology.[5]



Model of the C_{60} fullerene (buckminsterfullerene)

Buckminsterfullerene

Main article: Buckminsterfullerene

Buckminsterfullerene is the smallest fullerene molecule containing pentagonal and hexagonal rings in which no two pentagons share an edge (which can be destabilizing, as in pentalene). It is also most common in terms of natural occurrence, as it can often be found in soot.

The empirical formula of buckminsterfullerene is C_{60} and its structure is a truncated icosahedron, which resembles an association football ball of the type made of twenty hexagons and twelve pentagons, with a carbon atom at the vertices of each polygon and a bond along each polygon edge.

The van der Waals diameter of a buckminsterfullerene molecule is about 1.1 nanometers (nm). The nucleus to nucleus diameter of a buckminsterfullerene molecule is about 0.71 nm.

The buckminsterfullerene molecule has two bond lengths. The 6:6 ring bonds (between two hexagons) can be considered "double bonds" and are shorter than the 6:5 bonds (between a hexagon and a pentagon). Its average bond length is 1.4 angstroms.

Applications

Fullerenes have been extensively used for several biomedical applications including the design of high-performance MRI contrast agents, X-ray imaging contrast agents, photodynamic therapy and drug and gene delivery, summarized in several comprehensive reviews.

Medical research

In April 2003, fullerenes were under study for potential medicinal use: binding specific antibiotics to the structure to target resistant bacteria and even target certain cancer cells such as melanoma. The October 2005 issue of *Chemistry & Biology* contained an article describing the use of fullerenes as light-activated antimicrobial agents.

Tumor research

While past cancer research has involved radiation therapy, photodynamic therapy is important to study because breakthroughs in treatments for tumor cells will give more options to patients with different conditions. Recent experiments using HeLa cells in cancer research involves the development of new photosensitizers with increased ability to be absorbed by cancer cells and still trigger cell death. It is also important that a new photosensitizer does not stay in the body for a long time to prevent unwanted cell damage.

Fullerenes can be made to be absorbed by HeLa cells. The C_{60} derivatives can be delivered to the cells by using the functional groups L-phenylalanine, folic acid, and L-arginine among others.

Functionalizing the fullerenes aims to increase the solubility of the molecule by the cancer cells. Cancer cells take up these molecules at an increased rate because of an upregulation of transporters in the cancer cell, in this case amino acid transporters will bring in the L-arginine and L-phenylalanine functional groups of the fullerenes.

Once absorbed by the cells, the C_{60} derivatives would react to light radiation by turning molecular oxygen into reactive oxygen which triggers apoptosis in the HeLa cells and other cancer cells that can absorb the fullerene molecule. This research shows that a reactive substance can target cancer cells and then be triggered by light radiation, minimizing damage to surrounding tissues while undergoing treatment.

When absorbed by cancer cells and exposed to light radiation, the reaction that creates reactive oxygen damages the DNA, proteins, and lipids that make up the cancer cell. This cellular damage forces the cancerous cell to go through apoptosis, which can lead to the reduction in size of a tumor. Once the light radiation treatment is finished the fullerene will reabsorb the free radicals to prevent damage of other tissues.[77] Since this treatment focuses on cancer cells, it is a good option for patients whose cancer cells are within reach of light radiation. As this research continues, the treatment may penetrate deeper into the body and be absorbed by cancer cells more effectively.

HIIGH TEMPERATURE MATERIALS

Ultra-high-temperature ceramics (**UHTCs**) are a class of refractory ceramics that offer excellent stability at temperatures exceeding 2000 °C[1] being investigated as possible thermal protection system (TPS) materials, coatings for materials subjected to high temperatures, and bulk materials for heating elements. Broadly speaking, UHTCs are borides, carbides, nitrides, and oxides of early transition metals. Current efforts have focused on heavy, early transition metal borides such as hafnium diboride (HfB_2) and zirconium diboride (ZrB_2); additional UHTCs under investigation for TPS applications include hafnium nitride (HfN), zirconium nitride (ZrN), titanium carbide (TiC), titanium nitride (TiN), thorium dioxide (ThO_2), tantalum carbide (TaC) and their associated composites.

Beginning in the early 1960s, demand for high-temperature materials by the nascent aerospace industry prompted the Air Force Materials Laboratory to begin funding the development of a new class of materials that could withstand the environment of proposed hypersonic vehicles such as Dyna-soar and the Space Shuttle at Manlabs Incorporated. Through a systematic investigation of the refractory properties of binary ceramics, they discovered that the early transition metal borides, carbides, and nitrides had surprisingly high thermal conductivity, resistance to oxidation, and reasonable mechanical strength when small grain sizes were used. Of these, ZrB_2 and HfB_2 in composites containing approximately 20% volume SiC were found to be the best performing.[12]

UHTC research was largely abandoned after the pioneering mid-century Manlabs work due to the completion of the Space Shuttle missions and the elimination of the Air force spaceplane development. Three decades later, however, research interest was rekindled by a string of 1990s era NASA programs aimed at developing a fully reusable hypersonic spaceplane such as the National Aerospace Plane, Venturestar/X-33, Boeing X-37, and the Air Force's Blackstar program.[13] New research in UHTCs was led by NASA Ames, with research at the center continuing to the present through funding from the NASA Fundamental Aeronautics Program. UHTCs also saw expanded use in varied environments, from nuclear engineering to aluminum production. Production of a hafnium diboride set of fins via robocasting, a 3D Printing technique. 0.41mm nozzle, 4x speed.

In order to test real world performance of UHTC materials in reentry environments, NASA Ames conducted two flight experiments in 1997 and 2000. The slender Hypersonic Aero-thermodynamic Research Probes (SHARP B1 and

B2) briefly exposed the UHTC materials to actual reentry environments by mounting them on modified nuclear ordnance Mk12A reentry vehicles and launching them on Minuteman III ICBMs. Sharp B-1 had a HfB2/SiC nosecone with a tip radius of 3.5 mm which experienced temperatures well above 2815 °C during reentry, ablating away at an airspeed of 6.9 km/s as predicted; however, it was not recovered and its axially-symmetric cone shape did not provide flexural strength data needed to evaluate the performance of UHTCs in linear leading edges. To improve the characterization of UHTC mechanical strength and better study their performance, SHARP-B2, was recovered and included four retractable, sharp wedge-like protrusions called "strakes" which each contained three different UHTC compositions which were extended into the reentry flow at different altitudes.

Physical properties

Most research conducted in the last two decades has focused on improving the performance of the two most promising compounds developed by Manlabs, ZrB_2 and HfB_2, though significant work has continued in characterizing the nitrides, oxides, and carbides of the group four and five elements.[16][17][18][19] In comparison to carbides and nitrides, the diborides tend to have higher thermal conductivity but lower melting points, a tradeoff which gives them good thermal shock resistance and makes them ideal for many high-temperature thermal applications. The melting points of many UHTCs are shown in Table 1.[11] Despite the high melting points of pure UHTCs, they are unsuitable for many refractory applications because of their high susceptibility to oxidation at elevated temperatures.

Table 1. Crystal structures, densities, and melting points of selected UHTCs.

Material	**Formula**	**Crystal structure**	**Lattice parameters (Å)**			**Density (g/cm³)**	**Melting point**	
			a	**b**	**c**		**(°C)**	**(°F)**
Hafnium carbide	HfC	FCC	4.638	4.638	4.638	12.76	3958	7156
Tantalum carbide	TaC	Cubic	4.455	4.455	4.455	14.50	3768	6814
Niobium carbide	NbC	Cubic	-	-	-	7.820	3490	-
Zirconium carbide	ZrC	FCC	4.693	4.693	4.693	6.56	3400	6152
Hafnium nitride	HfN	FCC	4.525	4.525	4.525	13.9	3385	6125
Hafnium boride	HfB_2	Hexagonal	3.142	–	3.476	11.19	3380	6116
Zirconium boride	ZrB_2	Hexagonal	3.169	–	3.530	6.10	3245	5873
Titanium boride	TiB_2	Hexagonal	3.030	–	3.230	4.52	3225	5837
Titanium carbide	TiC	Cubic	4.327	4.327	4.327	4.94	3100	5612
Niobium boride	NbB_2	Hexagonal	3.085	-	3.311	6.97	3050	
Tantalum boride	TaB_2	Hexagonal	3.098	–	3.227	12.54	3040	5504
Titanium nitride	TiN	FCC	4.242	4.242	4.242	5.39	2950	5342

Zirconium nitride	ZrN	FCC	4.578	4.578	4.578	7.29	2950	5342
Silicon carbide	SiC	Polymorphic	–	Various	–	3.21	2545	4613
Vanadium carbide	VC	Cubic	-	-	-	5.77	2810 unstable	-
Tantalum nitride	TaN	Cubic	4.330	4.330	4.330	14.30	2700	4892
Niobium nitride	NbN	Cubic	-	-	-	8.470	2573	-
Vanadium nitride	VN	Cubic	-	-	-	6.13	2050 unstable ?	-

Biomaterial

A **biomaterial** is a substance that has been engineered to interact with biological systems for a medical purpose, either a therapeutic (treat, augment, repair, or replace a tissue function of the body) or a diagnostic one. As a science, **biomaterials** is about fifty years old. The study of biomaterials is called **biomaterials science** or **biomaterials engineering**. It has experienced steady and strong growth over its history, with many companies investing large amounts of money into the development of new products. Biomaterials science encompasses elements of medicine, biology, chemistry, tissue engineering and materials science.

Note that a biomaterial is different from a biological material, such as bone, that is produced by a biological system. Additionally, care should be exercised in defining a biomaterial as biocompatible, since it is application-specific. A biomaterial that is biocompatible or suitable for one application may not be biocompatible in another.[

Self-assembly

Self-assembly is the most common term in use in the modern scientific community to describe the spontaneous aggregation of particles (atoms, molecules, colloids, micelles, etc.) without the influence of any external forces. Large groups of such particles are known to assemble themselves into thermodynamically stable, structurally well-defined arrays, quite reminiscent of one of the seven crystal systems found in metallurgy and mineralogy (e.g. face-centered cubic, body-centered cubic, etc.). The fundamental difference in equilibrium structure is in the spatial scale of the unit cell (lattice parameter) in each particular case.

Molecular self assembly is found widely in biological systems and provides the basis of a wide variety of complex biological structures. This includes an emerging class of mechanically superior biomaterials based on microstructural features and designs found in nature. Thus, self-assembly is also emerging as a new strategy in chemical synthesis and nanotechnology. Molecular crystals, liquid crystals, colloids, micelles, emulsions, phase-separated polymers, thin films and self-assembled monolayers all represent examples of the types of highly ordered structures, which are obtained using these techniques. The distinguishing feature of these methods is self-organization.[7][8][9]

Structural hierarchy

Nearly all materials could be seen as hierarchically structured, since the changes in spatial scale bring about different mechanisms of deformation and damage. However, in biological materials, this hierarchical organization is inherent to the microstructure. One of the first examples of this, in the history of structural biology, is the early X-ray scattering work on the hierarchical structure of hair and wool by Astbury and Woods.[10] In bone, for example, collagen is the building block of the organic matrix, a triple helix with diameter of 1.5 nm. These tropocollagen molecules are intercalated with the mineral phase (hydroxyapatite, calcium phosphate) forming fibrils that curl into helicoids of alternating directions. These "osteons" are the basic building blocks of bones, with the volume fraction distribution between organic and mineral phase being about 60/40.

In another level of complexity, the hydroxyapatite crystals are mineral platelets that have a diameter of approximately 70 to 100 nm and thickness of 1 nm. They originally nucleate at the gaps between collagen fibrils.[11]

Similarly, the hierarchy of abalone shell begins at the nanolevel, with an organic layer having a thickness of 20 to 30 nm. This layer proceeds with single crystals of aragonite (a polymorph of $CaCO_3$) consisting of "bricks" with dimensions of 0.5 and finishing with layers approximately 0.3 mm (mesostructure).[12]

Crabs are arthropods, whose carapace is made of a mineralized hard component (exhibits brittle fracture) and a softer organic component composed primarily of chitin. The brittle component is arranged in a helical pattern. Each of these mineral ‘rods’ (1 μm diameter) contains chitin–protein fibrils with approximately 60 nm diameter. These fibrils are made of 3 nm diameter canals that link the interior and exterior of the shell.

Applications

Biomaterials are used in:

1. Joint replacements
2. Bone plates [13]
3. Intraocular lenses (IOLs) for eye surgery
4. Bone cement
5. Artificial ligaments and tendons

6. Dental implants for tooth fixation
7. Blood vessel prostheses
8. Heart valves
9. Skin repair devices (artificial tissue)
10. Cochlear replacements
11. Contact lenses
12. Breast implants
13. Drug delivery mechanisms
14. Sustainable materials
15. Vascular grafts
16. Stents
17. Nerve conduits
18. Surgical sutures, clips, and staples for wound closure
19. Pins and screws for fracture stabilisation
20. Surgical mesh

Biomaterials must be compatible with the body, and there are often issues of biocompatibility, which must be resolved before a product can be placed on the market and used in a clinical setting. Because of this, biomaterials are usually subjected to the same requirements as those undergone by new drug therapies. All manufacturing companies are also required to ensure traceability of all of their products, so that if a defective product is discovered, others in the same batch may be traced.

Heart valves

In the United States, 49% of the 2.5 lakh valve replacement procedures performed annually involve a mechanical valve implant. The most widely used valve is a bileaflet disc heart valve or St. Jude valve. The mechanics involve two semicircular discs moving back and forth, with both allowing the flow of blood as well as the ability to form a seal against backflow. The valve is coated with pyrolytic carbon and secured to the surrounding tissue with a mesh of woven fabric called Dacron (du Pont's trade name for polyethylene terephthalate). The mesh allows for the body's tissue to grow, while incorporating the valve.

Skin repair

Main article: Tissue engineering

Most of the time, "**Artificial' tissue**" is grown from the patient's own cells. However, when the damage is so extreme that it is impossible to use the patient's own cells, artificial tissue cells are grown. The difficulty is in finding a scaffold that the cells can grow and organize on. The characteristics of the scaffold must be that it is biocompatible, cells can adhere to the scaffold, mechanically strong and biodegradable. One successful scaffold is a copolymer of lactic acid and glycolic acid.

THERMO ELECTRONIC MATERIALS

Thermoelectric materials show the thermoelectric effect in a strong or convenient form.

The *thermoelectric effect* refers to phenomena by which either a temperature difference creates an electric potential or an electric potential creates a temperature difference. These phenomena are known more specifically as the Seebeck effect (creating a voltage from temperature difference), Peltier effect (driving heat flow with an electric current), and Thomson effect (reversible heating or cooling within a conductor when there is both an electric current and a temperature gradient). While all materials have a nonzero thermoelectric effect, in most materials it is too small to be useful. However, low-cost materials that have a sufficiently strong thermoelectric effect (and other required properties) are also considered for applications including power generation and refrigeration. The most commonly used thermoelectric material is based on bismuth telluride

Thermoelectric materials are used in thermoelectric systems for cooling or heating in niche applications, and are being studied as a way to regenerate electricity from waste heat.

Nanocrystal stability and thermal conductivity

Not all nanocrystalline materials are stable, because the crystal size can grow at high temperatures, ruining the materials' desired characteristics.

Nanocrystalline materials have many interfaces between crystals, which Physics of SASER scatter phonons so the thermal conductivity is reduced. Phonons are confined to the grain, if their mean free path is larger than the material grain size.

Nanocrystalline transition metal silicides

Nanocrystalline transition metal silicides are a promising material group for thermoelectric applications, because they fulfill several criteria that are demanded from the commercial applications point of view. In some nanocrystalline transition metal silicides the power factor is higher than in the corresponding polycrystalline material but the lack of reliable data on thermal conductivity prevents the evaluation of their thermoelectric efficiency.

Nanostructured skutterudites

Skutterudites, a cobalt arsenide mineral with variable amounts of nickel and iron, can be produced artificially, and are candidates for better thermoelectric materials.

One advantage of nanostructured skutterudites over normal skutterudites is their reduced thermal conductivity, caused by grain boundary scattering. ZT values of ~0.65 and > 0.4 have been achieved with $CoSb_3$ based samples; the former values were 2.0 for Ni and 0.75 for Te-doped material at 680 K and latter for Au-composite at $T > 700$ K.

Even greater performance improvements can be achieved by using composites and by controlling the grain size, the compaction conditions of polycrystalline samples and the carrier concentration.

Graphene

Graphene is known for its high electrical conductivity and Seebeck coefficient at room temperature. However, from thermoelectric perspective, its thermal conductivity is notably high, which in turn limits its ZT. Several approaches were suggested to reduce the thermal conductivity of graphene without altering much its electrical conductivity. These include, but not limited to, the following:

- Doping with carbon isotopes to form isotopic heterojunction such as that of ^{12}C and ^{13}C. Those isotopes possess different phonon frequency mismatch, which leads to the scattering of the heat carriers (phonons). This approach has been shown to affect neither the power factor nor the electrical conductivity.
- Wrinkles and cracks in the graphene structure were shown to contribute to the reduction in the thermal conductivity. Reported values of thermal conductivity of suspended graphene of size 3.8 μm show a wide spread from 1500 to 5000 W/(m·K). A recent study attributed that to the microstructural defects present in graphene, such as wrinkles and cracks, which can drop the thermal conductivity by 27%. These defects help scatter phonons.
- Introduction of defects with techniques such as oxygen plasma treatment. A more systemic way of introducing defects in graphene structure is done through O_2 plasma treatment. Ultimately, the graphene sample will contain prescribed-holes spaced and numbered according to the plasma intensity. People were able to improve ZT of graphene from 1 to a value of

2.6 when the defect density is raised from 0.04 to 2.5 (this number is an index of defect density and usually understood when compared to the corresponding value of the un-treated graphene, 0.04 in our case). Nevertheless, this technique would lower the electrical conductivity as well, which can be kept unchanged if the plasma processing parameters are optimized.

- Functionalization of graphene by oxygen. The thermal behavior of graphene oxide has not been investigated extensively as compared to its counterpart; graphene. However, it was shown theoretically by Density Functional Theory (DFT) model that adding oxygen into the lattice of graphene reduces a lot its thermal conductivity due to phonon scattering effect. Scattering of phonons result from both acoustic mismatch and reduced symmetry in graphene structure after doping with oxygen. The reduction of thermal conductivity can easily exceed 50% with this approach

NANO PHASE MATERIALS

Nanophase materials are materials that have grain sizes under 100 nanometres. They have different mechanical and optical properties compared to the large grained materials of the same chemical composition.

Transparency and different transparent colours can be achieved with nanophase materials by varying the grain size

Nanophase materials

- **Nanophase metals** usually are many times harder but more brittle than regular metals.
    - nanophase copper is a superhard material
    - nanophase aluminum

  - nanophase iron is iron with a grain size in the nanometer range. Nanocrystalline iron has a tensile strength of around 6 GPA, twice that of the best maraging steels.
- Nanophase ceramics usually are more ductile and less brittle than regular ceramics.
- Nanophase materials are materials with a grain size in the 1 to 100 nm range. Nanophase materials exhibit greatly altered mechanical properties compared to their normal, large-grained counterparts with the same chemical composition. For example, nanophase metals are up to five (5) times harder than the normal materials. While nanophase metals generally become harder and more brittle, nanophase ceramics become more ductile. In a typical nanophase material, 10 to 50% of the atoms are in grain boundary regions.
- Nanophase materials can be made using a number of methods. The two main methods involve consolidation of nanometer sized particles or the creation of small grains using mechanical attrition. For the first method, small particles are created using techniques such as inert gas condensation or through the use of chemical processing. In the second case, larger particles are milled for a long period of time to create a very small grain size.

Nanophase materials, with their grain sizes or phase dimensions in the nanometer size regime, are now being produced by a wide variety of synthesis and processing methods. The interest in these new ultrafine-grained materials results primarily from the special nature of their various physical, chemical, and mechanical properties and the possibilities of controlling these properties during the synthesis and subsequent processing procedures. Since it is now becoming increasingly apparent that their properties can be engineered effectively during synthesis and processing, and that they can also be produced in quantity, nanophase materials should have considerable potential for technological development in a variety of applications. Some of the recent research on nanophase materials related to their synthesis and properties is briefly reviewed and the future potential of these new materials is considered.

Synthesis and properties

A large number of methods exist for the synthesis of nanophase materials [4,7]. They include synthesis from atomic or molecular precursors (chemical or physical vapor deposition; gas- condensation; chemical precipitation; aerosol reactions; biological templating), from processing of bulk precursors (mechanical attrition; crystallization from the amorphous state; phase separation), and from nature. It is generally preferable to synthesize nanostructured materials from atomic or molecular precursors, in order to gain the greatest control over a variety of microscopic aspects of the condensed ensemble, but other methodologies can often yield very useful results. Several plasma-based methods have already been usefully applied to the synthesis of nanophase materials [S- 141, However, the surface chemistries of the plasma-produced powders need to be critically investigated for residual contamination from precursors, which can inhibit their subsequent utilization. Yet, novel high-temperature chemical synthesis and processing methods for creating tailored nanostructures are sorely needed, especially ones that can carefully control surface and interface chemistry. In the creation of nanophase materials, the ability to control the size and size distribution of the constituent phases or structures is of primary importance. While this is of course a necessary requirement of nanostructuring, it is generally not a sufficient condition for their application, as will be discussed below; surface chemistry can also play a decisive role. The desirable cluster or powder sizes are generally below 100 nm, since it is in this size range (and frequently below 10 nm) that various properties begin to change significantly owing to confinement effects. Spatial confinement can in general affect any property when the size of the atomic ensemble becomes comparable to or smaller than a critical length scale for the mechanism that is responsible for that property. Examples can be as diverse as the "blue" (high-frequency, short- wavelength) shifts of the optical absorption in semiconducting clusters when their sizes fall below the Bohr radii (ca. 5-50 nm) of the excitonic (electron-hole pair) states responsible for absorption and the increased strengthening of normally soft metals when their grain sizes fall below the critical length scales (ca. < 50 nm) for the sources of dislocations (the defect responsible for easy deformation) to easily operate at conventional applied stresses. The chemical compositions of the constituent phases in a nanostructured material are also of fundamental importance, as they are to the performance of conventional materials. This not only relates to average compositions, but also invariably to chemical gradients within the constituent phases or structures and especially those near surfaces and interfaces. Indeed, the chemistry of the surfaces of the constituents, as well as that of the subsequently formed interfaces on assembly, can often play a crucial role in the ability to use these materials. This can be a real problem in the synthesis of nanophase powders from gaseous or liquid precursors, where residues in the form of surface contaminants (even at submonolayer levels) can prevent the subsequent use of these powders in consolidated or high-surface-area forms. Another aspect of nanostructured materials that one would like to be able to control in their synthesis is the nature of the interfaces created between constituent phases and, hence, the nature of the interactions across the interfaces. Both the local structure and chemistry of the interfaces are important in this regard. The properties of nanophase materials are determined by the' interplay among these three features (domain size, composition, and interfaces). In some cases, one or more of these features may dominate the particular property in question. Thus, one wants to be able to synthesize nanophase materials under well-controlled conditions, but with an eye toward the particular property or properties of interest in subsequent applications. The degree of control available, of course, depends upon the particular synthesis method being used to create the given material. In some cases, a rather simple nanophase synthesis and processing route can yield the desired property. In other cases, a considerably greater degree of sophistication will be required to effect the required property or properties. An example of the former case could be the relatively simple need for a stronger copper conductor. Examples of the latter case may be the need to nanostructure a functionally-gradient material or a multifuntional, smart material with a variety of constituents and structural scales.

Applications

Among the various artificially synthesized nanostructures, multilayered niaterials have had the longest history, one that has already seen applications in semiconductor devices, strained-layer superlattices, and magnetic multilayers. The technological potential of multilayered quantum heterostructure semiconductor devices was recognized as early as the 1970s in the rapidly expanding electronics and computer industries and helped to drive advances in this exciting new field. Since the 1980s there has been a rapid expansion of research on isolated atom clusters and an increased understanding of their potential as the constituents of new materials J. During the past several years, exciting progress has been made in the physics, chemistry, biology, and materials research communities in characterizing and understanding these materials. A few examples are given here. The chemical reactivity of nanophase materials, with their potentially high surface areas compared to conventional materials, can also be significantly enhanced, a property long utilized in the catalysis community. Since clusters or ultrafine powders can be assembled by means of a variety of methods, there can be an excellent degree of control over the total available surface area in the resulting self-supported nanophase ensembles. Thus, one can maximize porosity for obtaining very high surface areas, remove most of it via consolidation, but retain some to facilitate low-temperature doping or other processing, or fully densify the nanophase material. Also, control of chemical composition can be readily achieved, since rapid atomic diffusion paths are plentiful and diffusion distances are short in the clusters. Measurements of the decomposition of hydrogen sulfide over lightly consolidated, high-surface-area nanophase titanium dioxide with a rutile crystal structure have clearly demonstrated the potential for enhanced chemical reactivity of nanophase materials Nanophase rutile is far more reactive initially than other available forms of titanium dioxide and, more importantly, remains so even after extended exposure to the hydrogen sulfide at 500°C. This enhanced activity results from a combination of unique and controllable features of the nanophase material, its high surface area combined with its rutile structure and its oxygen deficient composition. Such behavior should have significant future impact in a variety of catalytic and sensor applications, but great care must be exercised in the synthesis and processing routes to ensure proper control of surface chemistry and atomic defect populations.

SMART MATERIALS

Smart materials, also called intelligent or responsive materials, are designed materials that have one or more properties that can be significantly changed in a controlled fashion by external stimuli, such as stress, moisture, electric or magnetic fields, light, temperature, pH, or chemical compounds. Smart materials are the basis of many applications, including sensors and actuators, or artificial muscles, particularly as electroactive polymers

Types

There are a number of types of smart material, of which are already common. Some examples are as following:

- Piezoelectric materials are materials that produce a voltage when stress is applied. Since this effect also applies in a reverse manner, a voltage across the sample will produce stress within sample. Suitably designed structures made from these materials can, therefore, be made that bend, expand or contract when a voltage is applied.
- Shape-memory alloys and shape-memory polymers are materials in which large deformation can be induced and recovered through temperature changes or stress changes (pseudo elasticity). The shape memory effect

results due to respectively martensitic phase change and induced elasticity at higher temperatures.

- Photovoltaic materials or optoelectronics convert light to electrical current.
- Electroactive polymers (EAPs) change their volume by voltage or electric fields.
- Magnetostrictive materials exhibit a change in shape under the influence of magnetic field and also exhibit a change in their magnetization under the influence of mechanical stress.
- Magnetic shape memory alloys are materials that change their shape in response to a significant change in the magnetic field.
- Smart inorganic polymers showing tunable and responsive properties.
- pH-sensitive polymers are materials that change in volume when the pH of the surrounding medium changes.
- Temperature-responsive polymers are materials which undergo changes upon temperature.
- Halochromic materials are commonly used materials that change their color as a result of changing acidity. One suggested application is for paints that can change color to indicate corrosion in the metal underneath them.
- Chromogenic systems change color in response to electrical, optical or thermal changes. These include electrochromic materials, which change their colour or opacity on the application of a voltage (e.g., liquid crystal displays), thermochromic materials change in colour depending on their temperature, and photochromic materials, which change colour in response to light—for example, light-sensitive sunglasses that darken when exposed to bright sunlight.
- Ferrofluids are magnetic fluids (affected by magnets and magnetic fields).
- Photomechanical materials change shape under exposure to light.
- Polycaprolactone (polymorph) can be molded by immersion in hot water.

- Self-healing materials have the intrinsic ability to repair damage due to normal usage, thus expanding the material's lifetime.
- Dielectric elastomers (DEs) are smart material systems which produce large strains (up to 500%) under the influence of an external electric field.
- Magnetocaloric materials are compounds that undergo a reversible change in temperature upon exposure to a changing magnetic field.
- Smart self-healing coatings heal without human intervention.
- Thermoelectric materials are used to build devices that convert temperature differences into electricity and vice versa.
- Chemo responsive materials change size or volume under the influence of external chemical or biological compound.

Smart materials have properties that react to changes in their environment. This means that one of their properties can be changed by an external condition, such as temperature, light, pressure, electricity, voltage, pH, or chemical compounds. This change is reversible and can be repeated many times. There is a wide range of different smart materials. Each offer different properties that can be changed. Some materials are very good and cover a huge range of the scales.

NLO MATERIALS

NLO materials has distinct crystal structure which is anisotropic with respect to electromagnetic radiation. **NLO materials** are used in photonic systems including high-speed optical modulators, ultra-fast optical switches and high-density optical storage media.

onlinear optics (**NLO**) is the branch of optics that describes the behaviour of light in *nonlinear media*, that is, media in which the polarization density **P** responds non-linearly to the electric field **E** of the light. The non-linearity is typically observed only at very high light intensities (values of atomic electric fields, typically 10^8 V/m) such as those provided by lasers. Above the Schwinger limit, the vacuum itself is expected to become nonlinear. In nonlinear optics, the superposition principle no longer holds.

Nonlinear optical processes

Nonlinear optics explains nonlinear response of properties such as frequency, polarization, phase or path of incident light. These nonlinear interactions give rise to a host of optical phenomena:

Frequency-mixing processes

- Second-harmonic generation (SHG), or *frequency doubling*, generation of light with a doubled frequency (half the wavelength), two photons are destroyed, creating a single photon at two times the frequency.
- Third-harmonic generation (THG), generation of light with a tripled frequency (one-third the wavelength), three photons are destroyed, creating a single photon at three times the frequency.
- High-harmonic generation (HHG), generation of light with frequencies much greater than the original (typically 100 to 1000 times greater).
- Sum-frequency generation (SFG), generation of light with a frequency that is the sum of two other frequencies (SHG is a special case of this).
- Difference-frequency generation (DFG), generation of light with a frequency that is the difference between two other frequencies.
- Optical parametric amplification (OPA), amplification of a signal input in the presence of a higher-frequency pump wave, at the same time generating an *idler* wave (can be considered as DFG).
- Optical parametric oscillation (OPO), generation of a signal and idler wave using a parametric amplifier in a resonator (with no signal input).
- Optical parametric generation (OPG), like parametric oscillation but without a resonator, using a very high gain instead.
- Half-harmonic generation, the special case of OPO or OPG when the signal and idler degenerate in one single frequency,

- Spontaneous parametric down-conversion (SPDC), the amplification of the vacuum fluctuations in the low-gain regime.
- Optical rectification (OR), generation of quasi-static electric fields.
- Nonlinear light-matter interaction with free electrons and plasmas.

Other nonlinear processes

- Optical Kerr effect, intensity-dependent refractive index (a effect).
- Self-focusing, an effect due to the optical Kerr effect (and possibly higher-order nonlinearities) caused by the spatial variation in the intensity creating a spatial variation in the refractive index.
- Kerr-lens modelocking (KLM), the use of self-focusing as a mechanism to mode-lock laser.
- Self-phase modulation (SPM), an effect due to the optical Kerr effect (and possibly higher-order nonlinearities) caused by the temporal variation in the intensity creating a temporal variation in the refractive index.
- Optical solitons, an equilibrium solution for either an optical pulse (temporal soliton) or spatial mode (spatial soliton) that does not change during propagation due to a balance between dispersion and the Kerr effect (e.g. self-phase modulation for temporal and self-focusing for spatial solitons).
- Self-diffraction, splitting of beams in a multi-wave mixing process with potential energy transfer.
- Cross-phase modulation (XPM), where one wavelength of light can affect the phase of another wavelength of light through the optical Kerr effect.
- Four-wave mixing (FWM), can also arise from other nonlinearities.
- Cross-polarized wave generation (XPW), a effect in which a wave with polarization vector perpendicular to the input one is generated.

- Modulational instability.
- Raman amplification.
- Optical phase conjugation.
- Stimulated Brillouin scattering, interaction of photons with acoustic phonons
- Multi-photon absorption, simultaneous absorption of two or more photons, transferring the energy to a single electron.
- Multiple photoionisation, near-simultaneous removal of many bound electrons by one photon.
- Chaos in optical systems.

Related processes

In these processes, the medium has a linear response to the light, but the properties of the medium are affected by other causes:

- Pockels effect, the refractive index is affected by a static electric field; used in electro-optic modulators.
- Acousto-optics, the refractive index is affected by acoustic waves (ultrasound); used in acousto-optic modulators.
- Raman scattering, interaction of photons with optical phonons.

Higher-order frequency mixing

- The above holds for processes. It can be extended for processes where is nonzero, something that is generally true in any medium without any symmetry restrictions; in particular resonantly enhanced sum or difference frequency mixing in gasses is frequently used for extreme or "vacuum" Ultra Violet light generation. In common scenarios, such as mixing in dilute gases, the non-linearity is weak and so the light beams are focused which, unlike the plane wave approximation used above, introduces a pi phase shift on each light beam, complicating the phase matching requirements. Conveniently, difference frequency mixing with cancels this focal phase shift and often has a nearly self-canceling overall phase matching condition, which relatively simplifies broad wavelength tuning compared to sum frequency generation. In all four frequencies are mixing simultaneously, as opposed to sequential mixing via two processes.

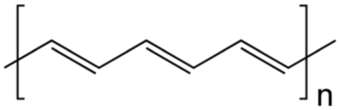
- The Kerr effect can be described as a as well. At high peak powers the Kerr effect can cause filamentation of light in air, in which the light travels without dispersion or divergence in a self-generated waveguide.[20] At even high intensities the Taylor series, which led the domination of the lower orders, does not converge anymore and instead a time based model is used. When a noble gas atom is hit by an intense laser pulse, which has an electric field strength comparable to the Coulomb field of the atom, the outermost electron may be ionized from the atom. Once freed, the electron can be accelerated by the electric field of the light, first moving away from the ion, then back toward it as the field changes direction. The electron may then recombine with the ion, releasing its energy in the form of a photon. The light is emitted at every peak of the laser light field which is intense enough, producing a series of attosecond light flashes. The photon energies generated by this process can extend past the 800th harmonic order up to a few KeV. This is called high-order harmonic generation. The laser must be linearly polarized, so that the electron returns to the vicinity of the parent ion. High-order harmonic generation has been observed in noble gas jets, cells, and gas-filled capillary waveguides.

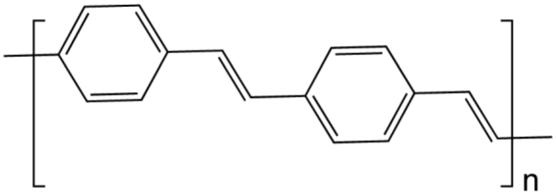
Molecular nonlinear optics

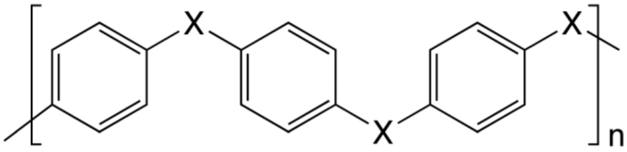
- The early studies of nonlinear optics and materials focused on the inorganic solids. With the development of nonlinear optics, molecular optical properties were investigated, forming molecular nonlinear optics. The traditional approaches used in the past to enhance nonlinearities include extending chromophore π-systems, adjusting bond length alternation, inducing intramolecular charge transfer, extending conjugation in 2D, and engineering multipolar charge distributions. Recently, many novel directions were proposed for enhanced nonlinearity and light manipulation, including twisted chromophores, combining rich density of states with bond alternation, microscopic cascading of second-order nonlinearity, etc. Due to the distinguished advantages, molecular nonlinear optics have been widely used in the biophotonics field, including bioimaging,

CONDUCTING POLYMERS

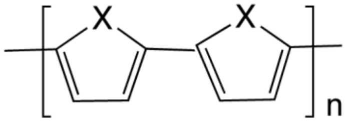
Conductive polymers or, more precisely, **intrinsically conducting polymers (ICPs)** are organic polymers that conduct electricity.[1][2] Such compounds may have metallic conductivity or can be semiconductors. The biggest advantage of conductive polymers is their processability, mainly by dispersion. Conductive polymers are generally not thermoplastics, *i.e.*, they are not thermoformable. But, like insulating polymers, they are organic materials. They can offer high electrical conductivity but do not show similar mechanical properties to other commercially available polymers. The electrical properties can be fine-tuned using the methods of organic synthesis and by advanced dispersion techniques







(X = NH/N, S)



(X = NH, S)

Chemical structures of some conductive polymers. From top left clockwise: polyacetylene; polyphenylene vinylene; polypyrrole (X = NH) and polythiophene (X = S); and polyaniline (X = NH) and polyphenylene sulfide (X = S).

Types

Linear-backbone "polymer blacks" (polyacetylene, polypyrrole, polyindole and polyaniline) and their copolymers are the main class of conductive polymers. Poly(p-phenylene vinylene) (PPV) and its soluble derivatives have emerged as the prototypical electroluminescent semiconducting polymers. Today, poly(3-alkylthiophenes) are the archetypical materials for solar cells and transistors.[3]

The following table presents some organic conductive polymers according to their composition. **The well-studied classes are written in bold** and *the less well studied ones are in italic.*

The main chain contains	**No heteroatom**	**Heteroatoms present**	
		Nitrogen-containing	**Sulfur-containing**
Aromatic cycles	• *Poly(fluorene)s* • *polyphenylenes* • *polypyrenes* • *polyazulenes* • *polynaphthalenes*	The N is in the aromatic cycle: • **poly(pyrrole)s (PPY)** • *polycarbazoles* • *polyindoles* • *polyazepines* The N is outside the aromatic cycle:	The S is in the aromatic cycle: • **poly(thiophene)s (PT)** • **poly(3,4-ethylenedioxythiophene) (PEDOT)** The S is outside the aromatic cycle:

		- **polyanilines (PANI)**	- **poly(p-phenylene sulfide) (PPS)**
Double bonds	- **Poly(acetylene)s (PAC)**		
Aromatic cycles and double bonds	- **Poly(p-phenylene vinylene) (PPV)**		

Synthesis

Conductive polymers are prepared by many methods. Most conductive polymers are prepared by oxidative coupling of monocyclic precursors. Such reactions entail dehydrogenation:

$$n\ \mathrm{H{-}[X]{-}H} \rightarrow \mathrm{H{-}[X]_n{-}H} + 2(n-1)\ \mathrm{H}^+ + 2(n-1)\ e^-$$

The low solubility of most polymers presents challenges. Some researchers add solubilizing functional groups to some or all monomers to increase solubility. Others address this through the formation of nanostructures and surfactant-stabilized conducting polymer dispersions in water. These include polyaniline nanofibers and PEDOT:PSS. In many cases, the molecular weights of conductive polymers are lower than conventional polymers such as polyethylene. However, in some cases, the molecular weight need not be high to achieve the desired properties.

There are two main methods used to synthesize conductive polymers, chemical synthesis and electro (co)polymerization. The chemical synthesis means connecting carbon-carbon bond of monomers by placing the simple monomers under various condition, such as heating, pressing, light exposure and catalyst. The advantage is high yield. However, there are many impurities plausible in the end product. The electro (co)polymerization means inserting three electrodes (reference electrode, counter electrode and working electrode) into solution including reactors or monomers. By applying voltage to electrodes, redox reaction to synthesize polymer is promoted. Electro (co)polymerization can also be divided into Cyclic Voltammetry and Potentiostatic method by applying cyclic voltage and constant voltage. The advantage of Electro (co)polymerization are the high purity of products. But the method can only synthesize a few products at a time.

Properties and applications

Conductive polymers show promise in antistatic materials and they have been incorporated into commercial displays and batteries. Literature suggests they are also promising in organic solar cells, printed electronic circuits, organic light-emitting diodes, actuators, electrochromism, supercapacitors, chemical sensors, chemical sensor arrays, and biosensors, flexible transparent displays, electromagnetic shielding and possibly replacement for the popular transparent conductor indium tin oxide. Another use is for microwave-absorbent coatings, particularly radar-absorptive coatings on stealth aircraft. Conducting polymers are rapidly gaining attraction in new applications with increasingly processable materials with better electrical and physical properties and lower costs. The new nano-structured forms of conducting polymers particularly, augment this field with their higher surface area and better dispersability. Research reports showed that nanostructured conducting polymers in the form of nanofibers and nanosponges, showed significantly improved capacitance values as compared to their non-nanostructured counterparts.

With the availability of stable and reproducible dispersions, PEDOT and polyaniline have gained some large-scale applications. While PEDOT (poly(3,4-ethylenedioxythiophene)) is mainly used in antistatic applications and as a transparent conductive layer in form of PEDOT:PSS dispersions (PSS=polystyrene sulfonic acid), polyaniline is widely used for printed circuit board manufacturing – in the final finish, for protecting copper from corrosion and preventing its solderability.[4] Moreover, Polyindole is also starting to gain attention for various applications due to its high redox activity, thermal stability, and slow degradation properties than competitors polyaniline and polypyrrole.

Electroluminescence

Electroluminescence is light emission stimulated by electric current. In organic compounds, electroluminescence has been known since the early 1950s, when Bernanose and coworkers first produced electroluminescence in crystalline thin films of acridine orange and quinacrine. In 1960, researchers at Dow Chemical developed AC-driven electroluminescent cells using doping. In some cases, similar light emission is observed when a voltage is applied to a thin layer of a conductive organic polymer film. While electroluminescence was originally mostly of academic interest, the increased conductivity of modern conductive polymers means enough power can be put through the device at low voltages to generate practical amounts of light. This property has led to the development of flat panel displays using organic LEDs, solar panels, and optical amplifiers.

Barriers to applications

Since most conductive polymers require oxidative doping, the properties of the resulting state are crucial. Such materials are salt-like (polymer salt), which diminishes their solubility in organic solvents and water and hence their processability. Furthermore, the charged organic backbone is often unstable towards atmospheric moisture. The poor processability for many polymers requires the introduction of solubilizing or substituents, which can further complicate the synthesis.

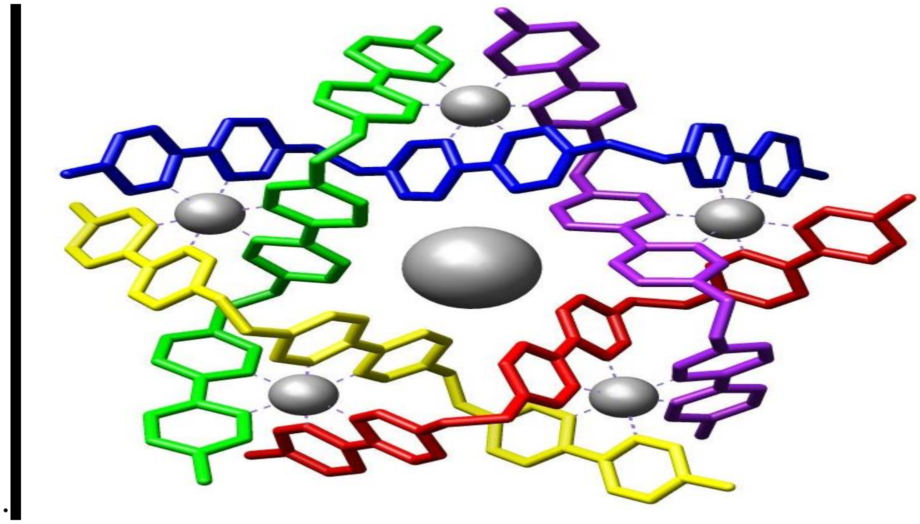
Experimental and theoretical thermodynamical evidence suggests that conductive polymers may even be completely and principally insoluble so that they can only be processed by dispersion. Trends

Most recent emphasis is on organic light emitting diodes and organic polymer solar cells. The Organic Electronics Association is an international platform to promote applications of organic semiconductors. Conductive polymer products with embedded and improved electromagnetic interference (EMI) and electrostatic discharge (ESD) protection have led to both prototypes and products. For example, Polymer Electronics Research Center at University of Auckland is developing a range of novel DNA sensor technologies based on conducting polymers, photoluminescent polymers and inorganic nanocrystals (quantum dots) for simple, rapid and sensitive gene detection. Typical conductive polymers must be "doped" to produce high conductivity. As of 2001, there remains to be discovered an organic polymer that is *intrinsically* electrically conducting. Recently (as of 2020), researchers from IMDEA Nanoscience Institute reported experimental demonstration of the rational engineering of 1D polymers that are located near the quantum phase transition from the topologically trivial to non-trivial class, thus featuring a narrow bandgap.

UNIT – III: SUPRA MOLECULAR CHEMISTRY

Supramolecular chemistry refers to the area of chemistry concerning chemical systems composed of a discrete number of molecules. The strength of the forces responsible for spatial organization of the system range from weak intermolecular forces, electrostatic charge, or hydrogen bonding to strong covalent bonding, provided that the electronic coupling strength remains small relative to the energy parameters of the component. Whereas traditional chemistry concentrates on the covalent bond, supramolecular chemistry examines the weaker and reversible non-covalent interactions between molecules.[3] These forces include hydrogen bonding, metal coordination, hydrophobic forces, van der Waals forces, pi–pi interactions and electrostatic effects.

Important concepts advanced by supramolecular chemistry include molecular self-assembly, molecular folding, molecular recognition, host–guest chemistry, mechanically-interlocked molecular architectures, and dynamic covalent chemistry. The study of non-covalent interactions is crucial to understanding many biological processes that rely on these forces for structure and function. Biological systems are often the inspiration for supramolecular



The existence of intermolecular forces was first postulated by Johannes Diderik van der Waals in 1873. However, Nobel laureate Hermann Emil Fischer developed supramolecular chemistry's philosophical roots. In 1894, Fischer suggested that enzyme–substrate interactions take the form of a "lock and key", the fundamental principles of molecular recognition and host–guest chemistry. In the early twentieth century non-covalent bonds were understood in gradually more detail, with the hydrogen bond being described by Latimer and Rodebush in 1920.

The use of these principles led to an increasing understanding of protein structure and other biological processes. For instance, the important breakthrough that allowed the elucidation of the double helical structure of DNA occurred when it was realized that there are two separate strands of nucleotides connected through hydrogen bonds. The use of non-covalent bonds is essential to replication because they allow the strands to be separated and used to template new double stranded DNA. Concomitantly, chemists began to recognize and study synthetic structures based on non-covalent interactions, such as micelles and microemulsions.

Eventually, chemists were able to take these concepts and apply them to synthetic systems. The breakthrough came in the 1960s with the synthesis of the crown ethers by Charles J. Pedersen. Following this work, other researchers such as Donald J. Cram, Jean-Marie Lehn and Fritz Vögtle became active in synthesizing shape- and ion-selective receptors, and throughout the 1980s research in the area gathered a rapid pace with concepts such as mechanically interlocked molecular architectures emerging.

The importance of supramolecular chemistry was established by the 1987 Nobel Prize for Chemistry which was awarded to Donald J. Cram, Jean-Marie Lehn, and Charles J. Pedersen in recognition of their work in this area. The development of selective "host–guest" complexes in particular, in which a host molecule recognizes and selectively binds a certain guest, was cited as an important contribution.

In the 1990s, supramolecular chemistry became even more sophisticated, with researchers such as James Fraser Stoddart developing molecular machinery and highly complex self-assembled structures, and Itamar Willner developing sensors and methods of electronic and biological interfacing. During this period, electrochemical and photochemical motifs became integrated into supramolecular systems in order to increase functionality, research into synthetic self-replicating system began, and work on molecular information processing devices began. The emerging science of nanotechnology also had a strong influence on the subject, with building blocks such as fullerenes, nanoparticles, and dendrimers becoming involved in synthetic systems.

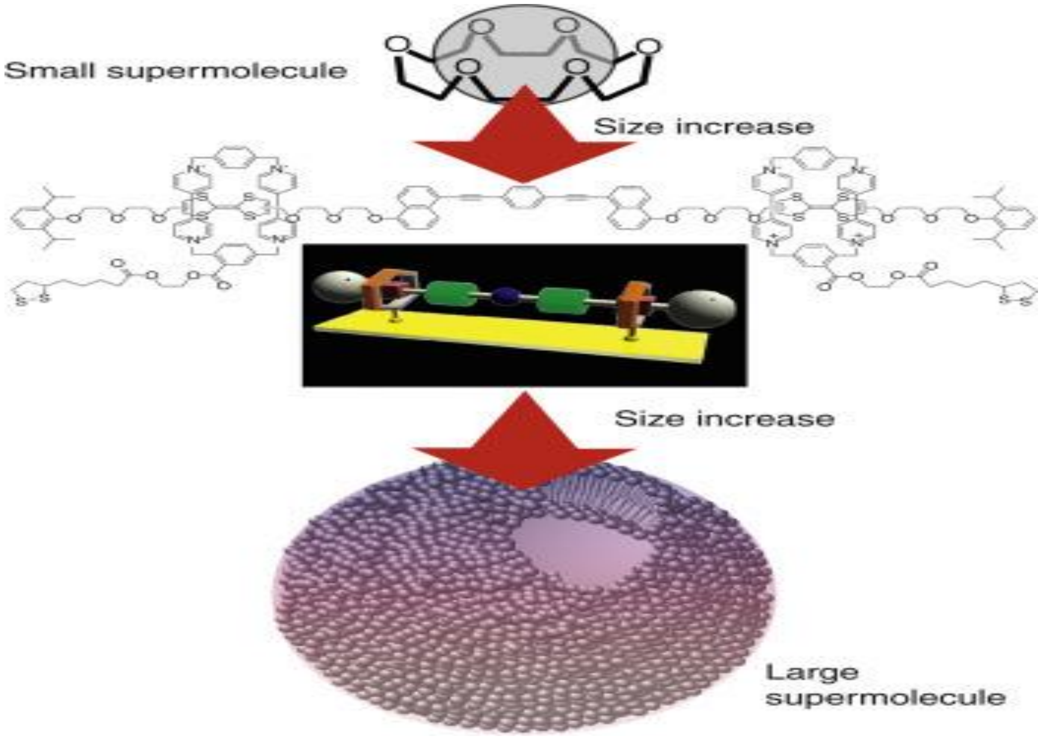
Supramolecular chemistry is an interdisciplinary field of science involving the chemical, physical, and biological features of molecular assemblies having a greater complexity than the individual molecules themselves. It is the study of the structures and functions of the supermolecules that result from the intermolecular binding interactions of two or more chemical entities in an organized manner. While traditional chemistry focuses on the covalent bond, supramolecular chemistry examines the weaker and reversible noncovalent interactions between molecules. This class of interactions spans a wide range of binding energies and encompasses electrostatic interactions, such as hydrogen bonding, dipole–dipole and ion–dipole interactions and hydrophobic interactions, such as van der Waals, π–π interactions, and dispersion interactions. The dimensions of supramolecular assemblies can range from nanometers to micrometers. Jean-Marie Lehn aptly described supramolecular chemistry as an ‘information science’: the instruction set for the creation of a large complex assembly is contained within its constituent components.[1] Nature provides the most spectacular examples of supramolecular chemistry. The enzyme–substrate complex, the DNA structure, its intricate packing and replication mechanisms, and protein–protein interactions are all examples of supramolecular chemistry at work. Supermolecules such as the octahedral iron storage vessel ferritin, for example, is assembled from many smaller repeated subunits that contain precise information for their correct integration into the larger structure. Supramolecular assemblies demonstrate cooperativity, which affects both the stability of the cluster and the mechanism of its formation and rearrangement. Detailed mechanistic studies of supramolecular assemblies are important not only for understanding the self-assembly processes but also for designing assemblies for specific applications. For the synthetic chemist, self-assembly represents a powerful synthetic methodology in the creation of large, discrete, ordered structures from relatively simple synthons. Increasingly, the focus is on application of these macromolecular systems to other chemistry problems: selective substrate binding, trapping reactive intermediates or protecting unstable species, influencing reaction chemistry within host cavities, or creating new nanodevices.

One of the major interests in supramolecular chemistry is the design of structurally well-defined architectures with dynamic and stimulus-responsive properties. Dynamic and adaptive supramolecular materials that self-assemble from multiple components will find a range of applications in materials and medicines. A number of fundamental studies in the field of supramolecular chemistry have demonstrated that more intricate and functional materials can be engineered from noncovalent complexes by carefully combining several intermolecular interactions. Chemical interactions between a protein and a drug, or a catalyst and its substrate, or a macrocyclic host and a guest; self-assembly of nanomaterials; and even some chemical reactions are dominated by noncovalent interactions. The use of a scaffold for self-assembly is a particularly interesting option, because a scaffold can guide the organization of weakly interacting molecules into well-defined self-assembled architectures. These supramolecules possess ample functionality such as catalytic, photophysical, electronic, or redox properties and are ideal building blocks for sensors, information storage materials, and nanodevices. In the last decades, scientists have made enormous strides toward creating nanoscale assemblies and structures with the aim of achieving applications ranging from targeted drug delivery to the development of functional materials. This article focuses on host–guest driven self-assembly, which has become a well-established methodology in supramolecular chemistry for constructing ensembles of varying structural motifs.

Basic Concepts of Supramolecular Chemistry

Followings are the important concepts developed during last decades which play important role in the understanding and developing several areas of applications. 2.1 Molecular self-assembly Molecular self-assemblyis the process by which molecules adopt a defined arrangement without external influences. There are two types of self-assembly—intermolecularself-assemblyandintra-molecularself-assembly. Commonly, the term molecular self-assembly refers to intermolecular self-assembly, while the intramolecular analog is more commonly called folding. Perhaps the best known intermolecular self-assembling structure in biological systems is naturally occurring DNA, which exists in a double helical form [35-37]. The two single strands are held together by a number of hydrogen bonds, involving acidic hydrogen atoms (hydrogen bonding donor), oxygen (hydrogen bonding acceptor), and nitrogen atoms (hydrogen bonding acceptor) of the purine and pyrimidine bases in order to maintain the double helical structure

Intra-molecular self-assembly or folding occurs infoldamers and polypeptides. A foldamer is a discrete chain molecule oroligomerthat folds into a conformationally ordered state in solution. They are artificial molecules that mimic the ability ofproteins,nucleic acids, andpolysaccharidestofoldinto well-defined conformations, such ashelicesandβ-sheets. The structure of a foldamer is stabilized bynon-covalent interactionsbetween nonadjacent monomers. Foldamers are studied with the main goal of designing large molecules with predictable structures. The study of foldamers is related to the themes of molecular self-assembly, molecular recognition and host-guest chemistry. Molecular self-assembly also allows the construction of larger structures such as micelles, membranes, vesicles, liquid crystals, and is important to crystal engineering. Micelle is an aggregate of surfactant molecules dispersed in a liquid colloid.



Supramolecular catalysis is not a well-defined field but it generally refers to an application of supramolecular chemistry, especially molecular recognition and guest binding, toward catalysis. This field was originally inspired by enzymatic system which, unlike classical organic chemistry reactions, utilizes non-covalent interactions such as hydrogen bonding, cation-pi interaction, and hydrophobic forces to dramatically accelerate rate of reaction and/or allow highly selective reactions to occur. Because enzymes are structurally complex and difficult to modify, supramolecular catalysts offer a simpler model for studying factors involved in catalytic efficiency of the enzyme. Another goal that motivates this field is the development of efficient and practical catalysts that may or may not have an enzyme equivalent in nature.

A closely related field of study is asymmetric catalysis which requires molecular recognition to differentiate two chiral starting material or chiral transition states and thus it could be categorized as an area of supramolecular catalysis, but supramolecular catalysis however does not necessarily have to involve asymmetric reaction. As there is another Wikipedia article already written about small molecule asymmetric catalysts, this article focuses primarily on large catalytic host molecules. Non-discrete and structurally poorly defined system such as micelle and dendrimers are not included.

Supramolecular catalysis involve two main steps-Binding which Selects the Substrate. Transformation of the bound species into product. Both the steps takes part in molecular recognition of the productive Substrate and require the correct molecular information in the reactive receptor.

For the catalysis process the binding should strain the substrate in order to bring towards the transition state of the reaction in order to lower the free energy of the activation.

In this module basically we focus on supramolecular chemical reactivity predominantlyin accelerating or understanding chemical reactions. There areclose parallels between artificial, abiotic supramolecular reactivity and biochemistry, for example in the study of enzymes and Nature's catalysts. Synthetic catalysts can both model natural ones and allow the design of new different kinds of reactions. Supramolecular catalysis lies some where between chemical catalysis (transition metal and organo catalysis) and biology. Supramolecular catalytic reactions involve binding of a well defined substrate(reactant) to the receptor (catalyst) and the catalytic process complete in three steps (see Figure 1)1) Selective binding of reactant(s) based on their recognition by the receptor that may bear reactive group(s). 2) Transformation of the bound species. 3) Release of the products and regeneration of the catalyst. First two steps binding and transformation in this catalytic process, are the important steps because both steps take part in the molecular recognition of the productive substrate and require the correct molecular information in the reactive receptor. Compared to molecular catalysis, a binding step is involved that selects the substrate and precedes the reaction it self.

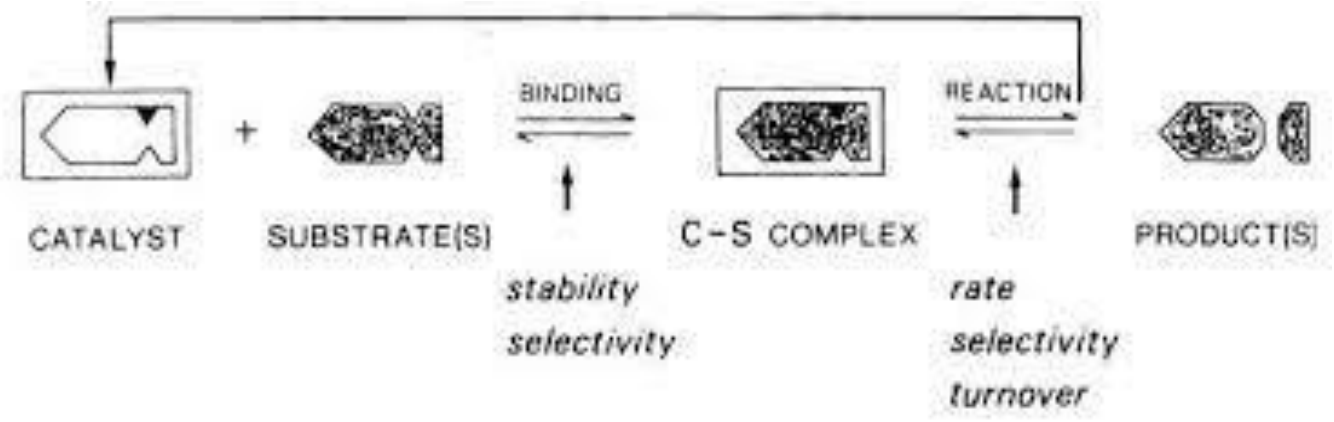
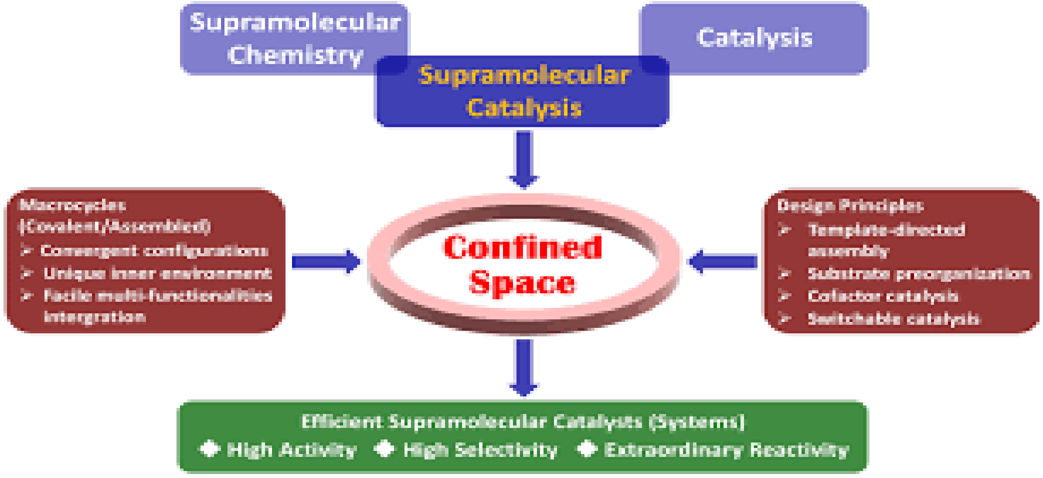


Fig. 6. Schematic representation of the supramolecular catalysis process.

[18]-O6macrocyclic polyether to bind primary ammonium ions which opens the possibility to induce chemical transformation on the sustrate. Supramolecular catalysis is always connected with substrate recognition in terms of shape, size and presence of specific functional groups to engage in weak intermolecular forces.

Catalysis by Reactive Macro cycliccation Receptor Molecules[18]-O_6 macrocyclic polyether to bind primary ammonium ions which opens the possibility to induce chemical transformation on the sustrate. Supramolecular catalysis is always connected with substrate recognition in terms of shape, size and presence of specific functional groups to engage in weak intermolecular forces.



Catalysis by Reactive Macrocyclic Cation Receptor Molecules. The most important example for catalysis by reactive macrocyclic cation receptors is the deacylation of O-acetyl hydroxylamine CH3COONH2 in presence of the macrocyclic polyether bearing four carbonyl groups derived from tartaric acid. The ability of [18]-O6macrocyclic poly ethers to bind primary ammonium ions opens the possibility to induce chemical transformations on such substrates (see Figure 3). Activation and orientation by binding was observed for the hydrolysis of O-acetyl hydroxyl amine, which forms such a stable complex with the macrocyclic tetra carboxylate receptor that it remains protonated and bound even at neutral pH, despite the low pKa(ca. 2.15) of the free species. As a consequence, its hydrolysis is accelerated and exclusively gives acetate and hydroxylamine, whereas in the presence of K+ions, which displace the substrate, it yields also acetyl hydroxamic acid, CH3CONH-OH (ca. 50%). Thus, strong binding may be sufficient for markedly accelerating a reaction and affecting its course, a result that also bears on enzyme- catalysed reactions. Chemical transformations may be induced by reaction between a bound substrate and functional groups borne by the macrocyclic receptor unit.

Catalysis by Reactive Anion Receptor Molecules Generally, the anion hosts are also obey the same rules that govern the magnitude of binding constants and host selectivity in cation hosts (primarily based on preorganisation, complementarity, salvation and size and shape effects), their application is made much more difficult because of some of the intrinsic properties of anions, listed below.•Anions are relatively large and therefore require receptors of considerably greater size than cations. For example, one of the smallest anions, F-, is comparable in ionic radius to K+(1.33Å versus 1.38Å).•Even simple inorganic anions occur in a range of shapes and geometries, e.g. spherical (halides), linear(SCN-, N3-), planar (NO3-, PtCl42-), tetrahedral (PO43-, SO42-), octahedral (PF6-, Fe(CN)63-) as well as more complicated examples as in the case of biologically important oligo phosphate anions.•In comparison to cations of similar size, anions have high free energies of solvation and hence anion hosts must compete more effectively with the surrounding medium, e.g. ΔGhydration(F-) = -465 kJ mol-1, ΔG hydration(K+) = -295 kJ mol-1. •Many anions exist only in a relatively narrow pH window, which can cause problems especially in the case of receptors based upon poly ammonium salts where the host may not be fully protonated in the pH region in which the anion is present in the desired form.•Anions are usually coordinatively saturated and therefore bind only via weak forces such as hydrogen bonding and van der Waals interactions, although they can form dative bonds.

The development of anion coordination chemistry and anion receptor molecules has made it possible to perform molecular catalysis on anionic substrates of chemical and biochemical interest, such as adenosine triphosphate(ATP).ATP hydrolysis was found' to be catalyzed by a number of protonated macrocyclic polyamines. In particular, [24]-N6O2(3) strongly binds ATP and markedly accelerates its hydrolysis to ADP and inorganic phosphate over a wide pH range. The reaction presents first-order kinetics and is catalytic with turnover. It proceeds via initial formation of a complex between ATP and protonated (3), followed by an intra complex reaction which may involve a combination of acid, electrostatic, and nucleophilic catalysis. Structure (4)represents one possible binding mode of the ATP-(3)complex and indicates how cleavage of the terminal phosphoryl groups might take place. A transient intermediate, identified as phosphoramidate (5), is formed by phosphorylation of the macrocycle by ATP and is subsequently hydrolyzed. Studies with analogues of ATP indicated that the mechanism was dissociative in character within a preassociative scheme resulting from receptor substrate binding. In this process, catalyst (3)presents prototypical ATPase activity; i.e., it behaves as a proto-ATPase.

Catalysis with Cyclophane Type Receptors

The term ‘cyclophane’ literally means any organic molecule containing a bridged aromatic ring. By definition, cyclophane hosts (e. g. calixarenes and resorcarenes) must contain at least one macrocyclic ring and thus must achieve closure by some means of curvature. Cyclophane hosts commonly bind both neutral molecules and organic cations, and there is sometimes even some ambiguity as to whether a guest is protonated by, for example, a hydrogen bond acid host or vice versa, resulting in charge-assisted binding. Cyclophanes may or may not contain a molecular cavity large enough to host guest species, but in some cases cavities are unnecessary to achieve high binding affinity as long as binding sites exhibiting stereoelectronic (steric and electronic) complementary to the guest and are properly positioned (preorganised) on the surface of the host. Thus cyclophanes can exhibit capsular or nesting types of binding, or even apolar surface interactions, often leading to aggregation. Cavities are frequently encountered however, because of the entropic and enthalpic gains associated with spherical or three-dimensional encapsulation of the guest by a host with convergent binding sites. A number of studies have made use of functionalized cyclophanes for developing supramolecular catalysts and enzyme models. Their catalytic behaviour is based on the implementation of electrostatic, hydrophobic and metal coordination features for effecting various reactions in aqueous media. Hydrophobic species bearing hydrocarbon chains present vitamin B12or vitaminB6type activity. Such systems lend themselves to inclusion in membrane ormicellar media. They thus provide a link with catalysis in more or less organized media such as membranes, vesicles, micelles, polymers. Water soluble cyclophanes showing, for example, transaminase, acetyl CHEMISTRY Paper 14: Organic Chemistry-IV (Advanced Organic Synthesis, supramolecular chemistry and carbocyclic rings)Module 19: Supramolecular reactivity and catalysis transfer, pyruvate oxidaseor nucleophilic substitution activity have been described. Cyclophane catalysts offer a rich playground for developing novel reactions and enzyme models in view of the variety of their structural types, the large cavities they contain and the possibility to attach several functional groups.

Supramolecular Metallocatalysis

Supramolecular metallocatalysts consist in principle of the combination of a recognition subunit (such as a macrocycle, a cyclodextrin, a cyclophane, etc.)that selects the substrate(s) and of a metal ion, bound to another subunit that is the reactive site. Complexed metal ions presenting free coordination positions may present a variety of substrate activation and functionalization properties. Heterotopic coreceptors such as (7)bind simultaneously a substrate and a metal ion bringing them into proximity, thus potentially allowing reaction between them. Approaches towards the development of artificial metallo enzymes have been made, based on cyclodextrins or macrocycles and involving various metal ions, such as Zn(ll), Cu(ll), Co(lll), for facilitating hydrolysis, epoxidation, hydrogen transfer, etc. Metalloporphyrins have been used for epoxidation and hydroxylation and a phosphine-rhodium complex for isomerization and hydrogenation. CytochromeP-450 model systems are represented by a porphyrin-bridged cyclophane, macrobicyclic transition metal cyclidenesor β-cyclodextrin-linked porphyrin complexes that may bind substrates and perform oxygenation reactions on them. A cyclodextrin connected to a coenzyme B12unit forms a potential enzyme-coenzyme mimic. Recognition directed, specific DNA cleavage reagents also make use of the reactivity features of various complexed metallic sites. The remarkable facilitation of amide hydrolysis by di nuclear copper complexes and related processes may open routes towards metallo cleavage of proteins. Selective metallo processes, in particular asymmetric reactions utilizing externalchiral ligands, such as hydrogenation, epoxidation, hydroxylation, etc. are of great value for organic synthesis and are being actively investigated. Supermolecular metallocatalysts, by combining a substrate recognition unit with a catalytic metallic site, offer powerful entries to catalysts presenting shape, regio and stereoselectivity

Cocatalysis: Catalysis of Synthetic Reactions

A further step lies in the design of systems capable of inducing bond formation rather than bond cleavage, thus effecting synthetic reactions as compared to degradative ones. To this end, the presence of several binding and reactive groups is essential. Such is the case for corecept or molecules (7) in which subunits may cooperate for substrate binding and transformation. They should be able to perform cocatalysis by bringing together substrate(s) and cofactor(s) and mediating reactions between them within the supramolecular structure

BIOMOLECULAR AND ABIOTIC CATALYSIS

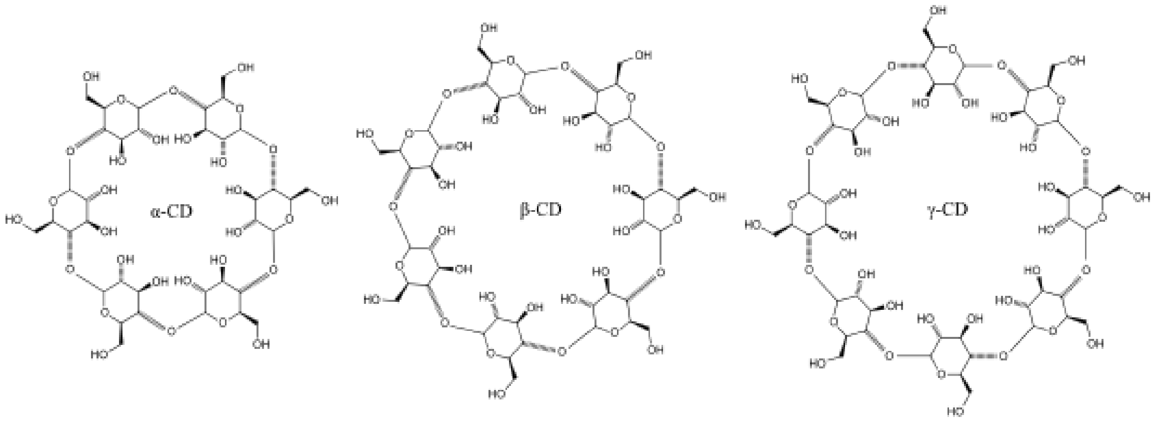
The design of supramolecular catalysts may make use of biological materials and processes for tailoring appropriate recognition sites and achieving high rates and selectivities of reactions. Modified enzymes obtained by chemical mutation or by protein engineering represent biochemical approaches to artificial catalysts. This is also the case for the generation of catalytic proteins by induction of antibodies. Antibodies to reactive haptens are able to facilitate the transformation of the bound species. Generating antibodies against analogues of transition states should lead to transition state stabilization and facilitate the process. Such catalytic antibodies or abzymes have been produced for a variety of reaction and an active field of research has developed along such lines. It represents an approach to substrate specific, efficient and selective catalysis of supramolecular type which is of much basic and applied interest. The strong affinity for the transition state (TS)of the reaction of a given substrate leads it along the way and thus facilitates the process. In line with the remarks made at the beginning of this chapter, the antibodies should be generated not against a transition state analogues (TSA)itself but against a (TSA-X) isostere lacking the group(s) X, which belong(s) to the reactive function(s) of the protein that is (are) expected to perform the reaction. This requires designing a (TSA-X) species in which the face presenting the (-X) gap be ideally chosen so as to lead to the induction in the antibody of the desired reactive functional group at the correct position.

CYCLODEXTRIN

Cyclodextrins are a family of cyclic oligosaccharides, consisting of a macrocyclic ring of glucose subunits joined by α-1,4 glycosidic bonds. Cyclodextrins are produced from starch by enzymatic conversion. They are used in food, pharmaceutical, drug delivery, and chemical industries, as well as agriculture and environmental engineering.

Cyclodextrins are composed of 5 or more α-D-glucopyranoside units linked 1->4, as in amylose (a fragment of starch). The largest cyclodextrin contains 32 1,4-anhydroglucopyranoside units, while as a poorly characterized mixture, at least 150-membered cyclic oligosaccharides are also known. Typical cyclodextrins contain a number of glucose monomers ranging from six to eight units in a ring, creating a cone shape:

- α (alpha)-cyclodextrin: 6 glucose subunits
- β (beta)-cyclodextrin: 7 glucose subunits
- γ (gamma)-cyclodextrin: 8 glucose subunits



Chemical structure of the three main types of cyclodextrins.

Applications

Drug delivery

Cyclodextrins are ingredients in more than 30 different approved medicines.[2] With a hydrophobic interior and hydrophilic exterior, cyclodextrins form complexes with hydrophobic compounds. Alpha-, beta-, and gamma-cyclodextrin are all generally recognized as safe by the U.S. FDA.[3][4] They have been applied for delivery of a variety of drugs, including hydrocortisone, prostaglandin, nitroglycerin, it raconazol, chloramphenicol. The cyclodextrin confers solubility and stability to these drugs.[1] The inclusion compounds of cyclodextrins with hydrophobic molecules are able to penetrate body tissues, these can be used to release biologically active compounds under specific conditions.[5] In most cases the mechanism of controlled degradation of such complexes is based on pH change of water solutions, leading to the loss of hydrogen or ionic bonds between the host and the guest molecules. Alternative means for the disruption of the complexes take advantage of heating or action of enzymes able to cleave α-1,4 linkages between glucose monomers. Cyclodextrins were also shown to enhance mucosal penetration of drugs.

Chromatography

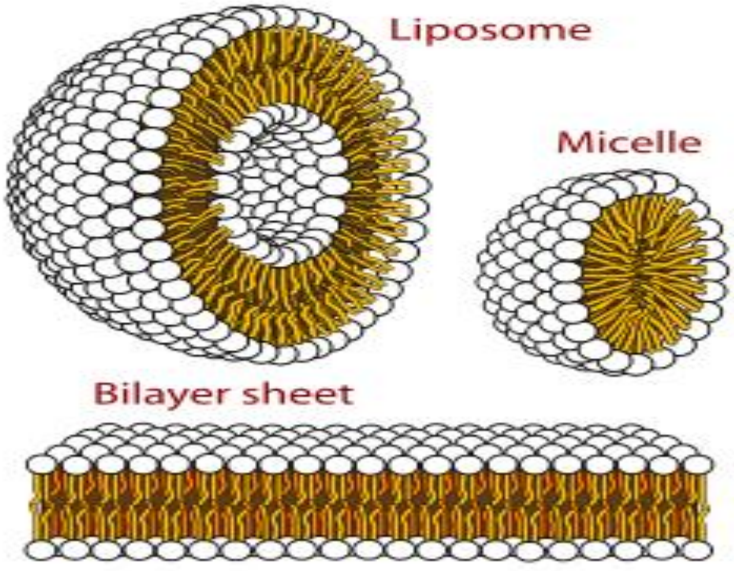
β-cyclodextrins are used to produce stationary phase media for HPLC separations

MICELLES

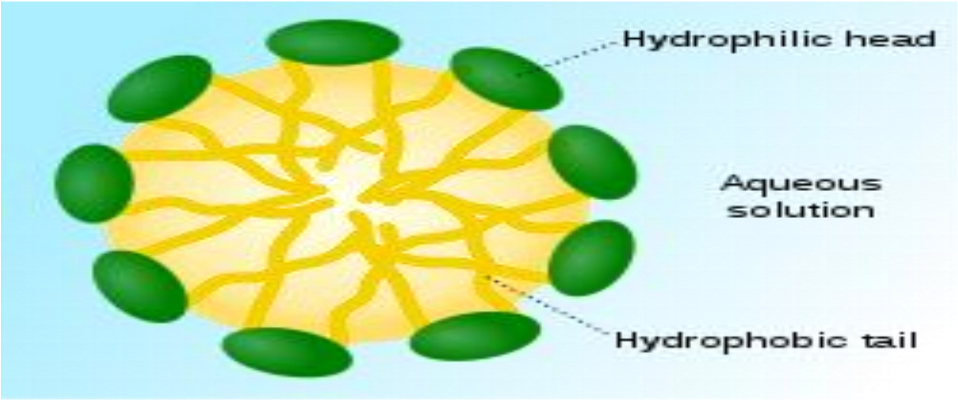
A micelle (plural micelles or micellae, respectively) is an aggregate (or supramolecular assembly) of surfactant molecules dispersed in a liquid, forming a colloidal suspension (also known as associated colloidal system). A typical micelle in water forms an aggregate with the hydrophilic "head" regions in contact with surrounding solvent, sequestering the hydrophobic single-tail regions in the micelle centre.

This phase is caused by the packing behavior of single-tail lipids in a bilayer. The difficulty filling all the volume of the interior of a bilayer, while accommodating the area per head group forced on the molecule by the hydration of the lipid head group, leads to the formation of the micelle. This type of micelle is known as a normal-phase micelle (oil-in-water micelle). Inverse micelles have the head groups at the centre with the tails extending out (water-in-oil micelle).

Micelles are approximately spherical in shape. Other phases, including shapes such as ellipsoids, cylinders, and bilayers, are also possible. The shape and size of a micelle are a function of the molecular geometry of its surfactant molecules and solution conditions such as surfactant concentration, temperature, pH, and ionic strength. The process of forming micelles is known as micellisation and forms part of the phase behaviour of many lipids according to their polymorphism.[5]



Cross-section view of the structures that can be formed by phospholipids in aqueous solutions (unlike this illustration, micelles are usually formed by single-chain lipids, since it is difficult to fit two chains into this shape)



Scheme of a micelle formed by phospholipids in an aqueous solution

Solvation

Individual surfactant molecules that are in the system but are not part of a micelle are called "monomers". Micelles represent a molecular assembly, in which the individual components are thermodynamically in equilibrium with monomers of the same species in the surrounding medium. In water, the hydrophilic "heads" of surfactant molecules are always in contact with the solvent, regardless of whether the surfactants exist as monomers or as part of a micelle. However, the lipophilic "tails" of surfactant molecules have less contact with water when they are part of a micelle—this being the basis for the energetic drive for micelle formation. In a micelle, the hydrophobic tails of several surfactant molecules assemble into an oil-like core, the most stable form of which having no contact with water. By contrast, surfactant monomers are surrounded by water molecules that create a "cage" or solvation shell connected by hydrogen bonds. This water cage is similar to a clathrate and has an ice-like crystal structure and can be characterized according to the hydrophobic effect. The extent of lipid solubility is determined by the unfavorable entropy contribution due to the ordering of the water structure according to the hydrophobic effect.

Micelles composed of ionic surfactants have an electrostatic attraction to the ions that surround them in solution, the latter known as counterions. Although the closest counterions partially mask a charged micelle (by up to 92%), the effects of micelle charge affect the structure of the surrounding solvent at appreciable distances from the micelle. Ionic micelles influence many properties of the mixture, including its electrical conductivity. Adding salts to a colloid containing micelles can decrease the strength of electrostatic interactions and lead to the formation of larger ionic micelles.[9] This is more accurately seen from the point of view of an effective charge in hydration of the system.

Uses

When surfactants are present above the critical micelle concentration (CMC), they can act as emulsifiers that will allow a compound that is normally insoluble (in the solvent being used) to dissolve. This occurs because the insoluble species can be incorporated into the micelle core, which is itself solubilized in the bulk solvent by virtue of the head groups' favorable interactions with solvent species. The most common example of this phenomenon is detergents, which clean poorly soluble lipophilic material (such as oils and waxes) that cannot be removed by water alone. Detergents clean also by lowering the surface tension of water, making it easier to remove material from a surface. The emulsifying property of surfactants is also the basis for emulsion polymerization.

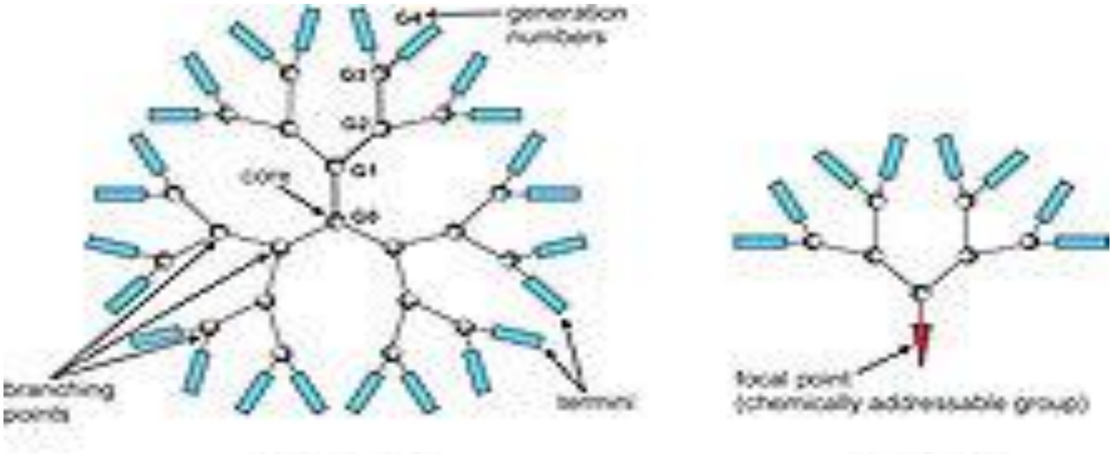
Micelle formation is essential for the absorption of fat-soluble vitamins and complicated lipids within the human body. Bile salts formed in the liver and secreted by the gall bladder allow micelles of fatty acids to form. This allows the absorption of complicated lipids (e.g., lecithin) and lipid-soluble vitamins (A, D, E, and K) within the micelle by the small intestine.

During the process of milk-clotting, proteases act on the soluble portion of caseins, κ-casein, thus originating an unstable micellar state that results in clot formation.

Micelles can also be used for targeted drug delivery as gold nanoparticles

DENDRIMERS

Dendrimers are highly ordered, branched polymeric molecules. The name comes from the Greek word (dendron) which translates to "tree". Synonymous terms for dendrimer include arborols and cascade molecules. Typically, dendrimers are symmetric about the core, and often adopt a spherical three-dimensional morphology. The word dendron is also encountered frequently. A dendron usually contains a single chemically addressable group called the focal point or core. The difference between dendrons and dendrimers is illustrated in the top figure, but the terms are typically encountered interchangeably.



DENDRIMER DENDRON

Dendrimer and Dendron

Properties

Dendritic molecules are characterized by structural perfection. Dendrimers and dendrons are monodisperse and usually highly symmetric, spherical compounds. The field of dendritic molecules can be roughly divided into low-molecular weight and high-molecular weight species. The first category includes dendrimers and dendrons, and the latter includes dendronized polymers, hyperbranched polymers, and the polymer brush.

The properties of dendrimers are dominated by the functional groups on the molecular surface, however, there are examples of dendrimers with internal functionality. Dendritic encapsulation of functional molecules allows for the isolation of the active site, a structure that mimics that of active sites in biomaterials. Also, it is possible to make dendrimers water-soluble, unlike most polymers, by functionalizing their outer shell with charged species or other hydrophilic groups. Other controllable properties of dendrimers include toxicity, crystallinity, tecto-dendrimer formation, and chirality.

Dendrimers are also classified by generation, which refers to the number of repeated branching cycles that are performed during its synthesis. For example, if a dendrimer is made by convergent synthesis (see below), and the branching reactions are performed onto the core molecule three times, the resulting dendrimer is considered a third generation dendrimer. Each successive generation results in a dendrimer roughly twice the molecular weight of the previous generation. Higher generation dendrimers also have more exposed functional groups on the surface, which can later be used to customize the dendrimer for a given application.

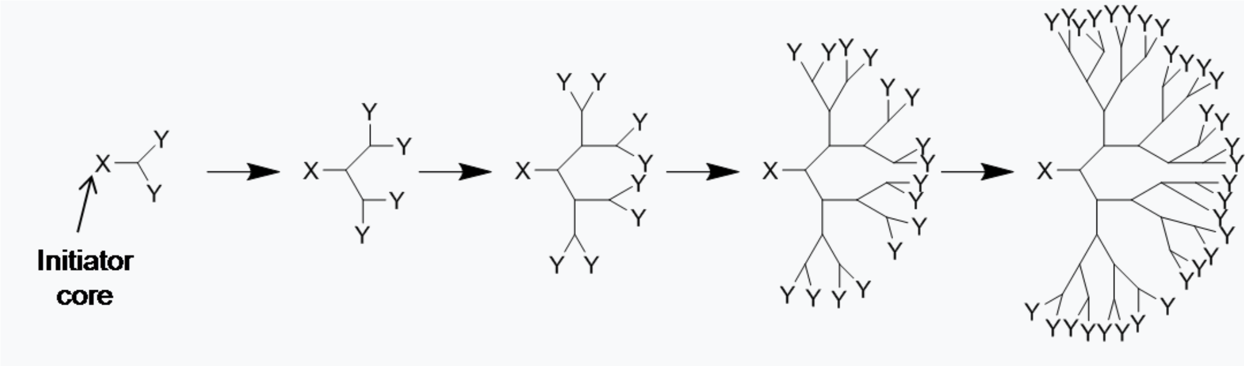
Synthesis

One of the first dendrimers, the Newkome dendrimer, was synthesized in 1985. This macromolecule is also commonly known by the name arborol. The figure outlines the mechanism of the first two generations of arborol through a divergent route (discussed below). The synthesis is started by nucleophilic substitution of 1-bromopentane by triethyl so diomethanetri carboxylate in dimethylformamide and benzene. The ester groups were then reduced by lithium aluminium hydride to a triol in a deprotection step. Activation of the chain ends was achieved by converting the alcohol groups to tosylate groups with tosyl chloride and pyridine. The tosyl group then served as leaving groups in another reaction with the tricarboxylate, forming generation two. Further repetition of the two steps leads to higher generations of arborol.

Poly(amidoamine), or PAMAM, is perhaps the most well known dendrimer. The core of PAMAM is a diamine (commonly ethylenediamine), which is reacted with methyl acrylate, and then another ethylenediamine to make the generation-0 (G-0) PAMAM. Successive reactions create higher generations, which tend to have different properties. Lower generations can be thought of as flexible molecules with no appreciable inner regions, while medium-sized (G-3 or G-4) do have internal space that is essentially separated from the outer shell of the dendrimer. Very large (G-7 and greater) dendrimers can be thought of more like solid particles with very dense surfaces due to the structure of their outer shell. The functional group on the surface of PAMAM dendrimers is ideal for click chemistry, which gives rise to many potential applications.

Dendrimers can be considered to have three major portions: a core, an inner shell, and an outer shell. Ideally, a dendrimer can be synthesized to have different functionality in each of these portions to control properties such as solubility, thermal stability, and attachment of compounds for particular applications. Synthetic processes can also precisely control the size and number of branches on the dendrimer. There are two defined methods of dendrimer synthesis, divergent synthesis and convergent synthesis. However, because the actual reactions consist of many steps needed to protect the active site, it is difficult to synthesize dendrimers using either method. This makes dendrimers hard to make and very expensive to purchase. At this time, there are only a few companies that sell dendrimers; Polymer Factory Sweden AB commercializes biocompatible bis-MPA dendrimers and Dendritechis the only kilogram-scale producers of PAMAM dendrimers. Nano Synthons, LLC from Mount Pleasant, Michigan, USA produces PAMAM dendrimers and other proprietary dendrimers.

Divergent methods



Schematic of divergent synthesis of dendrimers

The dendrimer is assembled from a multifunctional core, which is extended outward by a series of reactions, commonly a Michael reaction. Each step of the reaction must be driven to full completion to prevent mistakes in the dendrimer, which can cause trailing generations (some branches are shorter than the others). Such impurities can impact the functionality and symmetry of the dendrimer, but are extremely difficult to purify out because the relative size difference between perfect and imperfect dendrimers is very small.

GELATORS

gelators are a relatively new and dynamic soft materials capable of numerous possible applications; LMOGs are the monomeric sub-unit which form self-assembled fibrillar networks (SAFINs) that entrap solvent between the strands. SAFINs arise from the formation of strong non-covalent interactions between LMOG monomeric sub-units. As SAFINs are forming, the long fibers become intertwined and trap solvent molecules. Once solvent molecules are entrapped within the network, they are immobilized by surface tension effects. The stability of a gel is dependent on the equilibrium between the assembled network and the dissolved gelators. One characteristic of an LMOG, that demonstrates its stability, is its ability to contain an organic solvent at the boiling point of that solvent due to extensive solvent-fibrillar interactions. Gels self-assemble through non-covalent interactions such as π-stacking, hydrogen-bonding, or

Van der Waals interactions to form volume-filling 3D networks. Self-assembly is key to gel formation and dependent upon reversible bond formation. The propensity of a low molecular weight molecule to form LMOGs is classified by its Minimum Gelation Concentration (MGC). The MGC is the lowest possible gelator concentration needed to form a stable gel. A lower MGC is desired to minimize the amount of gelator material needed to form gels. Super gelators have a MGC of less than 1 wt%.

Gels can be organized according to multiple characteristics. The source of the gel (natural/artificial), the gel's medium (organic/aqueous/areo/xero), the constitution of the gel (macromolecular/supramolecular), and the type of crosslinking the gel forms (physical/chemical).

UNIT – IV (GREEN CHEMISTRY)

Green chemistry, also called sustainable chemistry, is an area of chemistry and chemical engineering focused on the design of products and processes that minimize or eliminate the use and generation of hazardous substances. While environmental chemistry focuses on the effects of polluting chemicals on nature, green chemistry focuses on the environmental impact of chemistry, including reducing consumption of nonrenewable resources and technological approaches for preventing pollution.

The overarching goals of green chemistry namely, more resource-efficient and inherently safer design of molecules, materials, products, and processes—can be pursued in a wide range of contexts.

The aim of green chemistry is to reduce chemical related impact on human health and virtually eliminate contamination of the environment through dedicated, sustainable prevention programs. Green chemistry searches for alternative, environmentally friendly reaction media and at the same time strives to increase reaction rates and lower reaction temperatures.

The green chemistry concept applies innovative scientific solutions to solve environmental issues posed in the laboratory. Paul T. Anastas, an organic chemist working in the Office of Pollution Prevention and Toxins at the EPA, and John C. Warner developed the Twelve Principles of Green Chemistry in 1991. These principles can be grouped into "Reducing Risk" and "Minimizing the Environmental Footprint."

Principles

In 1998, Paul Anastas (who then directed the Green Chemistry Program at the US EPA) and John C. Warner (then of Polaroid Corporation) published a set of principles to guide the practice of green chemistry. The twelve principles address a range of ways to reduce the environmental and health impacts of chemical production, and also indicate research priorities for the development of green chemistry technologies.

The principles cover such concepts as:

- the design of processes to maximize the amount of raw material that ends up in the product;
- the use of renewable material feedstocks and energy sources;
- the use of safe, environmentally benign substances, including solvents, whenever possible;
- the design of energy efficient processes;
- avoiding the production of waste, which is viewed as the ideal form of waste management.

The twelve principles of green chemistry are

1. Prevention. Preventing waste is better than treating or cleaning up waste after it is created.
2. Atom economy. Synthetic methods should try to maximize the incorporation of all materials used in the process into the final product. This means that less waste will be generated as a result.
3. Less hazardous chemical syntheses. Synthetic methods should avoid using or generating substances toxic to humans and/or the environment.
4. Designing safer chemicals. Chemical products should be designed to achieve their desired function while being as non-toxic as possible.
5. Safer solvents and auxiliaries. Auxiliary substances should be avoided wherever possible, and as non-hazardous as possible when they must be used.
6. Design for energy efficiency. Energy requirements should be minimized, and processes should be conducted at ambient temperature and pressure whenever possible.

7. Use of renewable feedstocks. Whenever it is practical to do so, renewable feedstocks or raw materials are preferable to non-renewable ones.
8. Reduce derivatives. Unnecessary generation of derivatives—such as the use of protecting groups—should be minimized or avoided if possible; such steps require additional reagents and may generate additional waste.
9. Catalysis. Catalytic reagents that can be used in small quantities to repeat a reaction are superior to stoichiometric reagents (ones that are consumed in a reaction).
10. Design for degradation. Chemical products should be designed so that they do not pollute the environment; when their function is complete, they should break down into non-harmful products.
11. Real-time analysis for pollution prevention. Analytical methodologies need to be further developed to permit real-time, in-process monitoring and control *before* hazardous substances form.
12. Inherently safer chemistry for accident prevention. Whenever possible, the substances in a process, and the forms of those substances, should be chosen to minimize risks such as explosions, fires, and accidental releases.

Trends

Attempts are being made not only to quantify the *greenness* of a chemical process but also to factor in other variables such as chemical yield, the price of reaction components, safety in handling chemicals, hardware demands, energy profile and ease of product workup and purification. In one quantitative study,[14] the reduction of nitrobenzene to aniline receives 64 points out of 100 marking it as an acceptable synthesis overall whereas a synthesis of an amide using HMDS is only described as adequate with a combined 32 points.

Green chemistry is increasingly seen as a powerful tool that researchers must use to evaluate the environmental impact of nanotechnology.[15] As nanomaterials are developed, the environmental and human health impacts of both the products themselves and the processes to make them must be considered to ensure their long-term economic viability.[*citation needed*]

Green solvents

The major application of solvents in human activities is in paints and coatings (46% of usage). Smaller volume applications include cleaning, de-greasing, adhesives, and in chemical synthesis.[16] Traditional solvents are often toxic or are chlorinated. Green solvents, on the other hand, are generally less harmful to health and the environment and preferably more sustainable. Ideally, solvents would be derived from renewable resources and biodegrade to innocuous, often a naturally occurring product. However, the manufacture of solvents from biomass can be more harmful to the environment than making the same solvents from fossil fuels. Thus the environmental impact of solvent manufacture must be considered when a solvent is being selected for a product or process. Another factor to consider is the fate of the solvent after use. If the solvent is being used in an enclosed situation where solvent collection and recycling is feasible, then the energy cost and environmental harm associated with recycling should be considered; in such a situation water, which is energy-intensive to purify, may not be the greenest choice. On the other hand, a solvent contained in a consumer product is likely to be released into the environment upon use, and therefore the environmental impact of the solvent itself is more important than the energy cost and impact of solvent recycling; in such a case water is very likely to be a green choice. In short, the impact of the entire lifetime of the solvent, from cradle to grave (or cradle to cradle if recycled) must be considered. Thus the most comprehensive definition of a green solvent is the following: "*a green solvent is the solvent that makes a product or process have the least environmental impact over its entire life cycle.*"

By definition, then, a solvent might be green for one application (because it results in less environmental harm than any other solvent that could be used for that application) and yet not be a green solvent for a different application. A classic example is water, which is a very green solvent for consumer products such as toilet bowl cleaner but is not a green solvent for the manufacture of polytetrafluoroethylene. For the production of that polymer, the use of water as solvent requires the addition of perfluorinated surfactants which are highly persistent. Instead, supercritical carbon dioxide seems to be the greenest solvent for that application because it performs well without any surfactant. In summary, no solvent can be declared to be a "green solvent" unless the declaration is limited to a specific application.

PHOTO OXIDATION

Introduction:

In the aquatic and atmospheric environments, oxidation by free radicals, singlet oxygen (102) or ozone (03) can be an important fate process for many organic chemicals. An understanding of how these oxidants behave toward organic structures and their probable average concentrations in water or air is essential for predicting the rates and products of chemical oxidation reactions. Direct or sensitized photo oxidation also occurs in air or water for many chemicals that can form excited states with solar radiation. The excited state reacts directly with oxygen or cleaves to form radicals which then react with oxygen. Direct photo oxidation rates depend only on the absorption cross section of the molecule, the quantum yield of the process and the solar flux in the absorption spectrum of the chemical. The distinction between photooxidation and chemical oxidation is important if laboratory test procedures are to be developed that will accurately predict the rates of these processes in a different environments. In most cases the properties of a chemical and of an environment that must be characterized are quite different for these two kinds of processes. Scheme 1 illustrates the two processes and the rate laws that govern them.

PHOTOOXIDATION

AY+ hv-AY*

AY*- A·+Y·

AY* + O2--→ Products (several steps)

Or

y. or A· + O2 –Products----------------→ (several steps)

Rox = < pIAedAY]

General Considerations

Oxidation is the chemical process whereby reactive electron deficient species (oxidants) remove electrons from other more electron-rich molecules. 1 Examples of oxidants that may be found in the environment are peroxy radical (R02·), hydroxy radical (l:l0:), singlet oxygen (102), ozone (03), and photo-excited triplet diradicals (R-O). Oxygen (02) is itself rarely involved directly in reactions with stable molecules but does act as the ultimate electron sink in most environmental oxidation reactions. Predicting the rate of oxidation of a specific chemical in air or water requires three kinds of information and data: (1) The identities and concentrations of the oxidants in the environmental compartment. (2) The rate constant for oxidation by each oxidant at a specific site in a molecule. (3) The kinetic rate law for each process. The following sections discuss the oxidants in aquatic and atmospheric systems, the kinetics of oxidation reactions, structure-reactivity relationships for oxidation of organic molecules, and oxidation and photo oxidation chemistry.

Photodegradation is the alteration of materials by light. Typically, the term refers to the combined action of sunlight and air. Photodegradation is usually oxidation and hydrolysis. Often photodegradation is avoided, since it destroys paintings and other artifacts. It is however partly responsible for remineralization of biomass and is used intentionally in some disinfection technologies. Photodegradation does not apply to how materials may be aged or degraded via infrared light or heat, but does include degradation in all of the ultraviolet light wavebands.

APPLICATION

The protection of food from photodegradation is very important. Some nutrients, for example, are affected by degradation when exposed to sunlight. In the case of beer, UV radiation causes a process that entails the degradation of hop bitter compounds to 3-methyl-2-buten-1-thiol and therefore changes the taste. As amber-colored glass has the ability to absorb UV radiation, beer bottles are often made from such glass to prevent this process.

Paints, inks and dyes

Paints, inks and dyes that are organic are more susceptible to photodegradation than those that are not. Ceramics are almost universally colored with non-organic origin materials so as to allow the material to resist photodegradation even under the most relentless conditions, maintaining its color.

Pesticides and herbicides

The photodegradation of pesticides is of great interest because of the scale of agriculture and the intensive use of chemicals. Pesticides are however selected in part not to photodegrade readily in sunlight in order to allow them to exert their biocidal activity. Thus, additional modalities are implemented to enhance their photodegradation, including the use of photosensitizers, photocatalysts (e.g., titanium dioxide), and the addition of reagents such as hydrogen peroxide that would generate hydroxyl radicals that would attack the pesticides.

Pharmaceuticals

The photodegradation of pharmaceuticals is of interest because they are found in many water supplies. They have deleterious effects on aquatic organisms including toxicity, endocrine disruption, genetic damage. But also in the primary packaging material the photodegradation of pharmaceuticals has to be prevented. For this, amber glasses like Fiolax amber and Corning 51-L are commonly used to protect the pharmaceutical from UV radiations. Iodine (in the form of Lugol's solution) and colloidal silver are universally used in packaging that lets through very little UV light so as to avoid degradation.

Polymers

Photo-oxidation of polymers

Common synthetic polymers that can be attacked include polypropylene and LDPE, where tertiary carbon bonds in their chain structures are the centres of attack. Ultraviolet rays interact with these bonds to form free radicals, which then react further with oxygen in the atmosphere, producing carbonyl groups in the main chain. The exposed surfaces of products may then discolour and crack, and in extreme cases, complete product disintegration can occur.

In fibre products like rope used in outdoor applications, product life will be low because the outer fibres will be attacked first, and will easily be damaged by abrasion for example. Discolouration of the rope may also occur, thus giving an early warning of the problem.

Polymers which possess UV-absorbing groups such as aromatic rings may also be sensitive to UV degradation. Aramid fibres like Kevlar, for example, are highly UV-sensitive and must be protected from the deleterious effects of sunlight.

Many organic chemicals are thermodynamically unstable in the presence of oxygen; however, their rate of spontaneous oxidation is slow at room temperature. In the language of physical chemistry, such reactions are kinetically limited. This kinetic stability allows the accumulation of complex environmental structures in the environment. Upon the absorption of light, triplet oxygen converts to singlet oxygen, a highly reactive form of the gas, which effects spin-allowed oxidations. In the atmosphere, the organic compounds are degraded by hydroxyl radicals, which are produced from water and ozone.

Photochemical reactions are initiated by the absorption of a photon, typically in the wavelength range 290–700 nm (at the surface of the Earth). The energy of an absorbed photon is transferred to electrons in the molecule and briefly changes their configuration (i.e., promotes the molecule from a ground state to an excited state). The excited state represents what is essentially a new molecule. Often excited state molecules are not kinetically stable in the presence of O_2 or H_2O and can spontaneously decompose (oxidize or hydrolyze). Sometimes molecules decompose to produce high energy, unstable fragments that can react with other molecules around them. The two processes are collectively referred to as direct photolysis or indirect photolysis, and both mechanisms contribute to the removal of pollutants.

The United States federal standard for testing plastic for photodegradation

Protection against photodegradation

Photodegradation of plastics and other materials can be inhibited with polymer stabilizers, which are widely used. These additives include antioxidants, which interrupt degradation processes. Typical antioxidants are derivatives of aniline. Another type of additive are UV-absorbers. These agents capture the photon and convert it to heat. Typical UV-absorbers are hydroxy-substituted benzophenones, related to the chemicals used in sunscreen.

REMOVAL OF HAZARDOUS CHEMICALS FROM WATER

Ozone, hydrogen peroxide, UV light are used in such processes to oxidize and remove toxic chemicals treatment from wastewater. Therefore, this process is also called in situ chemical oxidation.

Introduction

The energy demand is expected to be greater than 25 TW by the year 2050. This increase is expected to pose undue burden on natural resources and create challenges for sustaining our environment and quality of human life. In addition to energy, the demand for clean water is also expected to rise rapidly due to increasing global population. In addition, with the expeditious pace of industrialization, the disposal of industrial effluents poses threats to the environment and is becoming the biggest concern for the sustainable development of human society. Wastewater reclamation and recycling are essential goals to protect the global ecosystem and improve the quality of the environment. Several methods have been utilized for the removal of pollutants from contaminated water sources . Among them, advanced oxidation processes (AOP) have emerged to be promising, efficient, economic, and reliable for the removal of pollutants from aquatic environments. Among the various AOP methods, heterogeneous photocatalysis, using titanium dioxide (TiO_2) based photocatalysts, has emerged as a viable process for degrading a wide variety of pollutants.

Although TiO_2 has several important properties, such as ease of synthesis, excellent photostability, nontoxicity, and valence bands that are located at high positive potentials, there are several drawbacks that impair the performance of TiO_2 in photocatalytic processes. The absorbance of TiO_2 is limited to the UV region, and, thus, only a small fraction of the solar spectrum is utilized. The fast recombination of the photoinduced electron-hole pairs impedes the efficiency of the overall photocatalysis reaction. In addition, the relatively low surface area of TiO_2 limits the number of adsorptive sites of the target pollutant molecule. To overcome these aforementioned challenges, researchers have developed TiO_2 based mixed oxide materials that can provide large number of adsorptive sites by dispersion of TiO_2 species into a porous support with large surface area. Silica has been widely employed as a robust and stable mesoporous support for immobilizing photoactive TiO_2 species. The TiO_2-

SiO_2 mixed oxide photocatalysts have shown significantly enhanced activities compared to pure TiO_2 for a number of photocatalytic reactions for environmental remediation. The improved photocatalytic performance over TiO_2-SiO_2 mixed oxide materials can be accredited to the presence of highly dispersed TiO_2 species in the SiO_2 support, the better adsorption of the pollutant, and the presence of Ti-O-Si bonds that favor the activation of the organic pollutant.

In this review, we will first discuss the different types of aqueous pollutants followed by a discussion of selected removal techniques and their basic principles. Then, a brief overview of the synthesis methods of titania-silica (TiO_2-SiO_2) mixed oxides is presented. This is followed by an extensive description of available characterization techniques of periodic and aperiodic titania-silica catalysts. Following this, the heterogeneous photocatalytic degradation of several pollutants, in particular, organic materials in aqueous phase, is discussed. Finally, the factors that influence the degradation reactions are critically reviewed.

1.1. Aquatic Pollution

Clean water is the most important and indispensable resource that maintains the demands for the daily activities of every aspect of human society, such as drinking, cleansing, industrial manufacture, and farm irrigation. However, the squandering of clean water at discretion and careless handling of wastewater to aquatic systems from households and industries severely contaminate the quality of natural aquatic environments. In general, the sources that result in water pollution can be classified as point and nonpoint sources . The former one contains pollutants that are discharged from industries, septic materials, animal feedlots, mines and oil industries, and so forth into water sources. The latter one includes runoffs from agriculture, sediment, animal wastes, and so forth. Nonpoint sources, due to their irregularity, are more difficult to be tracked compared to point sources. However, according to the Environmental Protection

Agency (EPA), nonpoint sources are claimed to be the major cause of aqueous pollutants. The existence of these pollutants in water systems can cause serious environmental issues and pose threat to public hygiene and health. For instance, the contamination of groundwater by pesticides can endanger aquatic ecosystems. As the fertilizer is discharged into water sources, it can boost the multiplication of algae, which interrupts the oxygen level and upsets the ecological balance in the water system. Moreover, close contact or drinking of the contaminated water can cause skin rashes and other severe diseases like typhoid fever and stomach illness in humans. Waste inorganic and/or organic chemicals, in particular heavy metal ions, in the water may be ingested by fish and may also cause infection in humans, who catch and consume it. In the following section, the most commonly occurring hazardous pollutants along with their effects will be discussed.

1.2. Hazardous Pollutants

The most commonly observed hazardous wastes that threaten the global aquatic system can be divided into four groups according to the classification by the EPA: (i) hazardous wastes from nonspecific industrial processes, (ii) hazardous wastes from specific industrial sources, (iii) commercial chemical products, and (iv) toxic wastes. The EPA estimates that the above-mentioned pollutants have been increasingly detected during the past few decades in rivers, lakes, and oceans. In the following part, we will discuss the some important inorganic and organic wastes in water.

1.2.1. Inorganic Wastes

Anionic Wastes. Phosphates and nitrates are the most prevalent pollutants in contaminated surface water. Phosphorus (P) and nitrogen (N) are indispensable elements used in fertilizers for agriculture. Application of extensive amounts of P and N containing fertilizers on arable lands causes extensive accumulation of the phosphate and nitrate in the soil. Due to the use of manual irrigation and/or natural rainfall, phosphates and nitrates can leach into ground and surface water sources, such as rivers and lakes. In addition to the P and N containing fertilizers, the manure from livestock is also a major source of phosphate and nitrate contaminants in water systems.

The contamination of water by nitrates poses a threat to the health of humans and other animals. Nitrate is found to be extremely toxic at high concentrations in water. It has been postulated to be the origin of methemoglobinemia in infants and it can cause toxic effects on livestock. Although phosphorus is not as toxic as nitrate in water, it can stimulate the growth of algae in water along with nitrate pollutants. Their excessive discharge to the surface water sources can lead to severe eutrophication in surface water sources. Eutrophication is the most widespread water contamination in global aquatic systems and it brings about numerous negative aftermaths to the environment and ecosystem. The most commonly observed consequence of eutrophication is that it causes the multiplication of algae and aquatic weeds, which give bad odor and taste of water in the aquatic systems, and prevents the use of such polluted systems as sources for clean water for industry, agriculture, and humans. In addition, eutrophication can induce the growth of phytoplankton and zooplankton in various aquatic environments. Besides, eutrophication is considered to be the cause for the disappearance of coral reefs and the extinction of several fish species.

Cyanides are another important class of anionic pollutants. Cyanides, which can be generated from either anthropogenic or natural sources, commonly exist in the form of cyanide salts, such as sodium cyanide and potassium cyanide, or in gaseous phase as hydrogen cyanide. Cyanides can be discharged into aquatic system from carelessly treated industry sewage, coal gasification, electroplating operations, and incomplete combustion of fuels. Cyanides cause severe threat to human life as the cyanide anion ( ) is recognized to be highly toxic. The ingestion and/or inhalation of cyanide anion () by humans can lead to low vitamin B_{12} levels in the human body and can be lethal.

Cationic Wastes. The most commonly seen inorganic cationic wastes in aquatic systems are heavy metal ions, such as lead () [21], arsenic () [22], mercury (Hg^{2+}) [23], chromium (Cr^{6+}) [24], nickel () [25], barium (), cadmium (Cd^{2+}) [26], cobalt (Co^{3+}) [27], selenium (Se^{2+}) [28], and vanadium (V^{5+}) [25]. These above-mentioned heavy metal ions can be introduced into aquatic system via diverse means [29]. For example, large amounts of heavy metal ions are produced from natural processes, such as weathering, volcano activities, and crustal movement. As in the modern society, the major sources of heavy metal pollutants are from human/industry activities, for instance, printed board and semiconductor manufacturing, metal finishing and plating, industrial dyeing processes, and so forth. Many heavy metal ions, for example, Fe^{3+}, Zn^{2+}, Cu^{2+}, Mn^{2+}, Co^{3+}, , and so forth, are actually essential trace elements (required in less than 100 mg per day) to maintain the daily metabolism of the human body. However, these heavy metal ions exhibit fatal toxicity and can poison humans and animals under excessive exposure and close contact. The indication of heavy metal poisoning in humans can be divided into acute and chronic symptoms. Acute symptoms include fatigue, hallucinations, headache, nausea, numbness, and abdominal pain. Chronic symptoms contain anxiety, dyslexia, lack of concentration, migraines, and so forth. Therefore, the removal of heavy metal ion pollutants from aquatic system is indispensable.

1.2.2. Organic Wastes

Organic pollutants are toxic molecular compounds and can cause significant diseases in humans, when exposed to high concentration levels. These organic compounds originate from a variety of industrial products such as detergents, petroleum hydrocarbons, plastics, organic solvents, pesticides, and dyes, and they can be found in diverse environments. In addition, these organic pollutants are a threat to wildlife and human, due to long-term deleterious effect and chemical complexity. In particular, thousands of persistent organic pollutants (POPs) are a family of chemicals consisting of a diverse group of organic substances, which are toxic, bioaccumulative, and prone to long range of transport. It was reported elsewhere that POPs mainly differ in the level of chlorine substitutions and persist in the environment with long lives particularly in soils, sediments, and air. They are released into the environment via municipal and industrial wastes, landfill effluents, agricultural practices, and so forth and undergo various reactions that validate their prevalence. There are a wide number of pollutants listed under the toxic and hazardous categories and some of the main types are detailed here.

Aliphatic organic compounds are mainly runoffs from the surface and are particularly seen in urban areas. In addition, the petroleum oils and the byproducts from the combustion of oil also are mostly aliphatic compounds. A variety of aliphatic organic compounds, that include alkenes, alkynes, dichlorodifluoromethane, 1,2-dichloroethane, 2-propanol, and tetramethylammonium ions, have been reported as toxic pollutants from aquatic environment mainly from surface runoffs. Polycyclic aromatic hydrocarbons (PAH) are another type of organic substances released to the environment from the incomplete combustion of organic substances including wood, carbon, and oil. They are neutral, nonpolar organic molecules consisting of two or more fused benzene rings and reported as a priority pollutant by the EPA. The extensive use of polychlorinated biphenyls (PCBs) in numerous industrial processes, electrical transformers, capacitors, carbonless copy paper, and plastics increases their penetration into the environment.

Surfactants are among the most versatile group of organic compounds utilized in industrial, household, personal care, and health products. Owing to their existence in anionic, cationic, nonionic, and amphoteric forms, they have the ability to alter the physicochemical state of the natural habitat. At high concentrations, they can form complexes in water and cause harmful effects to microorganisms. Pesticides are another type of organics found in diverse chemical structures and are used for various agricultural and nonagricultural applications such as herbicides, insecticides, fungicides, and germicides. Dyes are colored substances that have strong affinity for the substrate to which it is being applied. Dyes are applied to numerous substrates such as textiles, leather, plastic, and paper. Dyes can be classified under different categories according to their application method, chemical structure, usage, or the type of chromophore present in them.

Phenol and phenolic compounds byproducts formed from many industrial processes, such as the manufacturing of herbicides, plastics, polymer precursors, photographic developers, dyes, drugs, and pulp and paper industry. In addition, incomplete mineralization of the phenolic compounds ends up with natural organic byproducts that include humic substances, lignins, and tannins, which are prevalent in our environment. The toxicity of phenols and phenol derivatives is mainly attributed to the ease of donation of free electrons, forming phenoxy radicals and intermediates. These phenoxy radicals can penetrate the cell and damage membranes of endoplasmic reticulum, mitochondria, and nucleus and also their components like enzymes and nucleic acids. Furthermore, exposure to phenol may damage the skin through its reaction with amino acids in the epidermis.

2. Removal Techniques

Continuous increase of pollutants in water bodies has necessitated the need to develop cost-effective methods for their removal. Destroying the pollutants to benign chemicals and/or removing these pollutants from contaminated water is imperative for a green environment. There are numerous treatment processes that have been applied for pollutant removal from wastewater, such as electrochemical oxidation [40], biodegradation [41, 42] membrane process [43], coagulation [44, 45], adsorption [46–49], precipitation [50], sonochemical degradation [51, 52], micellar enhanced ultrafiltration, and AOP [4, 9, 10]. Though these methods are considered as efficient methods for pollutant removal, each method has its own benefits and drawbacks. In this section, we will explain some of the most common methods that are frequently used for pollutant removal and their basic principles.

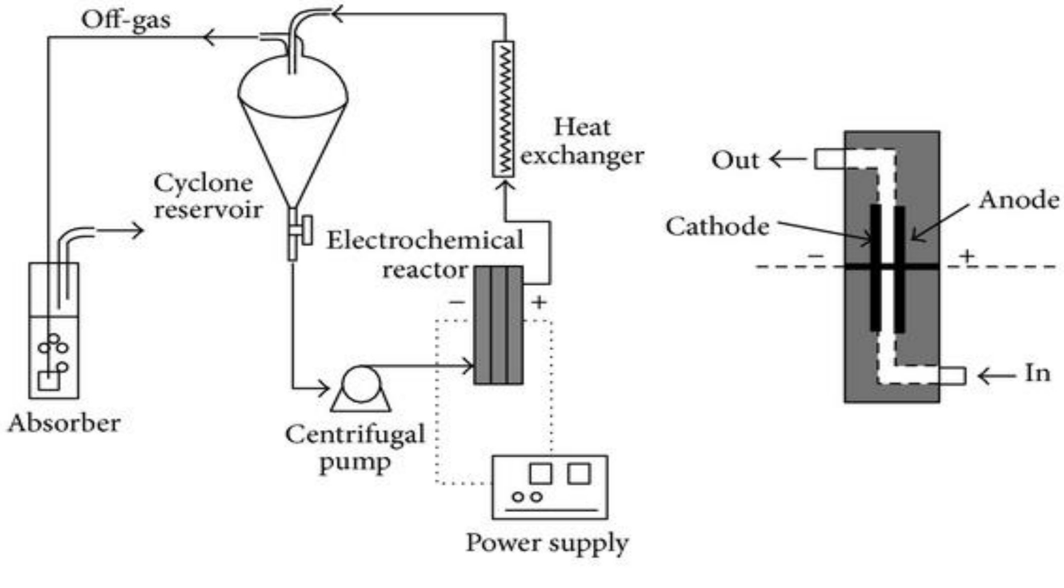
2.1. Electrochemical Oxidation

Electrochemical oxidation is an efficient and economic method, suitable when the wastewater contains nonbiodegradable organic pollutants. This method poses several advantages since it does not require auxiliary chemicals, high pressures, or high temperatures. In addition, owing to its versatility and cost-effectiveness, electrochemical techniques have gained great attention for the removal of pollutants. The process of electrochemical oxidation mechanism is mainly based on the generation of the hydroxyl radicals at the electrode surface.

Two different types of mechanisms have been elaborated for electrochemical oxidation, such as direct and indirect oxidation methods. In direct electrochemical oxidation, the degradation of organic compound occurs directly over the anode material, where the hydroxyl radical () or the reactive oxygen species react with the organic compound. The pollutants are first adsorbed at the surface of the anode and are then degraded by an anodic electron transfer reaction as given by

In the indirect electrochemical oxidation, the organics are treated in the bulk solution by oxidants, such as , Cl_2, hypochlorite (ClO^-), peroxodisulfate (), and ozone (O_3), which are electrochemically generated at the electrode surface. Even though high removal efficiencies are achieved by both the direct and indirect electrochemical oxidation processes, their effectiveness strongly depends on the treatment conditions including pH, current density, types and concentration of pollutants, supporting electrolyte, flow rate, electrode preparation method, and nature of the electrode materials. Several electrode materials that include Pt,

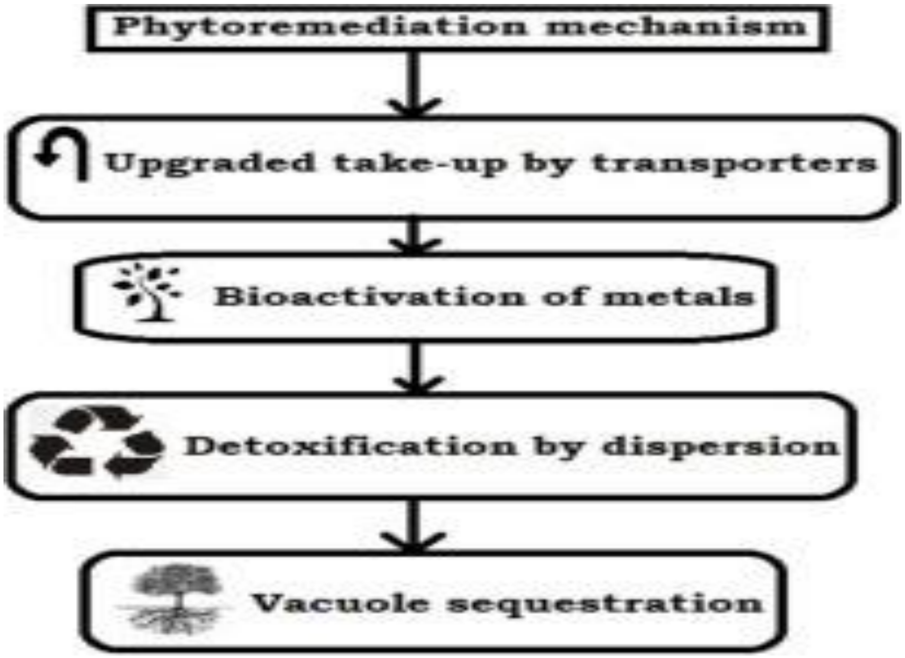
PbO_2, Ti-SnO_2, Ti/Pt, Ti/Pt–Ir, Ti/PbO_2, Ti/PdO–Co_3O_4, Ti/–TiO_2, Ti coated oxides of Ru/Ir/Ta, IrO_2, Ti/RuO_2, SnO_2, PbO_2, and so forth, and boron doped diamond (BDD) have been listed as efficient electrodes for the degradation of organics by electrochemical oxidation. Apart from these anode materials, graphite anodes are also considered as efficient materials for anodic oxidation of several organic pollutants. Particularly, the high oxygen overpotential, high electrocatalytic activity, chemical stability, long lifetime, and cost-effectiveness have been credited for the high efficiency of these graphite electrodes. In a recent publication, Govindaraj et al. investigated the electrochemical oxidation of bisphenol A (BPA) from aqueous solution using graphite electrodes. The effect of the supporting electrolyte (type and concentration), initial pH, and applied current density on the performance was discussed in their work. The oxidation of polyhydroxy benzenes was conducted using a single-compartment electrochemical flow cell as illustrated in Figure 1. Diamond-based material was used as the anode and stainless steel was used as the cathode.



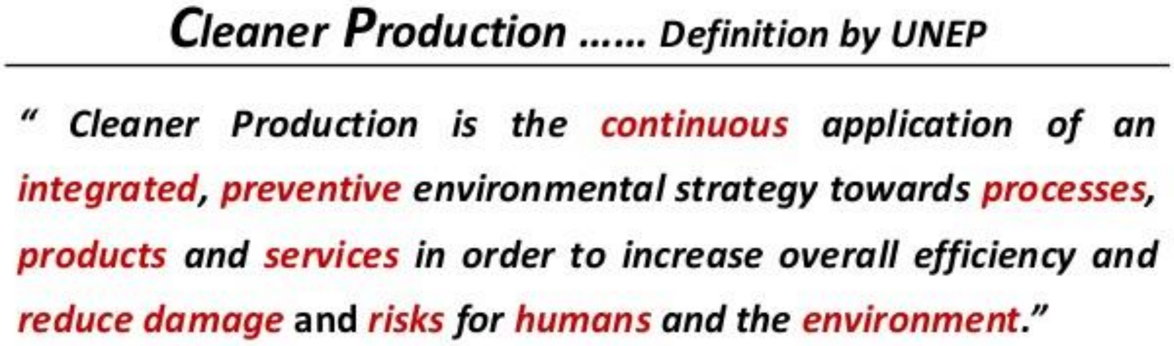
In this photocatalysis process, the contaminant molecule gradually breaks down by its reaction with highly reactive oxidative species (ROS), such as , and , which can be generated during the illumination process Frank and Bard have reported the heterogeneous photocatalytic oxidation of cyanide and sulfite in the presence of several semiconductors that include TiO_2, ZnO, CdS, Fe_2O_3, and WO_3, in aqueous medium under sunlight. It was noticed that TiO_2, ZnO, and CdS showed good activity for cyanide oxidation, and no oxidation was seen using Fe_2O_3 and WO_3. In addition, the rates of the photocatalytic oxidation were found to be greater for sulfite than cyanide. Among these oxides, titanium dioxide (TiO_2) is an effective semiconductor material that has been explored for numerous applications including adsorption, heterogeneous photocatalysis for splitting of water, solar cell applications, and degradation of pollutants.

The removal of inorganic anions that include cyanide, nitrite, and sulfite has been studied in the presence of TiO_2. In addition, the degradation of variety of pollutants that include several dye molecules, phenol and phenol derivatives [12, 46, 217, 218], and salicylic acid [219, 220] has also been researched.

Even though TiO_2 has been utilized as a photocatalyst for the degradation of a number of pollutants, its efficiency towards degradation is partly limited owing to its poor adsorptive property. In order to improve the efficiency of titania, researchers have prepared mixed oxide materials that can provide greater number of adsorptive sites; furthermore, by generating highly porous structures with large surface areas, effective dispersion of titania can also be achieved [221, 222]. Among the various mixed oxides, titania-silica has met the expectations of several researchers, due to the high surface area and the hydrophobic nature of silica

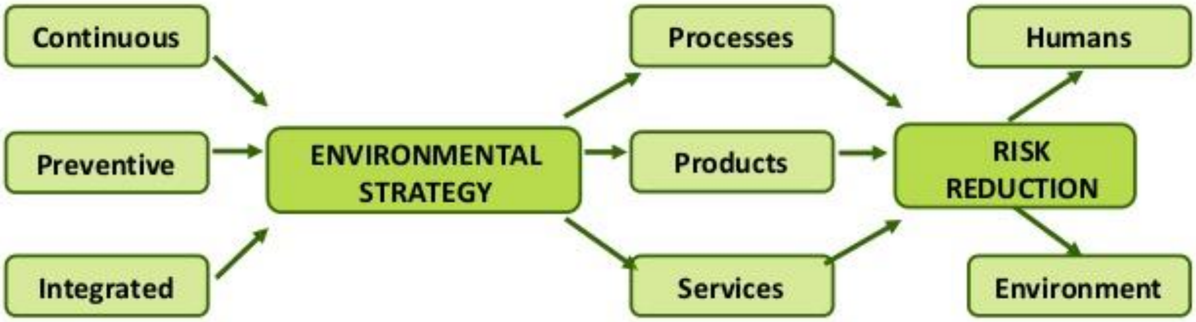


CLEANER PRODUCTION CONCEPT

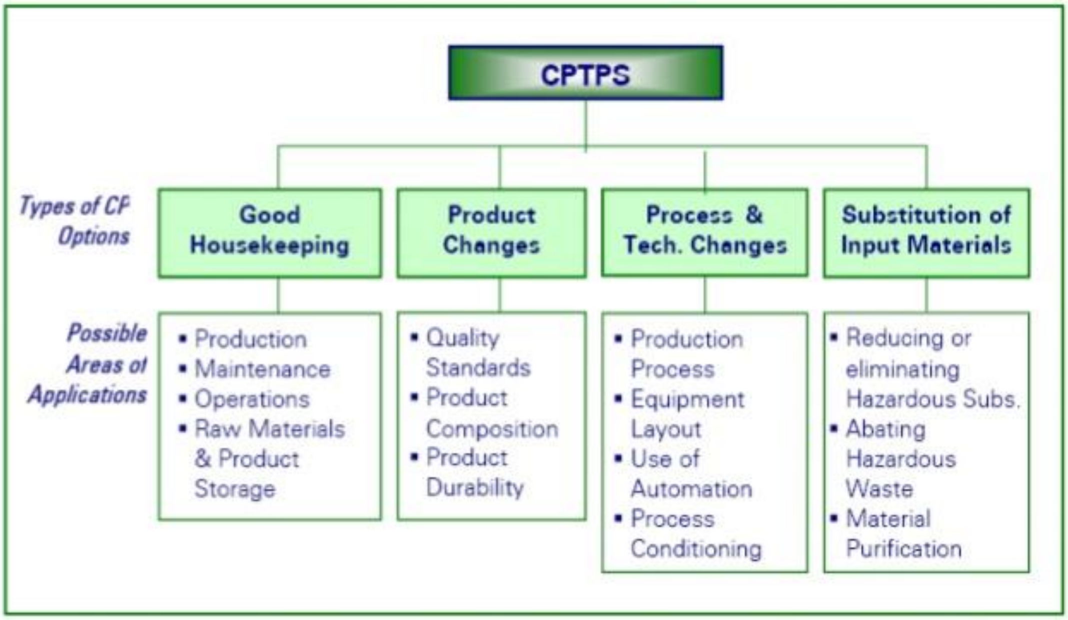


Cleaner Production *...... Definition by UNEP*

" Cleaner Production is the continuous application of an integrated, preventive environmental strategy towards processes, products and services in order to increase overall efficiency and reduce damage and risks for humans and the environment."



Cleaner production option



Definition

Cleaner production (CP) is a preventative approach to managing the environmental impacts of business processes and products. CP uses changes in technology, processes, resouces or practices to reduce waste, environmental and health risks; minimise environmental damage; use energy and resources more efficiently; increase business profitability and competitiveness; and increase the efficiency of production processes. Cleaner production is applicable to all businesses, regardless of size or type.

Main Features

Cleaner production is an ongoing process that can be applied to production processes; products; or services; or it can be extend to cover the entire lifecycle of a product or service. Some cleaner production techniques include:

- Changes in technology.
- Changes in input materials.
- Changes in operating practices.
- Changes in product design.
- Changes in waste use.
- Changes in maintenance.
- Changes in packaging.

Cleaner production is related to other sustainability concepts such as eco-efficiency; environmental sound technologies; life cycle assessment; green procurement and zero emissions. For cleaner production to succeed, senior management support, staff awareness and participation, and staff input is required.

The impetus behind cleaner production includes the reduction of operation or pollution license fees; regulations; peer pressure; corporate image; corporate environmental plans or policies; cost savings; and product bans. Barriers to implementing a CP program include: lack of finances (perceived or real); low environmental awareness or concern of the organisation; lack of organisational support; lack of human resources; and limited access to appropriate technology.

The CP technique employed by organisations differs, however, the basic CP process is:

- Planning and organisation - organisation are made aware of the CP process, stakeholder input sort, CP team formed, environmental policy reviewed or written, and budgets and program created.

- Assessment - material inputs and outputs identified and assessed, current processes and costs assessed, environmental and health impacts reviewed, CP options identified.
- Feasibility analysis - each CP option is assessed for its environmental impact and its technological and economical viability, final CP option selected.
- Implementation - selected CP option is implemented and a monitoring and evaluation program established.
- Continuation - regular audits conducted and findings feed back into the decision making process, stakeholders informed of progress and gains.I

IMPLEMENTATION GOVERNMENT ROLE

In some industrial chemical processes, not only waste products but also the reagents used for the production, may cause a threat to the environment. According to the principles of green chemistry, a threat can be eliminated in a simpler way, by applying safe raw materials for production process. Large amounts of adipic acid8 are used each year for the production of nylon, polyurethanes, lubricants and plasticizers. Benzene (a compound with carcinogenic properties) is a standard substrate for the production of this acid. Chemists from State University of Michigan developed green synthesis of adipic acid using a less toxic substrate. Furthermore, the natural source of this raw material, glucose is almost inexhaustible. The glucose can be converted into adipic acid by an enzyme discovered in genetically modificated bacteria. Such a manner of production of this acid guards the workers and the environment from exposure to hazardous chemical compounds. Conventional route to Adipic acid from Benzene S.Ravichandran /Int.J. ChemTech Res.2011,3(3) 1048 2 Green chemistry tries, when possible, to utilize benign, renewable feedstocks as raw materials. From the point view of green chemistry, combustion of fuels obtained from renewable feedstocks is more preferable than combustion of fossil fuels from depleting finite sources. For example, many vehicles around the world are fueled with diesel oil, and the production of biodiesel oil is a promising possibility. As the name indicates, biodiesel oil is produced from cultivated plants oil, e.g. from soya beans. It is synthesized from fats embedded in plant oils by removing the glycerine molecule. The advantages of using biodiesel oil are obvious. It’s fuel from renewable resources and contrary to normal diesel oil.

Survey of Industrial Implementation of Green Chemistry

The Roundtable surveyed green chemistry practitioners in the chemical manufacturing sector about their use of green chemistry principles and related metrics. For the three key survey topics (principles, metrics, priorities), the 2012 Roundtable survey results are presented and discussed on a topic by topic basis. In each case, the survey question is listed, results are provided, and implications of these results are discussed in light of recent chemical industry-wide sustainability reports to better illustrate the current state of green chemistry implementation in the sector.

Current Application of Green Chemistry Principles

The 12 principles (summarized in Figure 1) define the field of green chemistry. Practitioners were asked, “In your opinion, how frequently does your company implement the following principles of green chemistry?” on a scale of 1 to 4 (where 1 is never implemented and 4 is fully implemented).

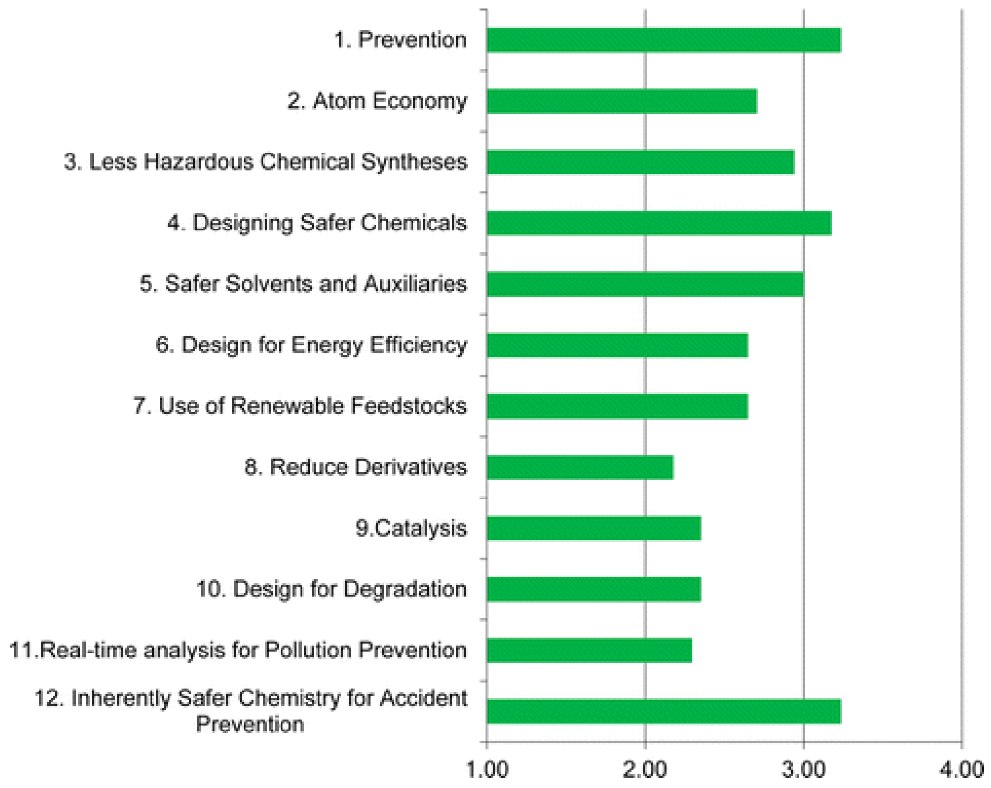


Figure 1. Frequency of the 12 principles of green chemistry implemented in chemical manufacturing. Average chemical manufacturer responses (n = 17) to the 2012 Roundtable survey question "In your opinion, how frequently does your company implement the following principles of green chemistry?" on a scale of 1 to 4, where 1 is never implemented (same value used for not applicable), 2 is rarely implemented, 3 is regularly implemented, and 4 is fully implemented. The magnitude of each bar is the average response calculated using the corresponding scale value (e.g., 3 for regularly implemented).

Unit-V Cheminformatics

Cheminformatics ; Introduction-Evalution-History and uses-molecular modelling using computer-Basic idea-Chemical information date base design and their management-database concepts-structural languages chemical database design chemical information sources- chemical information researches formula searching.

Cheminformatics (also known as **chemoinformatics**, **chemioinformatics** and **chemical informatics**) is the use of computer and informational techniques applied to a range of problems in the field of chemistry. These *in silico* techniques are used in, for example, pharmaceutical companies in the process of drug discovery. These methods can also be used in chemical and allied industries in various other forms.

Chemoinformatics is the mixing of those information resources to transform data into information and information into knowledge for the intended purpose of making better decisions faster in the area of drug lead identification and optimization. Since then, both spellings have been used, and some have evolved to be established as Cheminformatics, while European Academia settled in 2006 for Chemoinformatics. The recent establishment of the Journal of Cheminformatics is a strong push towards the shorter variant.

Basics

Cheminformatics combines the scientific working fields of chemistry, computer science and information science for example in the areas of topology, chemical graph theory, information retrieval and data mining in the chemical space. Cheminformatics can also be applied to data analysis for various industries like paper and pulp, dyes and such allied industries.

Applications

Storage and retrieval

Main article: Chemical database

The primary application of cheminformatics is in the storage, indexing and search of information relating to compounds. The efficient search of such stored information includes topics that are dealt with in computer science as data mining, information retrieval, information extraction and machine learning. Related research topics include:

- Unstructured data
    - Information retrieval
    - Information extraction
- Structured Data Mining and mining of Structured data
    - Database mining
    - Graph mining
    - Molecule mining
    - Sequence mining
    - Tree mining
- Digital libraries

Molecular modelling

- The backbone dihedral angles are included in the molecular model of a protein.
- Modeling of ionic liquid

Molecular modeling encompasses all theoretical methods and computational techniques used to model or mimic the behaviour of molecules. The techniques are used in the fields of computational chemistry, drug design, computational biology and materials science for studying molecular systems ranging from small chemical systems to large biological molecules and material assemblies. The simplest calculations can be performed by hand, but inevitably computers are required to perform molecular modelling of any reasonably sized system. The common feature of molecular modelling techniques is the atomistic level description of the molecular systems. This may include treating atoms as the smallest individual unit (the Molecular mechanics approach), or explicitly modeling electrons of each atom (the quantum chemistry approach)

Molecular mechanics

- Molecular mechanics is one aspect of molecular modelling, as it refers to the use of classical mechanics/Newtonian mechanics to describe the physical basis behind the models. Molecular models typically describe atoms (nucleus and electrons collectively) as point charges with an associated mass. The interactions between neighbouring atoms are described by spring-like interactions (representing chemical bonds) and van der Waals forces. The Lennard-Jones potential is commonly used to describe van der Waals forces. The electrostatic interactions are computed based on Coulomb's law. Atoms are assigned coordinates in Cartesian space or in internal coordinates, and can also be assigned velocities in dynamical simulations. The atomic velocities are related to the temperature of the system, a macroscopic quantity. The collective mathematical expression is known as a potential function and is related to the system internal energy (U), a thermodynamic quantity equal to the sum of potential and kinetic energies. Methods which minimize the potential energy are known as energy minimization techniques (e.g., steepest descent and conjugate gradient), while methods that model the behaviour of the system with propagation of time are known as molecular dynamics.

- $E = E_{\text{bonds}} + E_{\text{angle}} + E_{\text{dihedral}} + E_{\text{non-bonded}}$

- $E_{\text{non-bonded}} = E_{\text{electrostatic}} + E_{\text{van der Waals}}$

- This function, referred to as a potential function, computes the molecular potential energy as a sum of energy terms that describe the deviation of bond lengths, bond angles and torsion angles away from equilibrium values, plus terms for non-bonded pairs of atoms describing van der Waals and electrostatic interactions. The set of parameters consisting of equilibrium bond lengths, bond angles, partial charge values, force constants and van der Waals parameters are collectively known as a force field. Different implementations of molecular mechanics use different mathematical expressions and different parameters for the potential function. The common force fields in use today have been developed by using high level quantum calculations and/or fitting to experimental data. The technique known as energy minimization is used to find positions of zero gradient for all atoms, in other words, a local energy minimum. Lower energy states are more stable and are commonly investigated because of their role in chemical and biological processes. A molecular dynamics simulation, on the other hand, computes the behaviour of a system as a function of time. It involves solving Newton's laws of motion, principally the second law, $\mathbf{F} = m\mathbf{a}$. Integration of Newton's laws of motion, using different integration algorithms, leads to atomic trajectories in space and time. The force on an atom is defined as the negative gradient of the potential energy function. The energy minimization technique is useful for obtaining a static picture for comparing between states of similar systems, while molecular dynamics provides information about the dynamic processes with the intrinsic inclusion of temperature effects.

Applications

Molecular modelling methods are now routinely used to investigate the structure, dynamics, surface properties and thermodynamics of inorganic, biological and polymeric systems. The types of biological activity that have been investigated using molecular modelling include protein folding, enzyme catalysis, protein stability, conformational changes associated with biomolecular function, and molecular recognition of proteins, DNA, and membrane complexes.

BASIC IDEA

A collection of primitive operations for molecular diagram sketching has been developed. These primitives compose a concise set of operations which can be used to construct publication-quality 2 D coordinates for molecular structures using a bare minimum of input bandwidth. The input requirements for each primitive consist of a small number of discrete choices, which means that these primitives can be used to form the basis of a user interface which does not require an accurate pointing device. This is particularly relevant to software designed for contemporary mobile platforms. The reduction of input bandwidth is accomplished by using algorithmic methods for anticipating probable geometries during the sketching process, and by intelligent use of template grafting. The algorithms and their uses are described in detail.

A collection of primitive operations for molecular diagram sketching has been developed. These primitives compose a concise set of operations which can be used to construct publication-quality 2 D coordinates for molecular structures using a bare minimum of input bandwidth. The input requirements for each primitive consist of a small number of discrete choices, which means that these primitives can be used to form the basis of a user interface which does not require an accurate pointing device. This is particularly relevant to software designed for contemporary mobile platforms. The reduction of input bandwidth is accomplished by using algorithmic methods for anticipating probable geometries during the sketching process, and by intelligent use of template grafting. The algorithms and their uses are described in detai

Introduction

Molecular structure diagrams have been the mainstay of chemical communication since molecules began to be rationalised as Lewis structures. The basic ideas involved in representing structures have proven to be remarkably resilient. While typographic conventions used in the late 19th century differ slightly from modern publications, organic structures are mostly quite recognisable when compared to literature published more than a century ago.

Experimental

The objective of this work is to describe a collection of primitive drawing operations which provides a comprehensive set of editing capabilities. These can be used to compose complex diagrams with minimal effort on behalf of the operator.

Ideally, each primitive would be able to examine the molecule diagram thus far, determine what it is the user wants changed, and execute the change. In practice, several additional fields are required for most operations. The unit primitives which are described in this work operate as sequences of:

- select **subject**
- select **action**
- select **result**

The **subject** is an annotation to the existing structure, which consists of:

- current atom or current bond
- a set of selected atoms

At any time there may be a current atom or a current bond, but not both. Each atom of the existing structure is either selected or unselected. In the text that follows, the term subject atoms is defined as a set of:

- all selected atoms, if there are any;

- or: the current atom, if there is one;

- or: the two atoms of the current bond, if there is one;
- else: an empty set.

The **action** is the choice of primitive to apply to the current subject.

For many primitives, there is just one possible outcome when applied to a particular subject, e.g. changing atoms to a specific element, for which it is appropriate to design the primitive to have an unambiguous effect. For some of the more complicated primitives, there could be more than one possible outcome, e.g. attaching a template with multiple possible geometries. In these cases, the primitive may choose to generate a number of **results**. The list of results should be sorted so that the most plausible result is first, and the remaining possibilities in

Atoms

Atom modification primitives are mostly straightforward and unambiguous, such as changing an element label, or altering atom-centred properties such as charge or radical count. The number of primitives required depends on the number of editable atom properties used to describe the molecular structure. The following primitive classes are representative.

Add Atom

A new atom is created. Its position is determined automatically. If the structure already contains one or more atoms, it is along the top and to the right of the existing atoms.

One primitive is required for each element of the periodic table. The new atom will have the corresponding label, with default values for all other properties, and no bonds.

Set Element Label

The subject atoms have their atomic symbol changed. One primitive is required for each element of the periodic table. If there is no subject, then this primitive should be mapped to the corresponding Add Atom primitive.

Variations on this primitive should allow arbitrary values to be entered via an input dialog, for symbols which are not atomic elements, such as abbreviations or Markush structures.

Set Ionic Charge

The subject atoms have their ionic charge set to a specific value, such as 0, -1, +1, etc. The primitives in this class can either specify exact values for the charge, or they can be increment/decrement operations.

Set Unpaired Electrons

The subject atoms have the number of unpaired electrons (also known as radical count) set to a specific value, where 0 is for diamagnetic atoms, 1 is for radicals, 2 is for carbene-like species, etc. One primitive is needed for each available value.

Set Hydrogen Count

Some molecular structure formats allow the number of implicit hydrogens to be specified [14]. The default value should be automatic, whereby the number of implied hydrogens is calculated from the atomic element, charge, unpaired electron count and immediate bonding environment. A value of 0 implies that no additional hydrogens are attached, and a value of greater than zero specifies exactly how many are present. One primitive is needed for each possible value.

Set Isotope

The molecular mass of an atom defaults to the statistical average of its natural abundance. An atom can alternatively be defined to be a specific isotope. One primitive is required for each possible isotope of a given element.

Bonds

Modification of the properties of existing bonds is straightforward. Some interpretation is required in order to interpret the meaning of the incoming selection, but all changes can be applied in a straightforward way to the molecule connection table. Connecting or disconnecting atoms which already exist can be done explicitly with a different primitive class.

Set Bond Order

This class contains one primitive for each bond order supported by the molecular datastructure (e.g. 0, 1, 2, 3 and 4).

If the subject contains a single atom, this primitive is mapped to New Bond with Order, in the Geometry section, which creates a new atom and a new bond.

If the subject contains two atoms, and they are not currently bonded to each other, a new bond with the requested order is added between them.

Otherwise, all bonds between any two atoms within the subject set are set to the indicated bond order. Any of these bonds which previously had a specific stereo style is reset to the default non-stereochemical bond type.

Set Stereo Style

This class contains one primitive for each explicit bond stereo-style supported by the molecular datastructure, which includes: inclined bonds (upward wedge); declined bonds (hashed wedge); and unknown stereochemistry (often drawn as a wavy line). When used correctly, these types are sufficient to unambiguously resolve most kinds of stereoisomerism.

Similarly to the Set Bond Order class, if the subject contains a single atom, this primitive is mapped to New Bond with Stereo Style, in the Geometry section. .

Connect Atoms

Of all the subject atoms, any pairwise combination of two atoms which are not already bonded is considered. If there are any such atom pairs whose bond distances are approximately within the default bond distance (see Appendix 1) then all of these pairs are joined by adding a single bond between each pair.

If there are unbonded pairs, but none of them are close enough to the default bond distance, then only the closest pair of atoms is connected.

Disconnect Atoms

Any bond for which both the participating atoms are a part of the subject is deleted. The atoms themselves are not otherwise modified.

Deletion

Removal of atoms and bonds is straightforward, and requires only a small amount of logic to interpret the subject and apply the action to the molecule connection table.

Delete Atoms

All of the atoms in the subject set are deleted, as are any bonds which are connected to them.

Delete Bonds

Any bond which is between two atoms within the subject set is deleted. The atoms themselves are not modified.

Delete All

All atoms and bonds are deleted.

Merge Atoms

Each atom in the subject set is examined to see if it is particularly close to any other atom in the structure, typically set to a tolerance level which is significantly shorter than the default bond distance (see Appendix 1). For each of the subject atoms, a list is made of all other atoms to which the distance falls within the tolerance. From this list, one atom is selected to be retained, using the merging rules described in Appendix 2. The coordinates of the retained atom are set to the average position of the atoms in the list.

Movement

While the unit primitives for grafting new fragments onto an existing molecular sketch are entirely sufficient for building up many complex molecules, there will always be structures which need to be fine tuned, or drawn with nonstandard parameters. This is often the case around heavily congested atoms for which there is no non-overlapping planar layout that adheres to common conventions.

.

Move Atoms

The subject atoms are moved in a specific direction. There are twelve primitives in this class: four directions (left, right, up, down) by three extents (small nudge, large nudge, move to furthest extent).

The small and large nudges offset the X or Y coordinates of the subject atoms in the given direction by an offset, such as 0.1 or 0.5 Å.

When moving to the furthest extent, the distance needed to move the subject atoms 1 Å beyond any of the other atoms in the molecule is calculated, and used as the offset.

Scale Atoms

Two primitives are defined for this class: grow and shrink, which correspond to scaling factors of 1.25 and 0.8, respectively.

If the subject contains any selected atoms, then a central point is determined from the average positions of the selected atoms, unless there is also a current atom or bond, in which case its central position is used instead. Each of the subject atoms has its position recalculated by scaling its distance from the central point by the scaling factor associated with the primitive.

Scale Bond

As for the Scale Atoms class, two primitives are defined: grow and shrink, which correspond to scaling factors of 1.25 and 0.8, respectively.

The subject must include two atoms which are bonded to each other. Each side of the bond is assigned a weighting of 0, 0.5 or 1.

If the bond is acyclic, then the atoms of the connected components on either side of the bond are counted. If one side forms a component with more atoms than the other, then the smaller side is assigned a weighting of 1 and the larger side a weighting of 0. If both sides have the same size, or the bond is cyclic, then both sides are assigned a weighting of 0.5.

The bond length is scaled according to the scaling factor assigned to the primitive, and the weights that are assigned to both sides, i.e. if a side has a weighting of 0 it does not move. For acyclic bonds, when moving one side of the bond, all other atoms associated with that side are moved as well. For cyclic bonds, only the two atoms that make up the bond are extended.

Figure 1 illustrates increasing a bond length under three circumstances: unequal sides, equal sides, and a ring bond. The initial structures are shown on top, and the modified structures underneath.

Flip Atoms

Two primitives are defined for this class: horizontal and vertical flip.

If the subject contains some number of selected atoms, then these atoms are flipped about the indicated axis. The origin of the axis is calculated as the average position of the selected atoms, unless there is also a current atom or bond, in which case its central position is used

Rotate Atoms

Primitives in this class are defined to be common rotation increments, such as ± 1°, ± 5°, ± 15° and ± 30°.

Geometry

Because the information provided to the unit primitives cannot include spatial information such as bond direction, a crucial part of the design of the primitives is based on perception of atom geometry.

One of the most important sketching primitives is the ability to create a new atom which is bonded to an existing atom. With a traditional user interface this is done by using the mouse to drag a bond line in a particular direction, thus specifying bond angle and distance. Lacking such input, it is necessary for algorithms to be able to estimate the geometry of the atom, and from it, the most likely directions for a new bond.

Common geometries found in molecular sketches.

Most atom environments, when unconstrained, are drawn with complete or partial occupancy of one of these geometries. By examining the immediate bonding environment of an atom, it is often possible to make a reasonable estimate as to which of these geometry templates is most appropriate - and more importantly, which would be most appropriate in the context of adding an additional bond to a new atom. The process of assigning probable geometry based on topology and partial geometry is explained in Appendix 3.

New Bond with Order

When creating a new bond with a known bond order, the first step is to consider the subject atom with an additional bond with the requested order, connected to a newly created neutral carbon atom. In its new circumstances, the subject atom may have some number of preferred geometries. Consider the following cases shown in Figure 3: in each of these instances, the likely angles for the new bonds, indicated using dotted lines, are strongly suggested by the atom topology and the preexisting bond geometry.

Reasonable new bond geometries, based on existing layout and new bond order.

In the examples shown in Figure 4, the geometry for the new bond is less clear, either because the incoming geometry is irregular or the valence is full. New bond positions are instead defined by the set of interior angles of adjacent neighbours.

Potential new bond geometries for atom centres which do not match a common template.

Appendix 3 describes in detail the process of determining potential new bond angles. Once the list of angles has been generated, it is necessary to select one. For each of the angles, a point position is calculated by extending to the default bond length. The molecular congestion at each of these points is calculated (see Appendix 4), and the point which has the lowest congestion is used. A new carbon atom is created at this position, and a bond is created between the subject atom and the new atom.

New Bond with Style

The new atom position is determined using the same method as for New Bond with Order, given that the bond order is 1. The newly created bond has the indicated stereochemical style, e.g. inclined, declined or unknown. For wedge bonds, the atom direction emanates from the subject atom.

New Bond with Geometry

This class has one primitive for each of the 7 available geometries, which are shown in Figure 2. An attempt is made to create a new carbon atom and connect it to the subject atom via a single bond, using the indicated geometry.

The implementation is related to that of New Bond with Order, but more specific: if the current geometry about the subject atom does not match the indicated geometry with one angle missing, then the operation will instead be mapped to the corresponding Set Geometry primitive. If it does match, then all of the angles which are implied by matching the partial geometry are scored by calculating the congestion at the point of the implied new atom (see Appendix 4). The angle which corresponds to an atom with the least congestion is used to create the new atom and bond.

CHEMICAL DATA BASE DESIGN

A **chemical database** is a database specifically designed to store chemical information. This information is about chemical and crystal structures, spectra, reactions and syntheses, and thermophysical data.

Types of chemical databases

Chemical structures

Chemical structures are traditionally represented using lines indicating chemical bonds between atoms and drawn on paper (2D structural formulae). While these are ideal visual representations for the chemist, they are unsuitable for computational use and especially for search and storage. Small molecules (also called ligands in drug design applications), are usually represented using lists of atoms and their connections. Large molecules such as proteins are however more compactly represented using the sequences of their amino acid building blocks. Large chemical databases for structures are expected to handle the storage and searching of information on millions of molecules taking terabytes of physical memory...

Literature database

Chemical literature databases correlate structures or other chemical information to relevant references such as academic papers or patents. This type of database includes STN, Scifinder, and Reaxys. Links to literature are also included in many databases that focus on chemical characterization.

Crystallographic database

Crystallographic databases store X-ray crystal structure data. Common examples include Protein Data Bank and Cambridge Structural Database.

NMR spectra database

NMR spectra databases correlate chemical structure with NMR data. These databases often include other characterization data such as FTIR and mass spectrometry.

Reactions database

Most chemical databases store information on stable molecules but in databases for reactions also intermediates and temporarily created unstable molecules are stored. Reaction databases contain information about products, educts, and reaction mechanisms.

Thermophysical database

Thermophysical data are information about

- phase equilibria including vapor–liquid equilibrium, solubility of gases in liquids, liquids in solids (SLE), heats of mixing, vaporization, and fusion.
- caloric data like heat capacity, heat of formation and combustion,
- transport properties like viscosity and thermal conductivity

Chemical structure representation

There are two principal techniques for representing chemical structures in digital databases

- As connection tables / adjacency matrices / lists with additional information on bond (edges) and atom attributes (nodes), such as:

  MDL Molfile, PDB, CML

- As a linear string notation based on depth first or breadth first traversal, such as: SMILES/SMARTS, SLN, WLN, InChI

These approaches have been refined to allow representation of stereochemical differences and charges as well as special kinds of bonding such as those seen in organo-metallic compounds. The principal advantage of a computer representation is the possibility for increased storage and fast, flexible search.

Sixty-Four Free Chemistry Database

The open Web offers a rich collection of diverse chemical data sources - if you know where to look. It's been over four years since I wrote the previous post in this series describing some emerging chemical databases, and a lot has happened in this space. The time seems right for an update.

Although some of the original databases are no longer active, it's encouraging to see that a number of them continue to run and even prosper. It's of course likely that still more services will be created and retired in the coming years. If you know of a free chemistry database that's missing from this list, please leave a comment or contact me directly.

Below I give you, in no particular order, a collection of free chemistry databases.

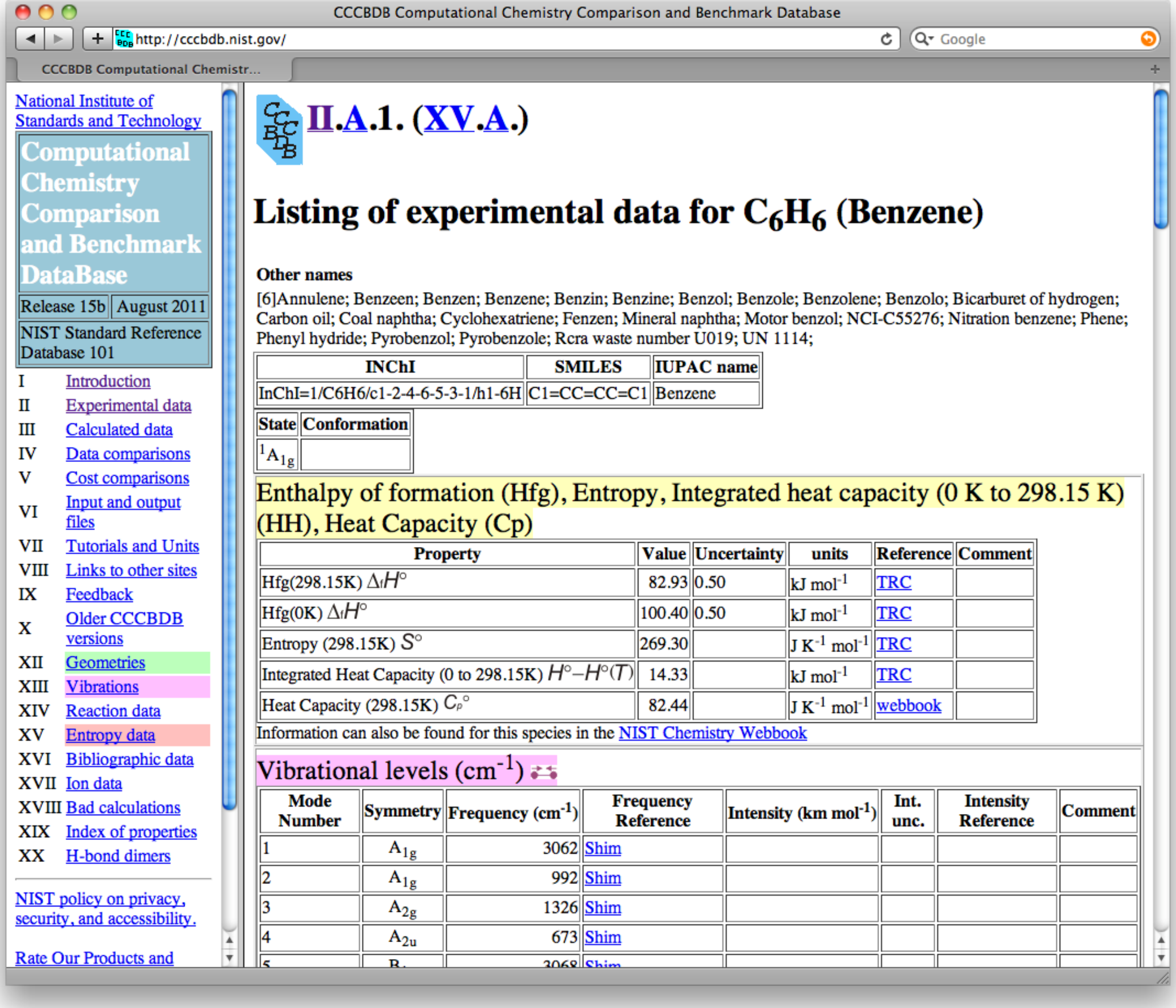
1. PubChem "... organized as three linked databases ... PubChem Substance, PubChem Compound, and PubChem Bio Assay."

- ZINC "... a free database of commercially-available compounds for virtual screening. ZINC contains over 13 million purchasable compounds in ready-to-dock, 3D formats."
- eMolecules "eMolecules discovers sources of chemical data by searching the Internet, and receives submissions from data providers such as chemical suppliers and academic research institutions
- ChEBI "Chemical Entities of Biological Interest (ChEBI) is a freely available dictionary of molecular entities focused on ‘small’ chemical compounds."
- NIST Chemistry WebBook "...provides thermochemical, thermophysical,

and ion energetics data compiled by NIST under the Standard Reference Data Program." VCVV

- ChemExper "This database contains chemicals with their physical characteristics. Everybody can submit chemical information and retrieve information with a Web browser."
- Compendium of Common Pesticide Names "This Compendium is believed to be the only place where all of the ISO-approved standard names of chemical pesticides are listed. It also includes more than 300 approved names from national and international bodies for pesticides that do not have ISO names."
- DrugBank "... a unique bioinformatics and cheminformatics resource that combines detailed drug (i.e. chemical, pharmacological and pharmaceutical) data with comprehensive drug target (i.e. sequence, structure, and pathway) information. The database contains 6707 drug entries including 1436 FDA-approved small molecule drugs, 134 FDA-approved biotech (protein/peptide) drugs, 83 nutraceuticals and 5086 experimental drugs."
- ChemBank "... includes freely available data derived from small molecules and small-molecule screens, and resources for studying the data so that biological and medical insights can be gained. ChemBank is intended to guide chemists synthesizing novel compounds or libraries, to assist biologists searching for small molecules that perturb specific biological pathways, and to catalyze the process by which drug hunters discover new and effective medicines."
- **National Institute of Allergy and Infectious Diseases Database** "There are three main search portals for the database: the chemical portal allows searches by compound structure or chemical characteristics, the biological portal performs searches based on compound activity against a specific pathogen or enzyme, and the literature portal supports searches based on publication information, such as author name or journal."

Computational Chemistry Comparison and Benchmark DataBase
"Experimental and computational thermochemical data for a selected set of 1420 gas-phase atoms and molecules.Tools for comparing experimental and computational ideal-gas thermochemical properties."



II.A.1. (XV.A.)

Listing of experimental data for C_6H_6 (Benzene)

Other names

[6]Annulene; Benzeen; Benzen; Benzene; Benzin; Benzine; Benzol; Benzole; Benzolene; Benzolo; Bicarburet of hydrogen; Carbon oil; Coal naphtha; Cyclohexatriene; Fenzen; Mineral naphtha; Motor benzol; NCI-C55276; Nitration benzene; Phene; Phenyl hydride; Pyrobenzol; Pyrobenzole; Rcra waste number U019; UN 1114;

INChI	SMILES	IUPAC name
InChI=1/C6H6/c1-2-4-6-5-3-1/h1-6H	C1=CC=CC=C1	Benzene

State	Conformation
$^1A_{1g}$	

Enthalpy of formation (Hfg), Entropy, Integrated heat capacity (0 K to 298.15 K) (HH), Heat Capacity (Cp)

Property	Value	Uncertainty	units	Reference	Comment
Hfg(298.15K) $\Delta_f H°$	82.93	0.50	kJ mol^{-1}	TRC	
Hfg(0K) $\Delta_f H°$	100.40	0.50	kJ mol^{-1}	TRC	
Entropy (298.15K) $S°$	269.30		J K^{-1} mol^{-1}	TRC	
Integrated Heat Capacity (0 to 298.15K) $H°-H°(T)$	14.33		kJ mol^{-1}	TRC	
Heat Capacity (298.15K) $C_p°$	82.44		J K^{-1} mol^{-1}	webbook	

Information can also be found for this species in the NIST Chemistry Webbook

Vibrational levels (cm^{-1})

Mode Number	Symmetry	Frequency (cm^{-1})	Frequency Reference	Intensity (km mol^{-1})	Int. unc.	Intensity Reference	Comment
1	A_{1g}	3062	Shim				
2	A_{1g}	992	Shim				
3	A_{2g}	1326	Shim				
4	A_{2u}	673	Shim				

- **Chem Mine** "ChemMine is a compound mining database that facilitates drug and agrochemical discovery and chemical genomics screens."
- **Organic Syntheses** "... Each procedure is written in considerably more detail as compared to typical experimental procedures in other journals, and each reaction and all characterization data has been carefully "checked" for reproducibility in the laboratory of a member of the Board of Editors."

- **Chem Synthesis** "ChemSynthesis is a freely accessible database of chemicals. This website contains substances with their synthesis references and physical properties such as melting point, boiling point and density. There are currently more than 40,000 compounds and more than 45,000 synthesis references in the database."
- **Chem Synthesis** "ChemSynthesis is a freely accessible database of chemicals. This website contains substances with their synthesis references and physical properties such as melting point, boiling point and density. There are currently more than 40,000 compounds and more than 45,000 synthesis references in the database."
- **Crystallography Open Database** "Open-access collection of crystal structures of organic, inorganic, metal-organic compounds and minerals, excluding biopolymers"
- **Crystallography Open Database** "Open-access collection of crystal structures of organic, inorganic, metal-organic compounds and minerals, excluding biopolymers"

Cheminformatics Services

Data Management

Exclusive Chemistry provides a service of creating and updating chemical databases. We can set up databases in Isis Base and SDF format, using any source of information given by the client. For example, you can send us a list with compound names and we will draw up a catalog, which will include the chemical structure, CAS number, MW and MF, order number, the compound name in IUPAC and CAS nomenclature and, wherever applicable, other trivial denominations. If required, we can also add each structure’s SMILES and InChi code.

Our company can convert your catalog from Excel, PDF or Word files into a chemical databank for Isis Base and/or SDF. Moreover, we render a SDF file error analysis service, where we check for possible errors in your SDF files (e.g. illegal valences, coincided coordinates of atoms or multiple fragments).

Structure-Searchable CD Catalogs

Exclusive Chemistry Ltd offers the ideal solution for companies that sell chemicals and send their product catalogs to customers. We can draw up a searchable CDROM catalog with your chemical structures. No matter whether you sell 50 or 50,000 chemicals – all data can easily be entered into one or several databanks. After your customer inserts the searchable CD catalog into his/her computer, the software automatically starts and opens all databases on the CDROM.

- **Features:**
  - The structures can be drawn manually, or imported from SDF files that can be created using a different software
  - A new database can be set up in a matter of minutes
  - There is password protection for the export, import and editing of data
  - No additional software is needed! The only requierement is a PC running Windows 98/2000/NT/XP
  - Your catalog can be searched using the structure. Many other CDROM catalog softwares provide searches by name only

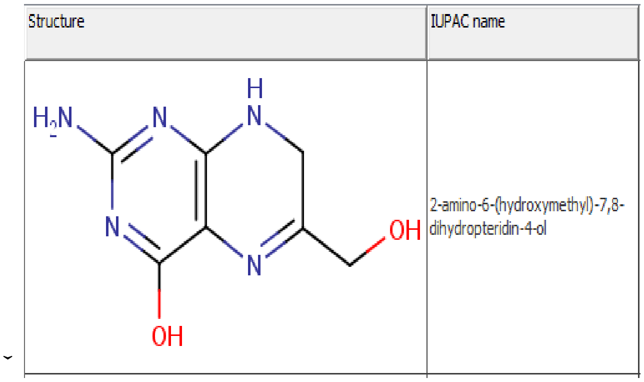
How to get started

Please contact us with your requirements and we will get a quote back to you as soon as possible (usually within the 2 - 24 hours). All enquiries and subsequent projects are of course undertaken in the strictest confidence and will be backed up by secrecy agreements if required.

Visualization of database content

Customised grid view for database content visualisation

The grid view provides a simple means to view tabular data (or spreadsheet like). When you import data, a corresponding grid view is automatically generated for you. The grid view offers a representation of the data in the table, enabling you to both view and edit the data. Because the view is synchronized with the database table, any edits you make will cause the database table to automatically update.



Structure	IUPAC name
	2-amino-6-(hydroxymethyl)-7,8-dihydropteridin-4-ol

Customised form view for database content visualisation

The form view allows the creation of more complex reports from relational data tables. The form builder allows multiple reports to be easily designed and laid out. You can add display widgets to the form, and bind them to particular field(s). Each widget can be re-sized and re-positioned, allowing your fine grain control of the design. Relational data can be displayed, with the contents of the widgets updating reflect the current content and selection. Forms can also be shared and copied. Furthermore, with the help of the Button Widget one can perform custom made actions, defined by the user in a Groovy script.

DATABASE CONCEPTS

A **database** is an organized collection of data.[1] The data is typically organized to model aspects of reality in a way that supports processes requiring information. For example, modelling the availability of rooms in hotels in a way that supports finding a hotel with vacancies.

Database management systems are computer software applications that interact with the user, other applications, and the database itself to capture and analyze data. A general-purpose DBMS is designed to allow the definition, creation, querying, update, and administration of databases. Well-known DBMSs include MySQL, PostgreSQL, Microsoft SQL Server, Oracle, Sybase and IBM DB2. A database is not generally portable across different DBMSs, but different DBMS can interoperate by using standards such as SQL and ODBC or JDBC to allow a single application to work with more than one DBMS. Database management systems are often classified according to the database model that they support; the most popular database systems since the 1980s have all supported the relational model as represented by the SQL language. Sometimes a DBMS is loosely referred to as a 'database'.

- **Data definition** – Creation, modification and removal of definitions that define the organization of the data.
- **Update** – Insertion, modification, and deletion of the actual data.
- **Retrieval** – Providing information in a form directly usable or for further processing by other applications. The retrieved data may be made available in a form basically the same as it is stored in the database or in a new form obtained by altering or combining existing data from the database.[4]
- **Administration** – Registering and monitoring users, enforcing data security, monitoring performance, maintaining data integrity, dealing with concurrency control, and recovering information that has been corrupted by some event such as an unexpected system failure.

Both a database and its DBMS conform to the principles of a particular database model. "Database system" refers collectively to the database model, database management system, and database.

Physically, database servers are dedicated computers that hold the actual databases and run only the DBMS and related software. Database servers are usually multiprocessor computers, with generous memory and RAID disk arrays used for stable storage. RAID is used for recovery of data if any of the disks fail. Hardware database accelerators, connected to one or more servers via a high-speed channel, are also used in large volume transaction processing environments. DBMSs are found at the heart of most database applications. DBMSs may be built around a custom multitasking kernel with built-in networking support, but modern DBMSs typically rely on a standard operating system to provide these functions. Since DBMSs comprise a significant economical market, computer and storage vendors often take into account DBMS requirements in their own development plans.[*citation needed*]

Databases and DBMSs can be categorized according to the database model(s) that they support (such as relational or XML), the type(s) of computer they run on (from a server cluster to a mobile phone), the query language(s) used to access the database (such as SQL or XQuery), and their internal engineering, which affects performance, scalability, resilience, and security.

Application areas of DataBase Manegement System

1. Banking: For customer information, accounts, and loans, and banking transactions.

2. Airlines: For reservations and schedule information. Airlines were among the first to use databases in a geographically distributed manner - terminals situated around the world accessed the central database system through phone lines and other data networks.

3. Universities: For student information, course registrations, and grades.

4. Credit card transactions: For purchases on credit cards and generation of monthly statements.

5. Telecommunication: For keeping records of calls made, generating monthly bills, maintaining balances on prepaid calling cards, and storing information about the communication networks.

6. Finance: For storing information about holdings, sales, and purchases of financial instruments such as stocks and bonds.

7. Sales: For customer, product, and purchase information.

8. Manufacturing: For management of supply chain and for tracking production of items in factories, inventories of items in warehouses / stores, and orders for items.

9. Human resources: For information about employees, salaries, payroll taxes and benefits, and for generation of paychecks.

Basic Concepts

A database is just what the name implies, a base collection of data. The data is organized in some manner so that the information contained within the database can be easily retrieved. Some of the simple databases that you might be familiar with are things like phone books or rolodexes. As data processing has become more sophisticated, so have methods for collecting, storing and retrieving information. Databases have become the cornerstone for an overwhelming amount of the computing environment in existence.

Basic Database concepts for the opening section

Field (Column): a single piece of information. Could be a name, or a number. In some cases, it may even be a null or empty value.

Record (Row): a collection of related fields. A number of pieces of information that relate to the same object. For example: If you keep records on an employee, you might have their name, address, social security number, phone number, etc…Each piece of the information relates back to one employee. This would be the employee's record.

Table (File): a collection of related records. If you put all the employee records together, you have a table of employees.

Database: a collection of tables. If you were keeping the company records, you might have a table for employees, a table for customers, and another for sales records. All these tables would be combined as a database.

Relational Database: a collection of related tables. The difference between a database and a relational database is in the way the tables are constructed. If you were keeping the company records on a series of Excel spreadsheets, you would have just a database. You could pull information from each table, but you wouldn't have the ability to use information from one spreadsheet as a basis for asking questions about the information contained on another sheet. In a relational database, the tables are constructed so that there is a logical link between them. Based on the information that's found in one table, you can follow this link and get relevant information from another table.

Structural languages

SQL - **Structured Query Language** is a special-purpose programming language designed for managing data held in a relational database management system

(RDBMS), or for stream processing in a relational data stream management system (RDSMS).

Originally based upon relational algebra and tuple relational calculus, SQL consists of a data definition language and a data manipulation language. The scope of SQL includes data insert, query, update and delete, schema creation and modification, and data access control. Although SQL is often described as, and to a great extent is, a declarative language (4GL), it also includes procedural elements.

SQL was one of the first commercial languages for Edgar F. Codd's relational model, as described in his influential 1970 paper, "A Relational Model of Data for Large Shared Data Banks."[10] Despite not entirely adhering to the relational model as described by Codd, it became the most widely used database language.[11][12]

SQL became a standard of the American National Standards Institute (ANSI) in 1986, and of the International Organization for Standardization (ISO) in 1987.[13] Since then, the standard has been revised to include a larger set of features. Despite the existence of such standards, though, most SQL code is not completely portable among different database systems without adjustments

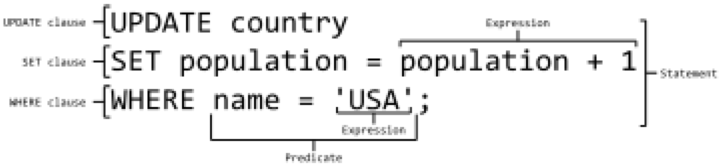
History

SQL was initially developed at IBM by Donald D. Chamberlin and Raymond F. Boyce in the early 1970s. This version, initially called *SEQUEL* (*Structured English QUEry Language*), was designed to manipulate and retrieve data stored in IBM's original quasi-relational database management system, System R, which a group at IBM San Jose Research Laboratory had developed during the 1970s. The acronym SEQUEL was later changed to SQL because "SEQUEL" was a trademark of the UK-based Hawker Siddeley aircraft company.

In the late 1970s, Relational Software, Inc. (now Oracle Corporation) saw the potential of the concepts described by Codd, Chamberlin, and Boyce, and developed their own SQL-based RDBMS with aspirations of selling it to the U.S. Navy, Central Intelligence Agency, and other U.S. government agencies. In June 1979, Relational Software, Inc. introduced the first commercially available implementation of SQL, Oracle V2 (Version2) for VAX computers.

After testing SQL at customer test sites to determine the usefulness and practicality of the system, IBM began developing commercial products based on their System R prototype including System/38, SQL/DS, and DB2, which were commercially available in 1979, 1981, and 1983, respectively.[16]

Language elements



```
UPDATE country
SET population = population + 1
WHERE name = 'USA';
```

A chart showing several of the SQL language elements that compose a single statement

The SQL language is subdivided into several language elements, including:

- *Clauses, which are constituent components of statements and queries. (In some cases, these are optional.*
- *Expressions, which can produce either scalar values, or tables consisting of columns and rows of data*
- *Predicates, which specify conditions that can be evaluated to SQL three-valued logic (3VL) (true/false/unknown) or Boolean truth values and are used to limit the effects of statements and queries, or to change program flow.*

- *Queries, which retrieve the data based on specific criteria. This is an important element of SQL.*
- *Statements, which may have a persistent effect on schemata and data, or may control transactions, program flow, connections, sessions, or diagnostics.*
    - *SQL statements also include the semicolon (";") statement terminator. Though not required on every platform, it is defined as a standard part of the SQL grammar.*
- *Insignificant whitespace is generally ignored in SQL statements and queries, making it easier to format SQL code for readability.*

Operators

Operator	***Description***	***Example***
=	*Equal to*	*Author = 'Alcott'*
<>	*Not equal to (many DBMSs accept != in addition to <>)*	*Dept <> 'Sales'*
>	*Greater than*	*Hire_Date > '2012-01-31'*
<	*Less than*	*Bonus < 50000.00*
>=	*Greater than or equal*	*Dependents >= 2*
<=	*Less than or equal*	*Rate <= 0.05*
BETWEEN	*Between an inclusive range*	*Cost BETWEEN 100.00 AND 500.00*
LIKE	*Match a character pattern*	*First_Name LIKE 'Will%'*

IN	*Equal to one of multiple possible values*	*DeptCode IN (101, 103, 209)*
IS or IS NOT	*Compare to null (missing data)*	*Address IS NOT NULL*
IS NOT DISTINCT FROM	*Is equal to value or both are nulls (missing data)*	*Debt IS NOT DISTINCT FROM - Receivables*
AS	*Used to change a field name when viewing results*	*SELECT employee AS 'department1'*

Conditional (CASE) expressions

SQL has the case/when/then/else/end expression, which was introduced in SQL-92. In its most general form, which is called a "searched case" in the SQL standard, it works like else if in other programming languages:

```
CASE WHEN n > 0
        THEN 'positive'
    WHEN n < 0
        THEN 'negative'
    ELSE 'zero'
END
```

SQL tests WHEN conditions in the order they appear in the source. If the source does not specify an ELSE expression, SQL defaults to ELSE NULL. An abbreviated syntax—called "simple case" in the SQL standard—mirrors switch statements:

```
CASE n WHEN 1
          THEN 'one'
      WHEN 2
          THEN 'two'
```

```
    ELSE 'I cannot count that high'
END
```

This syntax uses implicit equality comparisons, with the usual caveats for comparing with NULL.

Chemical database

A chemical database **is a database specifically designed to store chemical information. This information is about chemical and crystal structures, spectra, reactions and syntheses, and Chemical Information Sources/SIRCh/Chemistry Databases on the Web**

American Mineralogist Crystal Structure Database

Includes every structure published in the American Mineralogist, The Canadian Mineralogist, European Journal of Mineralogy and Physics and Chemistry of Minerals, as well as selected datasests from other journals. The database is maintained under the care of the Mineralogical Society of America and the Mineralogical Association of Canada, and financed by the National Science Foundation.

Atomic Reference Data for Electronic Structure Calculations

Contains total energies and orbital eigenvalues for the atoms hydrogen through uranium, as computed in several standard variants of density-functional theory.

Aureus Sciences Databases (Aureus Sciences)

Aureus Sciences helps researchers transform data into knowledge to accelerate the drug discovery process. AurSTORE is a comprehensive data structuring system particularly suited for the integration of proprietary biological and chemical information generated through the client's own research program. Databases cover ADME, Kinases, Nuclear Receptors, Proteases, Ion Channels and GPCR.

BIGG (University of California at San Diego)

The BiGG database allows the exploration of hundreds of human disorders involving metabolism. It includes more than 3,300 known human biochemical reactions and allows scientists to create any cell in silico.

Binding MOAD (University of Michigan)

Binding MOAD's goal is to be the largest collection of well resolved protein crystal structures with clearly identified biologically relevant ligands annotated with experimentally determined binding data (Kd, Ka, Ki, IC50) extracted from the literature. Currently has 9836 entries, with 2950 entries with binding data.

BindingDB (University of Maryland Biotechnology Institute)

The Binding Database aims to make experimental data on the noncovalent association of molecules in solution searchable via the WWW. The initial focus is on biomolecular systems, but data on host-guest and supramolecular systems are also important and will be included in time. The database currently contains data generated by isothermal titration calorimetry (ITC) and enzyme inhibition (Enz. Inhib.) methods. BindingDB contains 15,000 small molecule ligands with 30,000 measured affinities to proteins represented in the PDB.

Biochemical Pathways Database under C@ROL (BioPath) (University of Erlangen)

BioPath is designed to support scientists to understand the impact of gene regulations on biological systems for drug target identification and provides the following features:

- *1,175 molecules with connection tables including stereochemical information*
- *1,545 biochemical reactions stoichiometrically balanced, with marked reaction centers and atom-atom mapping numbers between educts an*

Types of chemical databases

Chemical structures

Chemical structures are traditionally represented using lines indicating chemical bonds between atoms and drawn on paper (2D structural formulae). While these are ideal visual representations for the chemist, they are unsuitable for computational use and especially for search and storage. Small molecules (also called ligands in drug design applications), are usually represented using lists of atoms and their connections. Large molecules such as proteins are however more compactly represented using the sequences of their amino acid building blocks. Large chemical databases for structures are expected to handle the storage and searching of information on millions of molecules taking terabytes of physical memory.

Literature database

Chemical literature databases correlate structures or other chemical information to relevant references such as academic papers or patents. This type of database includes STN, Scifinder, and Reaxys. Links to literature are also included in many databases that focus on chemical characterization.

Crystallographic database

Crystallographic databases store X-ray crystal structure data. Common examples include Protein Data Bank and Cambridge Structural Database.

NMR spectra database

NMR spectra databases correlate chemical structure with NMR data. These databases often include other characterization data such as FTIR and mass spectrometry.

Reactions database

Most chemical databases store information on stable molecules but in databases for reactions also intermediates and temporarily created unstable molecules are stored. Reaction databases contain information about products, educts, and reaction mechanisms.

Thermophysical database

Thermophysical data are information about

- phase equilibria including vapor–liquid equilibrium, solubility of gases in liquids, liquids in solids (SLE), heats of mixing, vaporization, and fusion.
- caloric data like heat capacity, heat of formation and combustion,
- transport properties like viscosity and thermal conductivity

Chemical structure representation

There are two principal techniques for representing chemical structures in digital databases, As connection tables / adjacency matrices / lists with additional information on bond (edges) and atom attributes (nodes), such as:

MDL Molfile, PDB, CML

- As a linear string notation based on depth first or breadth first traversal, such as:

  SMILES/SMARTS, SLN, WLN, InChI

These approaches have been refined to allow representation of stereochemical differences and charges as well as special kinds of bonding such as those seen in organo-metallic compounds. The principal advantage of a computer representation is the possibility for increased storage and fast, flexible search.

Chemical Information Sources

Main Topic	Includes
How and Where to Start	Publications, Guides, Computer Searching, Current Awareness, Reviews, Document Delivery, Background Reading
How and Where to Search: General	Authors, Citations, Subjects, Chemical Name, Formula, Structure Searching
How and Where to Search: Specialized	Synthesis, Reactions, Safety, Analytical, Physical, Patents
Communicating in Chemistry	Newsgroups, Listserves, Blogs, Visualization, Writing
Miscellaneous	History, Directories, Study, Teaching, Careers, Cheminformatics
Supplemental Resources	SIRCh, CIIM, Problem Sets, CRSD, CHMINF-L

CHEMICAL INFORMATION RESEARCHES FORMULA SEARCHING

Chemistry - How to Search Molecular Formulas

There are many ways of representing molecular formulas. One common format is the linear structure formula which shows how the atoms of a molecule are connected. For example, the acetic acid molecule can be written as either CH_3COOH or CH_3CO_2H. Linear formulas can also show how one group of atoms is attached to another. The linear formula for methylpropane (isobutane) is $CH(CH_3)_3$, indicating that there are three methyl groups attached to the central carbon atom.

Many chemical information search engines, such as Scifinder and Reaxys, prefer the molecular formula format, which is sometimes referred to as the Hill Order. This format is based on the actual number of atoms in a molecule, with carbon first, followed by hydrogen and then any other atoms in alphabetical order. For example, the molecular formula for methylpropane is C_4H_{10}, indicating that it has four carbon atoms and 10 hydrogen atoms. When you search a formula in Scifinder or Beilstein you should first convert it into the molecular formula format.

Scifinder

Although SciFinder prefers the Hill Order, it automatically arranges the atoms in the required order. So it doesn't matter what order you type them in as long as the count for each atom is correct. Spaces between each atom are optional.

Substance Type	Molecular Formula	Examples
Single component molecules not containing carbon	Atoms in alphabetical order	H_2O_4S H_2O_4S
Single component molecules containing carbon	Carbon first, then hydrogen, followed by atoms in alphabetical order	C4H12Si C4 H12 Si
Polymers	Component formulas enclosed in parantheses followed by 'x'	(C8H8)x (C6 H13 N O2)x
Coordination compounds	Individual compounds or ions follow rules for single-component substances	C14H10Fe2O4
Alloys	Atoms in alphabetical order separated by a period	Al.Cu.N

Mixtures	Components in alphabetical order separated by a period	C3H6N6O6.Al C9H8O3.C8H11N
Isotopic substances	Only isotopes of hydrogen (D, T) have special listing in the formula index. Isotopes of other atoms list symbol for atom only. Use "Refine" search option to limit by isotope-containing substances	C4H10SiT2 C4D10

Reaxys

Reaxys has two formula search fields, the Molecular Formula (MF) field and the Linear Structure Formula (LSF) field. As their names suggest, the MF field uses the molecular formula format (Hill Order) and the LSF takes the linear structure formula format.

Molecular Formula Field

Substance Type	Molecular Formula	Examples
Single component molecules not containing carbon (G)	Atoms in alphabetical order	H2O4S

Single component molecules containing carbon (B/G)	Carbon first, then hydrogen, followed by atoms in alphabetical order	C4H12Si
Polymers (B)	Not searchable. Search by Chemical Name, e.g. polyvinyl chloride	-
Coordination compounds (G)	Individual compounds or ions follow rules for single-component substances	C9H14Sn
Alloys (G)	Atoms in alphabetical order	Ni3Zr
Mixtures (B/G)	Components in alphabetical order separated by an asterisk	C8H11N*C9H8O3
Isotopic substances (B/G)	Not searchable. Use the Linear Structure Formula field instead	-

Linear Structure Formula Field

Substance Type	Linear Formula	Examples
Single component molecules (carbon or no carbon) (B/G)	Atoms in linear structure order	H2O4S Si(NH)2 C(N3)3H Si(CH3)2C2H5
Polymers (B)	Not searchable. Search by Chemical Name, e.g. polyvinyl chloride	-
Coordination compounds (G)	Individual compounds or ions follow rules for single-component substances	C6H5Sn(CH3)3
Alloys (G)	Atoms in linear structure order	ZrNi3
Mixtures (B/G)	Atoms in linear structure order with components separated by an asterisk	C9H8O3*C8H11N

Isotopic substances (B/G)	Atoms in linear structure order. Isotopes and charges must be enclosed in parantheses, e.g. (14)C, Al(2-), Si(2+)	C4D10 C6H11T C3(14)CH12N2 CO3(2-)

****