

Module-5

Instrumental Methods of Analysis and Nanomaterials



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Introduction

- Analytical chemistry is a branch of chemistry that deals with chemical analysis involves identifying and determining the percentage composition in a sample of a substance.
- The identification is carried out by qualitative analysis. Quantitative analysis gives the percentage composition of the constituents.
- The sample under analysis is an analyte. Some important techniques of quantitative analysis are titrimetry or volumetry, gravimetry and instrumental methods.

Colorimetry:

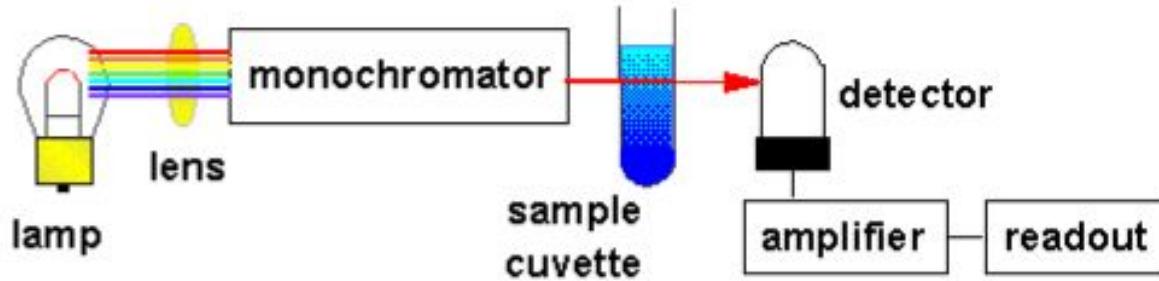
- Colorimetry is an analytical technique used for determination of concentration of compounds in a solution.
- It is used for solutions which are themselves coloured or which gives a colour when mixed with a suitable reagent.
- The intensity of the colour of the solution is a measure of the concentration of the substance. The intensities are determined visually or with the help of a colour.

Theory:

- When monochromatic light is passed through the solution to be analyzed when part of the light is absorbed by the solution. The extent of absorption depends on the concentration of the solution and on the path of the light through the solution.
- These generalizations are stated in the form of Beer-Lambert's law. $A = \epsilon ct$
Where A is the absorbance, c is the concentration of the solution, T is the path length and ϵ is the molar absorptivity which is a constant at a given wavelength.
- If the path length is kept constant, then A is proportional to c . i.e. $A \propto c$.

Instrumentation of Colorimetry:

The essential components of spectrophotometer instrumentation include:



Stable and cheap radiant energy source

- A monochromator, to break the polychromatic radiation into component wavelength (or) bands of wavelengths.
- Transport vessels (cuvettes), to hold the sample
- A Photosensitive detector and an associated readout system

Radiant Energy Sources:

- Materials which can be excited to high energy states by a high voltage electric discharge (or) by electrical heating serve as excellent radiant energy sources.

Sources of Ultraviolet radiation:

- Most commonly used sources of UV radiation are the hydrogen lamp and the deuterium lamp.
- Sources of Visible radiation: “Tungsten filament” lamp is the most commonly used source for visible radiation.

Wavelength selectors:

- Wavelength selectors are of two types, Filters, Monochromators

Filters:

- “Gelatin” filters are made of a layer of gelatin, colored with organic dyes and sealed between glass plates.

Monochromators :

- A monochromator resolves polychromatic radiation into its individual wavelengths and isolates these wavelengths into very narrow bands.

Grating:

- Gratings are often used in the monochromators of spectrophotometers operating ultraviolet, visible and infrared regions.

Sample Holder:

- Sample holder to carry sample known as Cuvette. They are made from quartz. Most of the spectrophotometric studies are made in solutions, the solvents assume prime importance.

Detection Devices:

- Most detectors depend on the photoelectric effect. The current is then proportional to the light intensity and therefore a measure of it. Important requirements for a detector include

Applications of Colorimetry

Qualitative Analysis:

- The visible and UV spectrophotometer may be used to identify classes of compounds in both the pure state and in biological preparations.

Quantitative Analysis:

- Spectrophotometer uses in the Quantitative analysis of Biochemistry practicals.
- Estimation of Proteins, tyrosine and Blood glucose levels.

Enzyme Assay:

- This is the basic application of spectrophotometry. This assay is carried out most quickly and conveniently when the substrate absorbs light in the UV range. Assay of Urease Enzyme Activity, Salivary Amylase enzyme activity, Effect of Temperature on Amylase activity

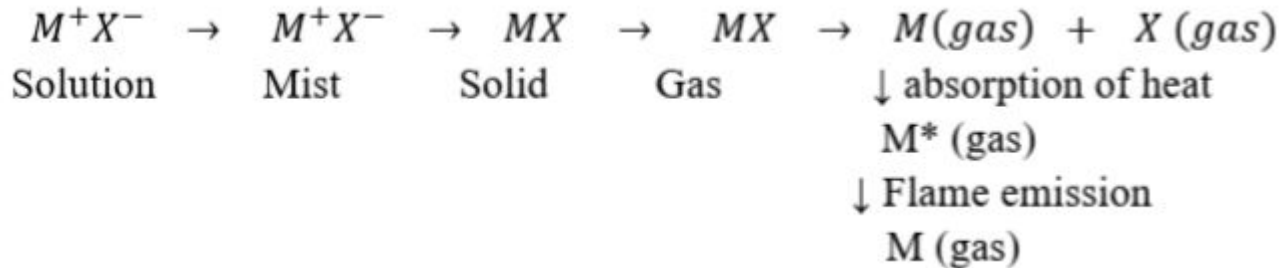
Molecular Weight determination:

- Molecular weights of amine, picrates, sugars and many aldehyde and ketone compounds have been determined by this method. Molecular weights of only small molecules may be determined by this method.

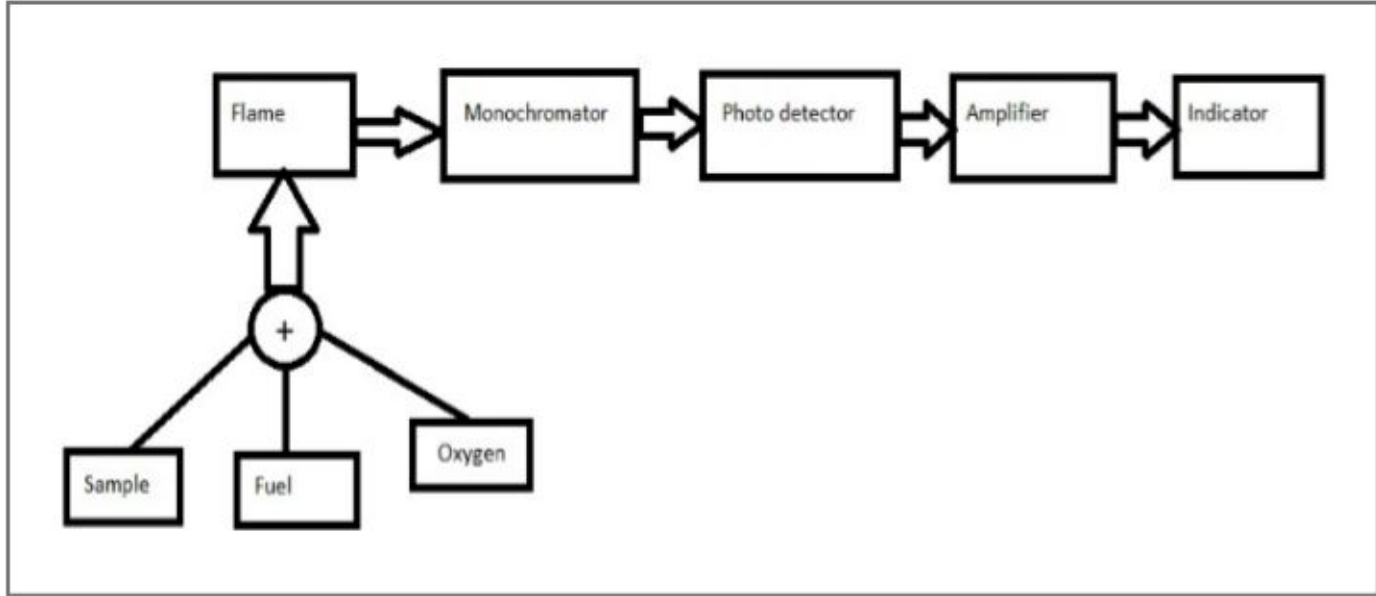
Flame Photometry

Principle:

- This relies on the principle that an alkali metal salt drawn into a non-luminous flame will ionise, absorb energy from the flame and then emit light of a characteristic wavelength as the excited atoms decay to the unexcited ground state.
- The sequence of changes taking place at the flame, when metal salt solution is aspirated may be summarized as follows:



Instrumentation:



A simple flame photometer consists of the following basic components:

Source of flame:

- A Burner in the flame photometer is the source of flame. It can be maintained in at a constant temperature. The temperature of the flame is one of the critical factors in flame photometry.

Nebuliser:

- Nebuliser is used to send homogeneous solution into the flame at a balanced rate.

Optical system:

- The optical system consists of convex mirror and convex lens. The convex mirror transmits the light emitted from the atoms. Convex mirror also helps to focus the emissions to the lens. The lens helps to focus the light on a point or slit.

Photo-detector:

- The intensity of radiation emitted by the flame is measured by photo detector. Here the emitted radiation is converted to an electrical signal with the help of photo detector. These electrical signals are directly proportional to the intensity of light.

Recorders and display:

- These are the devices to read out the recording from detectors.

Applications:

- Flame photometer can be applied both for quantitative and qualitative analysis of elements.
- For quantitative analysis to determine the concentration of group IA and IIA elements. For example, Concentration of Sodium, potassium in Urine
- Concentration of calcium and other elements in bio-glass and ceramic materials.
- Concentration of calcium in hard water.
- The concentrations of Na^+ and K^+ ions are very important in the human body for conducting various metabolic functions.
- Soft drinks, fruit juices and alcoholic beverages can also be analyzed by using flame photometry to determine the concentrations of various metals and elements.

Atomic absorption spectroscopy

- Is it the technique to study the absorption of electromagnetic radiations in relationship to molecular structure. It is a technique for measuring the concentration of various elements in the sample through their absorption of light.
- It is a relatively simple and reliable technique which uses absorption of optical radiation by free atoms for determining the contents of different elements.

Theory

- When a monochromatic radiation of frequency ν is incident on a molecule, the molecule in the gaseous state E_1 absorbs a photon of energy $h\nu$, it undergoes a transition from lower energy level to higher energy level.
- A detector is placed to collect the radiation after interaction with the molecule which shows that intensity has reduced. With wide range of frequencies, the detector shows the energy has been absorbed only from the frequency.

$$\nu = \Delta E/h$$

- Therefore we obtain an absorption spectrum which is defined as a record of the radiation absorbed by the given sample as a function of wavelength of radiation.
- The energy difference between the levels is given as

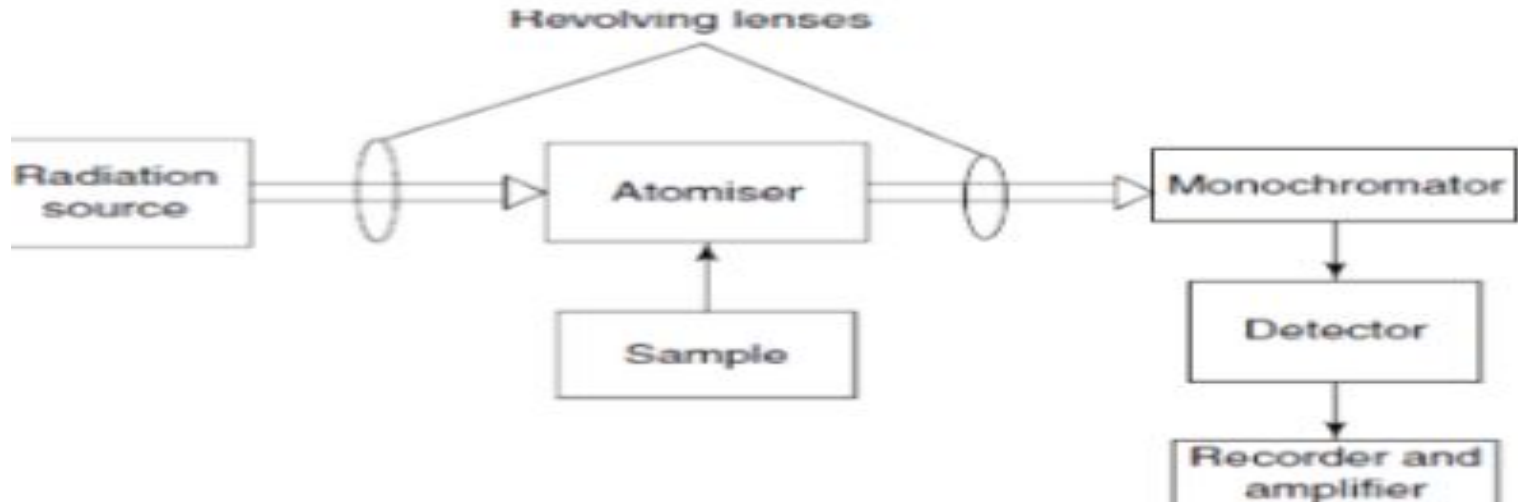
$$\Delta E = E_2 - E_1 = h\nu = hc/\lambda$$

Atomic absorption Spectroscopy Instrumentation:

The instrument is available as single and double beam instruments.

The Instrumentation includes:

- The atomizer (burner) to dry the sample and produce atoms.
- Sample container.
- Fuel and oxidant to burn the sample by heat.
- Hollow cathode lamp to produce light of the desired wavelength.
- Detector to detect the absorption intensity.
- Amplifier and data recorder.



- The sample from the capillary rises to the tip of burner where it is burned with the flame produced by the fuel and oxidant combination. The sample after evaporation leaves a fine residue of neutral atoms.

Sample container:

- This is a beaker-like a container of the sample which is placed below the burner preferably. A capillary tube drains the sample to the tip of the burner.

Fuel and oxidant:

- This is a very important part of the entire process to be remembered. If the heat produced is not sufficient then the sample doesn't form neutral atoms. If the heat of burner is more, the sample molecules may ionize instead of forming atoms. So both are undesirable for experimentation. Hence a proper combination of fuels and oxidant are to be used to produce recommended temperatures. Commonly used fuels include propane, Hydrogen, and acetylene and oxidants are mostly air or oxygen.

Light source:

- The light source should produce a narrow spectrum with little background noise. Besides the light should be stable and have sufficient intensity.
- Two types of light sources can be used based on the requirement.
Hollow cathode lamp and Electrode-less discharge lamps.

Detector:

- The detector consists of a photomultiplier tube or simple photocell.
- The current or potential recorded for the sample absorption is recorded in computer software and then analyzed.

Applications:

- Atomic spectroscopy is used for quantitative analysis of metal elements in samples like soil, plant material.
- It is especially useful to analyze ionic metal elements in blood, saliva, urine samples like sodium, potassium, magnesium, calcium and other body fluids.
- To determine heavy metals like iron, manganese, copper, zinc, mercury, lead, nickel, tin, etc. in urine, blood, etc.
- To determine metal elements in the food industry.
- To estimate Lead in petroleum products.
- To determine metal concentrations in groundwater and bore well samplings before using for drinking and irrigation.

Potentiometry:

- Potentiometry is one of the methods of electroanalytical chemistry. It is usually employed to find the concentration of a solute in solution.

Theory:

- It is based on the principle of Nernst equation
For a reaction $M^+ + ne \rightleftharpoons M$ is given by the expression.

$$E = E^\circ + \frac{RT}{nF} \log[Mn^+] \dots\dots\dots (1)$$

Where E is the electrode potential

E° is the standard electrode potential. n is the valency of the ions.

Mn^+ is the concentration of the metal ions surrounding the electrode surface.

Equation (1) can be written as $E = E^\circ + 0.0591/nF [\log Mn^+]$ at 25°C

- During titration concentration of ions changes, hence potential of the electrode changes. Change in the potential can be used to detect end point.
- An inert electrode such as platinum is used in the redox system where potential depends upon the concentration of the ions to be determined and is combined with a standard reference electrode such as calomel electrode.
- This involves the measurements of the emf between two electrodes and its changes during titration. The emf of the cell changes with titrant is gradual in the beginning and reaches maximum at the equivalence point and again becomes slow.

Instrumentation of Potentiometry:

Reference electrode:

- A half cell with an accurately known electrode potential E_{ref} , i.e., independent of the concentration of the analyte or any other ions in the solution.

Indicator electrode:

- which is immersed in a solution of the analyte, develops a potential E_{ind} , which depends on the activity of the analyte.

Salt bridge :

- Prevents the components of the analyte solution from mixing with those of reference electrode.
- Potassium chloride is an ideal electrolyte for the salt bridge because of the mobilities of K^+ and Cl^- ions are nearly equal.

Application:

- Clinical Chemistry: Ion-selective electrodes are important sensors for clinical samples because of their selectivity for analytes in complex matrices.
- The most common analytes are electrolytes, such as Na^+ , K^+ , Ca^{2+} , H^+ , and Cl^- , and dissolved gases such as CO_2 .
- Environmental Chemistry: For the analysis of CN^- , F^- , NH_3 , and NO_3^- in water and wastewater.

Potentiometric Titrations:

- For determining the equivalence point of an acid–base titration. Possible for acid–base, complexation, redox, and precipitation titrations, as well as for titrations in aqueous and non aqueous solvents.
- Agriculture: NO_3 , NH_4 , Cl , K , Ca , I , CN in soils, plant material, fertilizers and feed stuffs.
- Detergent Manufacture: Ca , Ba , F for studying effects on water quality.
- Food Processing: NO_3 , NO_2 in meat preservatives, Salt content of meat, fish, dairy products, fruit juices, brewing solutions. F in drinking water and other drinks.
- Ca in dairy products and beer. K in fruit juices and wine making. Corrosive effect of NO_3 in canned food

Conductometry:

- Conductometry is the measurement of the electrical conductivity of a solution. The conductance is defined as the current flow through the conductor. In other words, it is defined as the reciprocal of the resistance. The unit for the conductance is Siemens (S) which is the reciprocal of Ohm's (Ω^{-1}). This method is mainly used for the determination of the physico-chemical properties of the compounds.

Theory:

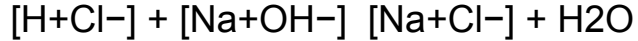
- Ohm's law states that the current I flowing through a conductor is directly proportional to the applied potential E and inversely proportional to the resistance R of the conductor. $I = E/R$
- Conductance measurements are used to determine the equivalence point in acid-base titration. There is a sudden change in conductance of the solution after the equivalence point. The equivalence point is determined graphically by plotting conductance against the titre values.
- In Conductometric titration, ions of a particular conductance are replaced by ions of different conductance.
- Consider the titration of hydrochloric acid with sodium hydroxide, a base. The conductance of the acid is due to the H^+ ions and Cl^- ions. When $NaOH$ is added, the H^+ are gradually replaced by Na^+ . The Na^+ ions have lower mobility than H^+ ions.
- Hence on addition of $NaOH$, the conductance gradually decreases until the acid is completely neutralized. Addition of base beyond the neutralization point leads to an increase in number of more mobile OH^- ions and conductance increases.
- Therefore during the titration the conductance initially decreases, reaches minimum value and again increases. A plot of conductance against volume of base gives two straight lines. The point of intersection of the two lines gives the neutralization point.

Types of the Conductometric Titrations

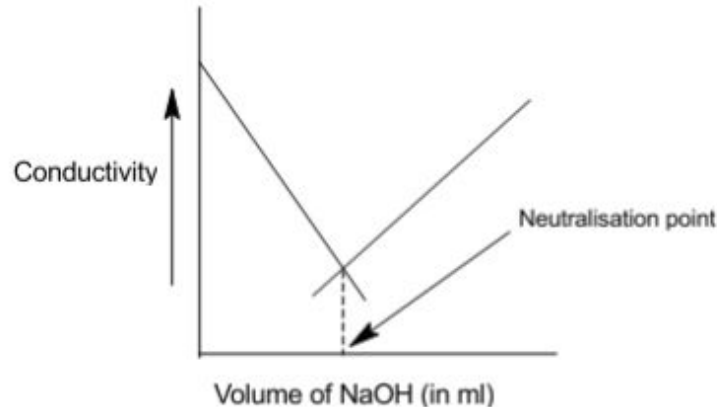
Acid–base titrations:

In this method, the conductance of the hydrogen ions and hydroxyl ions are compared with the conductivity of the sample solution.

Strong acid with a strong base

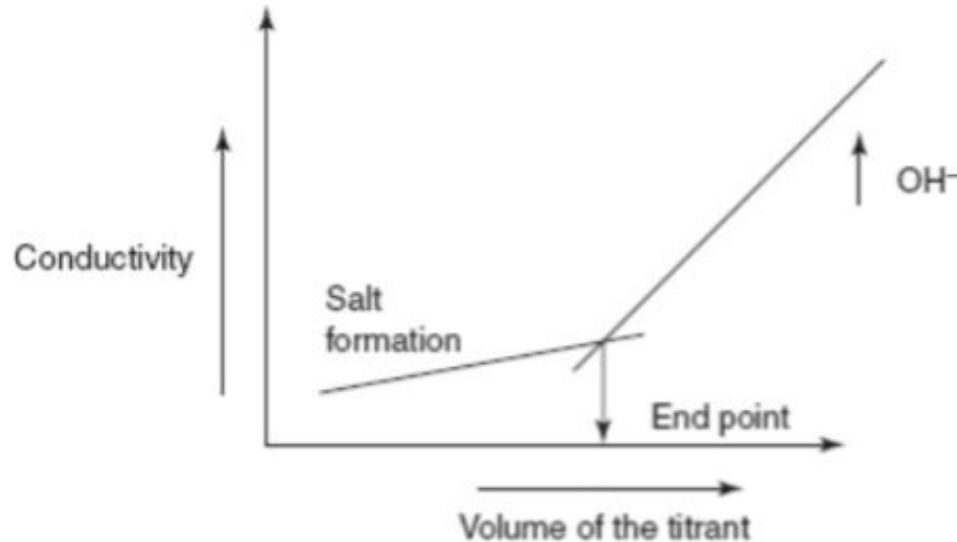


- Consider the titration of HCl against NaOH. The conductance initially falls till the equivalence point. This is due to the replacement of highly mobile H^+ ions by the less mobile Na^+ .
- After the equivalence point the conductance rapidly rises with further additions of strong base. This is due to increase in the concentration of the OH^- ions.
- A plot of conductance against volume of NaOH gives a graph as shown in fig. The point of intersection of the curves gives the end point.



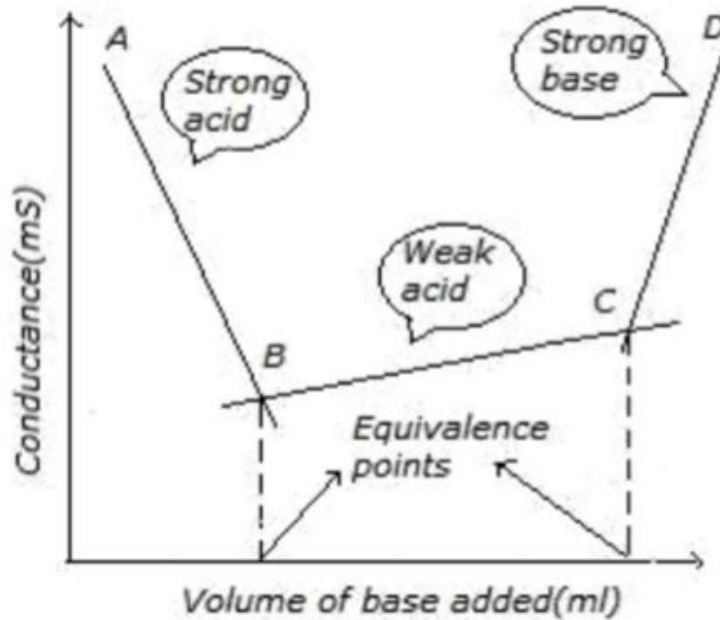
Weak acid with a strong base:

- The weak acid such as acetic acid is titrated with the strong base such as sodium hydroxide.
$$\text{CH}_3\text{COOH} + \text{NaOH} \longrightarrow \text{CH}_3\text{COONa} + \text{H}_2\text{O}$$
- The acetic acid dissociates to produce the H^+ ions which shows the high conductivity and is titrated with the sodium hydroxide which is dissociated to produce the OH^- ions which shows slight increase in the conductivity by the formation of the CH_3COONa at the equivalence point.
- Then it shows the gradual increase in the conductivity by the addition of excess titrant.
- Then plot the graph between the conductivity and the volume of the titrant which shows the plateau.



Mixture of a Strong Acid and a Weak Acid vs. a Strong Base:

- In this curve there are two break points. The first break point corresponds to the neutralization of strong acid. When the strong acid has been completely neutralized only then the weak acid starts neutralizing.
- The second break point corresponds to the neutralization of weak acid and after that the conductance increases due to the excess of OH⁻ ions in case of a strong base as the titrant.



Applications:

- Used in the determination of the basicity of the acids.
- The basicity is defined as the number of carboxylic acid groups attached to the molecules.
- Used in the determination of the sparingly soluble salts such as barium sulphate and lead sulphate.
- Used in the determination of the purity of the water.
- Used in the determination of the salinity of the sea water.
- Used in the determination of the ionic product of the water.
- Used in the quantitative analysis of the compounds.

Nanomaterials

Introduction:

- Nanomaterials are corner stones of nanoscience and nanotechnology.
- Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years.
- It has the potential for revolutionizing the ways in which materials and products are created and the range and nature of functionalities that can be accessed. It is already having a significant commercial impact, which will assuredly increase in the future.

What are nanomaterials?

- Nanoscale materials are defined as a set of substances where at least one dimension is less than approximately 100 nanometers.
- A nanometer is one millionth of a millimeter - approximately 100,000 times smaller than the diameter of a human hair.
- Nanomaterials are of interest because at this scale unique optical, magnetic, electrical, and other properties emerge. These emergent properties have the potential for great impacts in electronics, medicine, and other fields.

Size dependent properties:

Surface area:

- Nanomaterials have a significant proportion of atoms existing at the surface. Properties like catalytic activity, gas adsorption and chemical reactivity depend on the surface area. Therefore nanomaterials can show specific related properties that are not observed in bulk materials.

Electrical properties:

- The electronic bands in bulk materials are continuous due to overlapping of orbits of billions of atoms. But in the nanomaterials, very few atoms or molecules are present so the electric band becomes separate and the separation between different electric states varies with the size of the nanomaterials. Hence, some metals which are good conductors in bulk become semiconductors and insulator as their size is decreased to nanolevel.

•Optical properties:

- Nanomaterials in general can have particular optical properties as a result of the way light intersects with their fine nanostructures. The discrete electronic states of nanomaterials allow absorption and emission of light at specific wavelength. Hence, differing magnetic properties. Bulk gold and platinum are non magnetic but at the nano size they act as magnetic particles. Gold nanoparticles become ferromagnetic when they are capped with nanomaterials exhibit unique colours different from bulk materials.

Catalytic properties:

- Nanomaterial-based catalysts are usually heterogeneous catalysts broken up into metal nanoparticles in order to speed up the catalytic process. Metal nanoparticles have a higher surface area so there is increased catalytic activity because more catalytic reactions can occur at the same time

Thermal properties:

- Thermo physical properties such as thermal conductivity, latent heat, viscosity and super cooling of phase change materials (PCM) could be changed for different physical properties of dispersed nanoparticles.

Synthesis of nanomaterials:

- The topdown process: Where the material is prepared by the structural decomposition of coarser-grained structures as the result of severe plastic deformation.
Ex: Milling and mechanical grinding
- The bottom up process: where materials containing the desired precursors are mixed in a controlled fashion to form a colloidal.
Ex: Sol-gel, Precipitation, Gas condensation, Chemical vapour condensation, Hydro thermal & Thermolysis

Sol-Gel-Method.

- The -gel process has been mainly used in the synthesis of mono dispersed nanoparticles of metal oxide and temp sensitive organic- inorganic hybrid material. The following steps are involved in the synthesis of nanomaterials by -gel process.

Sol-Gel processing:

- It is one of the methods used to produce nanomaterials with novel, predefined properties in a simple process & relatively low process cost.
- The sol-gel process consists of the following steps.

Preparation of precursor solution:

- Common metal organic precursors for the sol-gel process are metal alkoxides. In a typical sol-gel process, the precursor is subjected to a series of hydrolysis & polymerization reactions to form a colloidal suspension (the sol).
- Metal alkoxides is dissolved in alcohol & then water is added under acidic, neutral or basic conditions. Addition of water leads to hydrolysis in which alkoxides ligand is replaced with a hydroxyl group.



Formation of gel phase:

- The polymerization reaction between MOH & MOR results in the formation of an oxide or alcohol-bridged network (the gel). Gel formation results in a dramatic increase in the viscosity of the solution.



Aging of the gel (Synthesis):

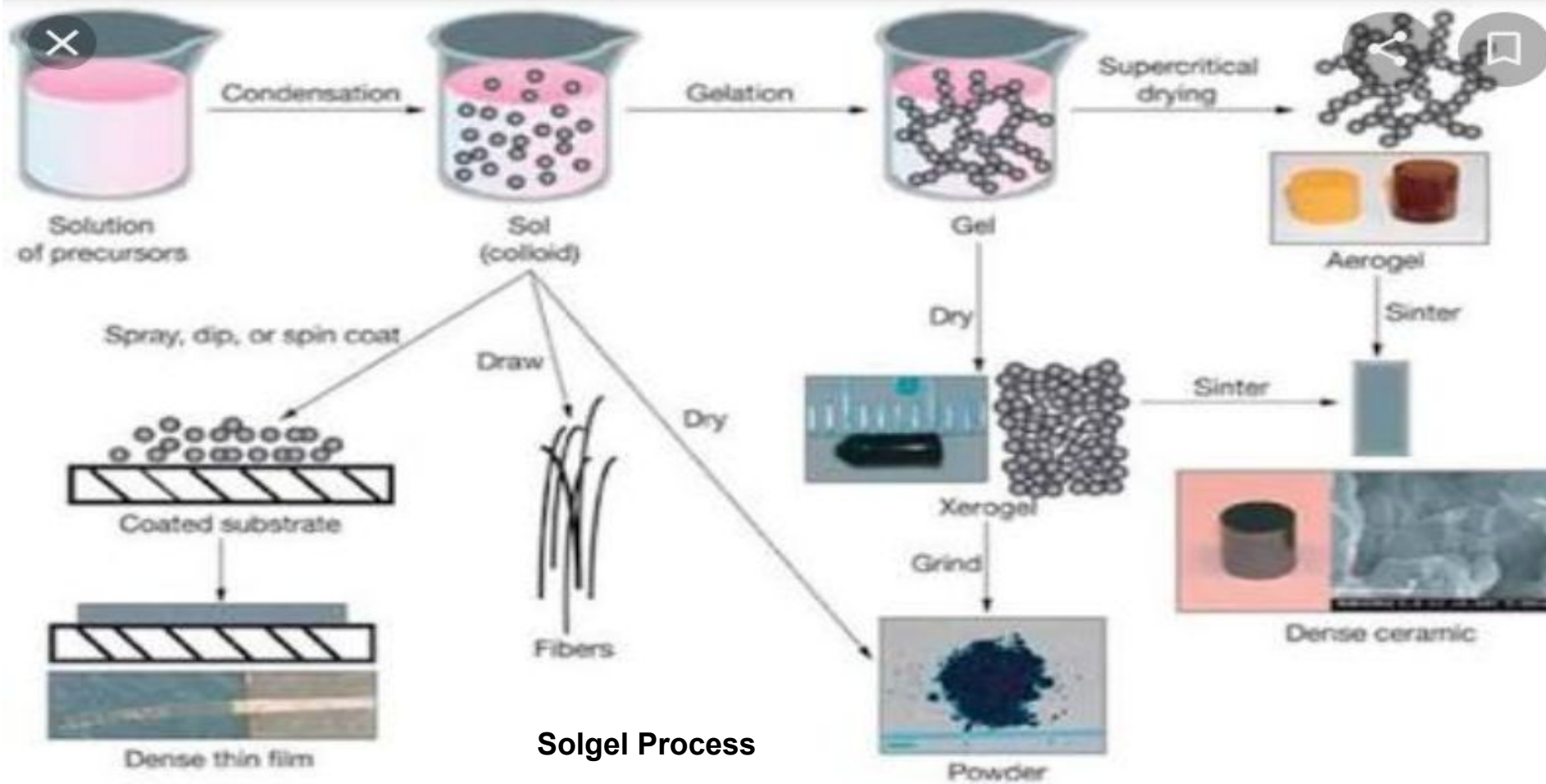
- The reaction mixture is allowed to continue polycondensation reaction until the gel transforms into a solid mass, accompanied by contraction of the gel network & expulsion of solvent from gel pores. Phase transformation may occur concurrently with syneresis.

Drying of the gel:

- Water & other volatile liquids are removed from the gel network.

Dehydration:

- During dehydration, surface-bound M-OH groups are removed, thereby stabilizing the gel against rehydration. This is normally achieved by calcining at temperature up to 800°C.

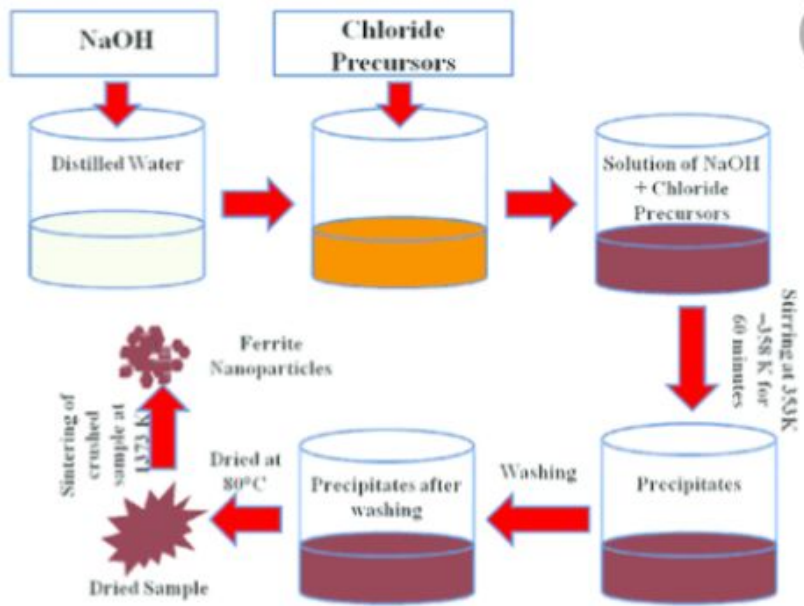


Precipitation process:

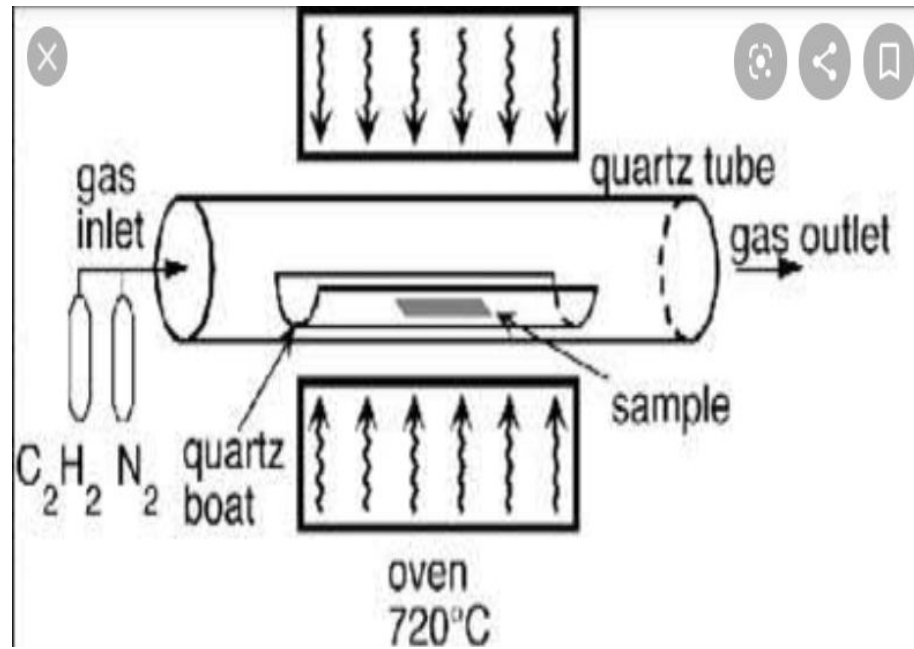
- This method relies on the precipitation of nanometer-sized particles in a continuous fluid solvent.
- An inorganic metal salt such as chloride, nitrate, sulphate, etc., is dissolved in water.
- Metal cations exist in the form of metal hydrate species, for example, $[\text{Al}(\text{H}_2\text{O})]^{3+}$ or $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$.
- These metal hydrates are treated with base such as NaOH or NH_4OH .
- The precipitate is then washed, filtered & dried
- The dried powder on subsequent calcinations to obtain the final crystalline metal oxide.

Chemical Vapor Condensation process.

- It involves the conversion of metal organic precursors into vapors in a reduced pressure.
- Chemical reactions among the gas molecules are induced by an input of energy such as resistant heating, laser & plasma.
- The precursors are transported into a bubbler & then passed into a heated furnace by helium gas, where they are later decomposed.
- The residence time of the precursor in the reactor determines the nature of particles or the film formed.
- By adjusting the gas flow rate, pressure difference between the precursor delivery system & the main chamber as well as the temperature of the hot walls of the reactor, the production of nanoparticles of metals & ceramics is achieved.



Precipitation



Chemical Vapour Deposition

Nanoscale materials:

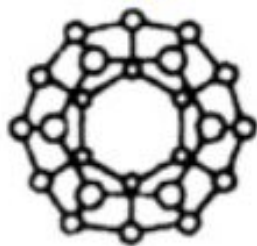
Fullerenes:

- A fullerene is a pure carbon molecule composed of at least 60 atoms of carbon.
- Fullerenes are made by heating of graphite in an electric arc in the presence of inert gases such as helium or argon.
- Fullerenes are cage like molecules. C₆₀ molecule has a shape like soccer ball & called Buckminsterfullerene.
- It contains twenty- six membered rings & twelve five membered rings.
- All the carbon atoms are equal & they are sp² hybridized. Each carbon atom forms three sigma bonds with other three carbon atoms. The remaining electron at each carbon is delocalized in molecular orbital, which in turn, give aromatic character to molecule.
- The bond lengths of each C-C & C=C are 143.5pm & 138.3pm respectively.

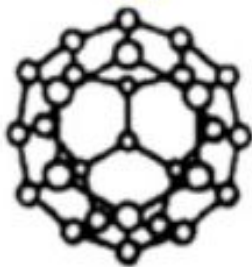
Uses of Fullerene:

- It is used in electrographic imaging, solar cells, non linear optical thin films, magneto optical recording.
- It is used in making carbon films, tunnel diodes, photolithography, double layer capacitor & storage devices.
- It is widely used for the conversion of diamond.
- In the separation of chromatography materials, absorbent for gases etc.
- It is used as gas sensor, temperature sensor, particle sensor & in the detection of organic vapours.
- Used as lubricants, adhesives, charge transfer complexes, cosmetics, catalysis etc.

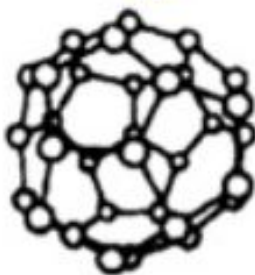
C_{24}



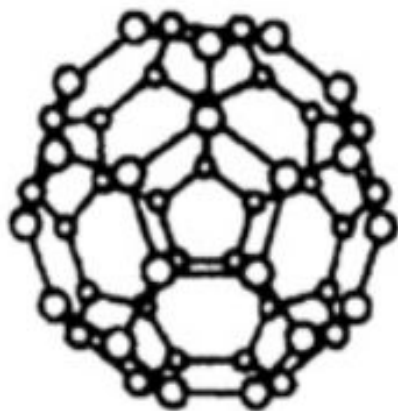
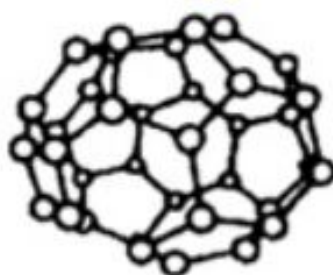
C_{28}



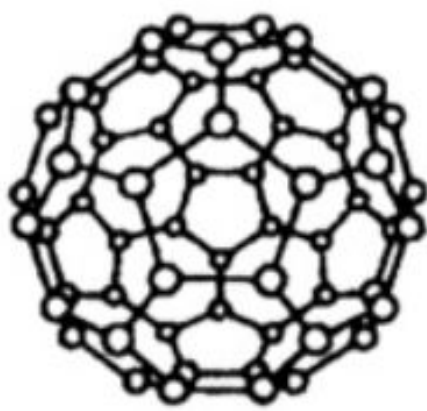
C_{32}



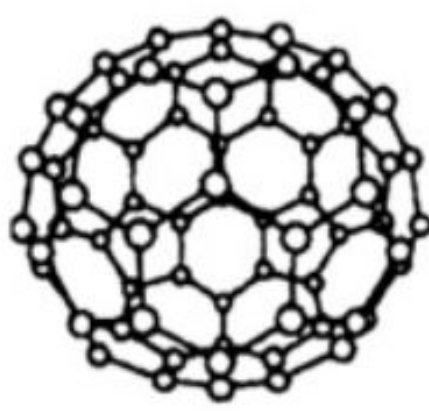
C_{36}



C_{50}



C_{60}



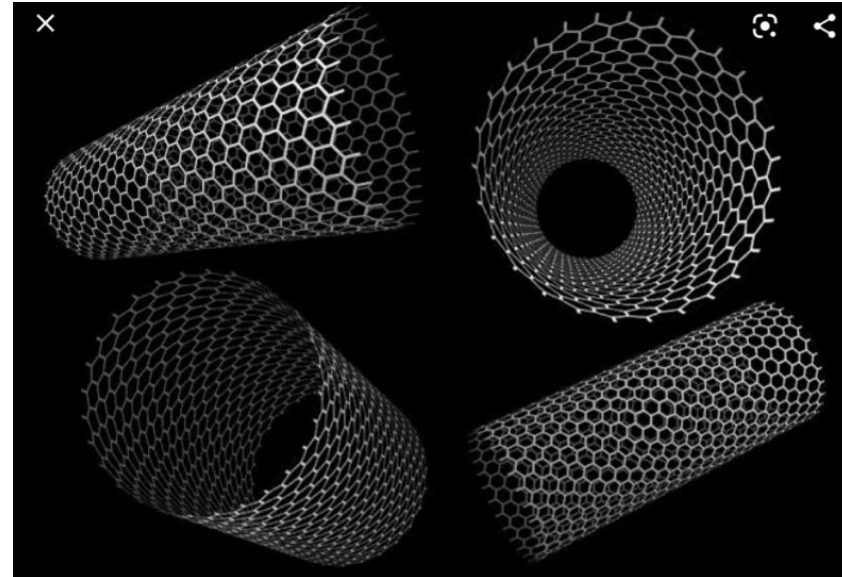
C_{70}

Carbon nanotubes:

- Carbon nanotubes are members of the fullerene structure family.
- Their name is derived from their long; hallow structure with the walls formed by one-atom-thick sheets of carbon, called graphene.
- Carbon nanotubes are single sheets of graphene rolled into cylinders.
- The diameter of the tubes is typically of nanometer dimensions, while the lengths are typically micrometers.
- Individual nanotubes naturally align themselves into ropes held together by vander Waals forces.
- Carbon nanotubes are generally produced by three main techniques, arc discharge, laser ablation

Uses of carbon nanotubes

- Field emitters / emission: Conductive or reinforced plastics.
- CNT based non-volatile RAM, CNT based transistors.
- CNT based fibers & fabrics.
- CNT based ceramics.
- Biomedical applications.

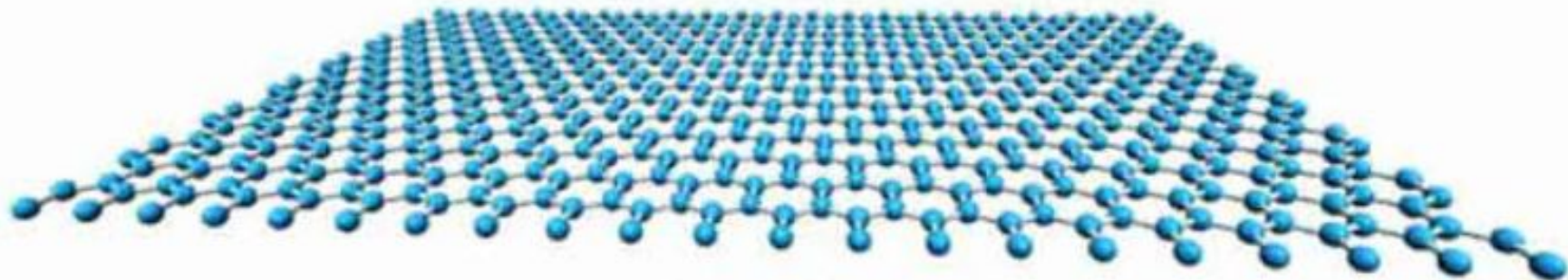


Graphenes:

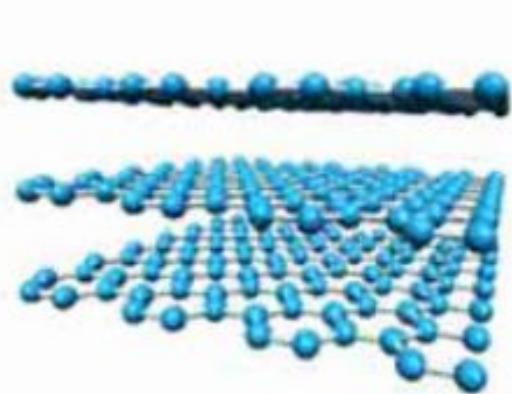
- Graphene is the thinnest material known to man at one atom thick, and also incredibly strong about 200 times stronger than steel. On top of that, graphene is an excellent conductor of heat and electricity and has interesting light absorption abilities. It is truly a material that could change the world, with unlimited potential for integration in almost any industry.
- Graphene is an extremely diverse material, and can be combined with other elements (including gases and metals) to produce different materials with various superior properties.
- Researchers all over the world continue to constantly investigate and patent graphene to learn its various properties and possible applications, which include:
- Touch screens (for LCD or OLED displays), transistors, computer chips, batteries, energy generation, super capacitors, DNA sequencing, water filters, antennas, solar cells,
- Spintronics-related products

Properties:

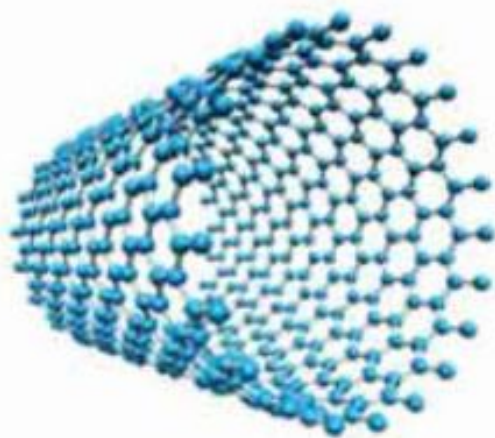
- Graphene is an amazingly pure substance, thanks largely to its simple, orderly structure based on tight, regular, atomic bonding. Carbon is a nonmetal, so you might expect graphene to be one too.
- In fact, it behaves much more like a metal (though the way it conducts electricity is very different), and that's led some scientists to describe it as a semimetal or a semiconductor (a material mid-way between a conductor and an insulator, such as silicon and germanium). Even so, it's as well to remember that graphene is extraordinary—and quite possibly unique.



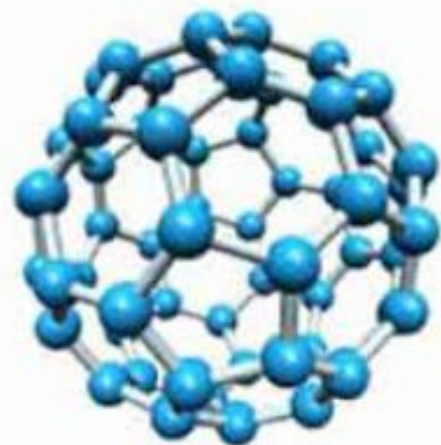
Monolayer Graphene



Multilayer Graphene



Carbon Nanotube



Buckyball