

Atomic and Molecular NanochemistryDalton's atomic theory

1. Everything is made up of atoms, which are the indivisible building blocks of matter, and cannot be destroyed.
2. All Atoms of an element are identical.
3. Atoms of different elements vary in size and mass.
4. Compounds are formed by the different whole number combinations of atoms.
5. A chemical reaction results in the rearrangement of atoms.

Atomic Number: Atomic number is described as the number of units of positive charge (protons) present in the nucleus.

- denoted by Z
- determines the chemical properties of an atom.

Isotopes: Nuclei with the same number of protons, but diff. no. of neutrons are called isotopes.

Mass number: sum of the no. of protons and the no. of neutrons present in the nucleus of an atom.

For eg. the 3 isotopes of hydrogen; hydrogen, deuterium and tritium have the same atomic number (1) but have different mass numbers (1, 2 and 3 respectively) because they each have a different number of neutrons.

Isotones: 2 or more species that have the same number of neutrons are called isotones. eg. Chlorine - 37 and Potassium - 39.

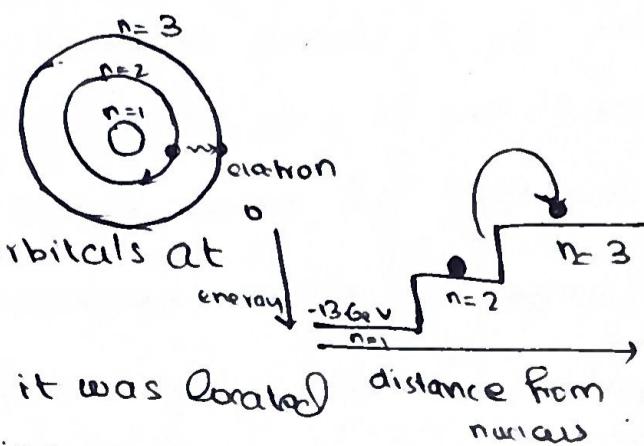
Chlorine: 17 protons 20 neutrons

Potassium: 19 protons 20 neutrons

Size of an atom: between 0.3 and 3 \AA

Bohr's Structure of an atom:

- Electrons can only be allowed in specific allowed orbitals at different energy levels.
- An electron can disappear from the orbit where it was located and reappear in a new orbit, without ever appearing anywhere in between the 2 energy levels.
- This is called a quantum jump.



Bond Formation

2.

(1) By the exchange / transfer of electrons

- (a) Ionic bond - electrons are transferred from one atom to another.
e.g. NaCl
- (b) covalent bond - electrons are shared between neighbouring atoms e.g. CH₄
- (c) metallic bonds - electrons are shared betw with all the atoms in a material (in metals)

(2) Bonding without the exchange/ transfer of electrons

Polar Bonds: • molecules that have charge separation

- The internal forces of the molecule are such that all the negative charge is clustered at one end, while all the positive charge is on the other end.
- The molecule is neutral as a whole, even though the positive and negative charges are found at different places.
- For eg. in H₂O, the electrons are usually found near the oxygen atom, making it electron rich, while the region with the hydrogen atoms are electron deficient.

Hydrogen Bonding - a special type of polar bonding

- When hydrogen forms a covalent bond with another atom, electrons move towards that atom, leaving hydrogen with a partial positive charge.
- This partial positive charge, causes the attraction of another negatively charged atom of the same / diff. molecule
- This type of attraction leads to a bridge-like structure between 2 atoms and molecules - called hydrogen bonding.
- For eg. - Found in DNA.

Vander Waals Forces

- A type of weak bonding that occurs in electrically neutral atoms
- When 2 atoms approach each other, their electron clouds exert repulsive forces, which leaves the atoms polarized.
- In such a situation, it is possible for that the electrical attraction between the nucleus of 1 atom and the electrons of the other are

- able to overcome the repulsive forces between electrons and thereby form weak bonds.
- For e.g. it is seen in the case of graphite, where the carbon atoms are held together in sheets by strong covalent bonds, but the sheets are held together only by weak Van der Waals' forces.

Electrical Properties

Conductors: In materials that are bound by metallic bonds, electrons float loosely between the metal ions.

- In such a case, if an electric field is applied, then the electrons would be able to move from one end to another, i.e. electric current is able to flow.
- The material is said to be a conductor of electricity.

Insulators: In materials like ceramics and plastics, the electrons are bound in ionic or covalent bonds.

- If an electric field is applied between the ends of such materials, no electric current would flow as the electrons are not free to move.
- Such materials are called insulators.

Magnetic Properties

Atoms behaving like magnets: An electron in orbit is a miniature loop of electric current.

- According to the laws of electromagnetism, such a loop will create a magnetic field.
- The magnetic fields, along with the intrinsic fields of the electrons and the nucleus, together determine the magnetic field of an atom.

Paramagnetism: Atomic magnets point in random directions in most cases,

- The material itself is not magnetic.
- Under the influence of a strong magnetic field, the atomic magnets line up, strengthening the external field.
- This phenomenon is called paramagnetism.

Ferromagnetism: In some metals, such as iron, the interatomic forces are such that the atomic magnets are lined up in some regions a few atoms across.

- Those regions are called domains.
- Under normal circumstances, the domains are randomly oriented, so the material is not magnetic.
- But if the material is subjected to a strong external magnetic field the domains will line up, and remain lined up, even after the external field is removed.
- As a result, the material now possesses a strong magnetic field.
- This phenomenon is called ferromagnetism
- Permanent magnets are made in this manner.

Nuclear Forces

- Within the nucleus, protons repel each other due to electrical forces, but are attracted to each other due to gravitation.
- As in the Bohr's model of an atom, the nucleus also has different energy levels, that correspond to the quantum jumps that the protons and neutrons make between their allowed orbits.
- Since the energies in the nucleus are much greater than what is associated with electrons, the transitions of the photons that are emitted/absorbed happen in the electromagnetic spectrum (i.e gamma rays and X-rays), rather than in the visible region.

Heisenberg's Uncertainty Principle : It is impossible to predict both the path and position of an electron simultaneously with precision.

Predicting the Location of an electron around the nucleus

- According to atomic theory and quantum mechanics, a mathematical function (wave function Ψ) is used to determine the probability of finding an electron in a particular location around the nucleus.
- Consider a hydrogen atom. An electron can be found at 'x' distance from the nucleus.
- However, it does not stay there, it moves frequently from one location to another.

- Thus, by locating the different positions of the electron, a 3D model of where the electron may be found is gradually built up.
- The electron can be found anywhere within a spherical space surrounding the nucleus.

Orbital: A well defined region around the nucleus, where the electron can be found is called an orbital.

Different orbitals and their shapes

First Level

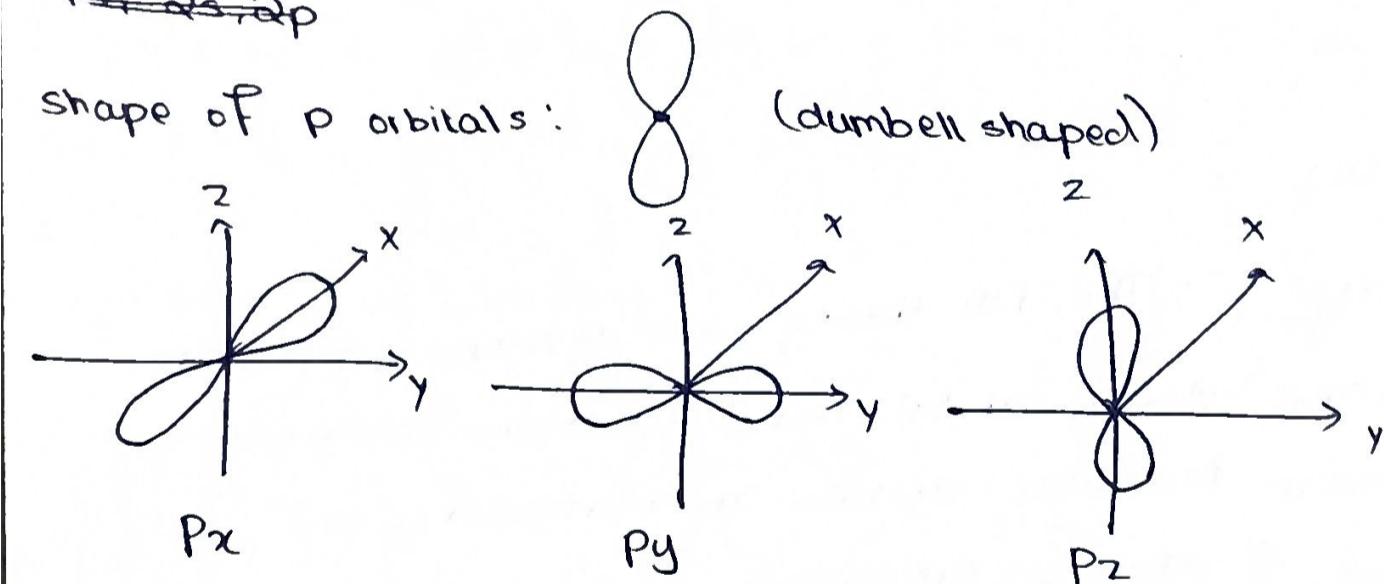
- $1s$: $1 \Rightarrow$ represents the orbital closest to the nucleus
 \Rightarrow shape of the orbital, i.e., spherical

Note: $1s$ is the closest to the nucleus. The $2s, 3s, 4s$ progressively get farther and farther away.

Second Level

- has s & p orbitals Total orbitals: 4
 ~~$1s\ 2s\ 2p$~~

Shape of p orbitals:



Note: At higher levels, the lobes of the p-orbital become elongated, indicating that they are farther away from the nucleus.

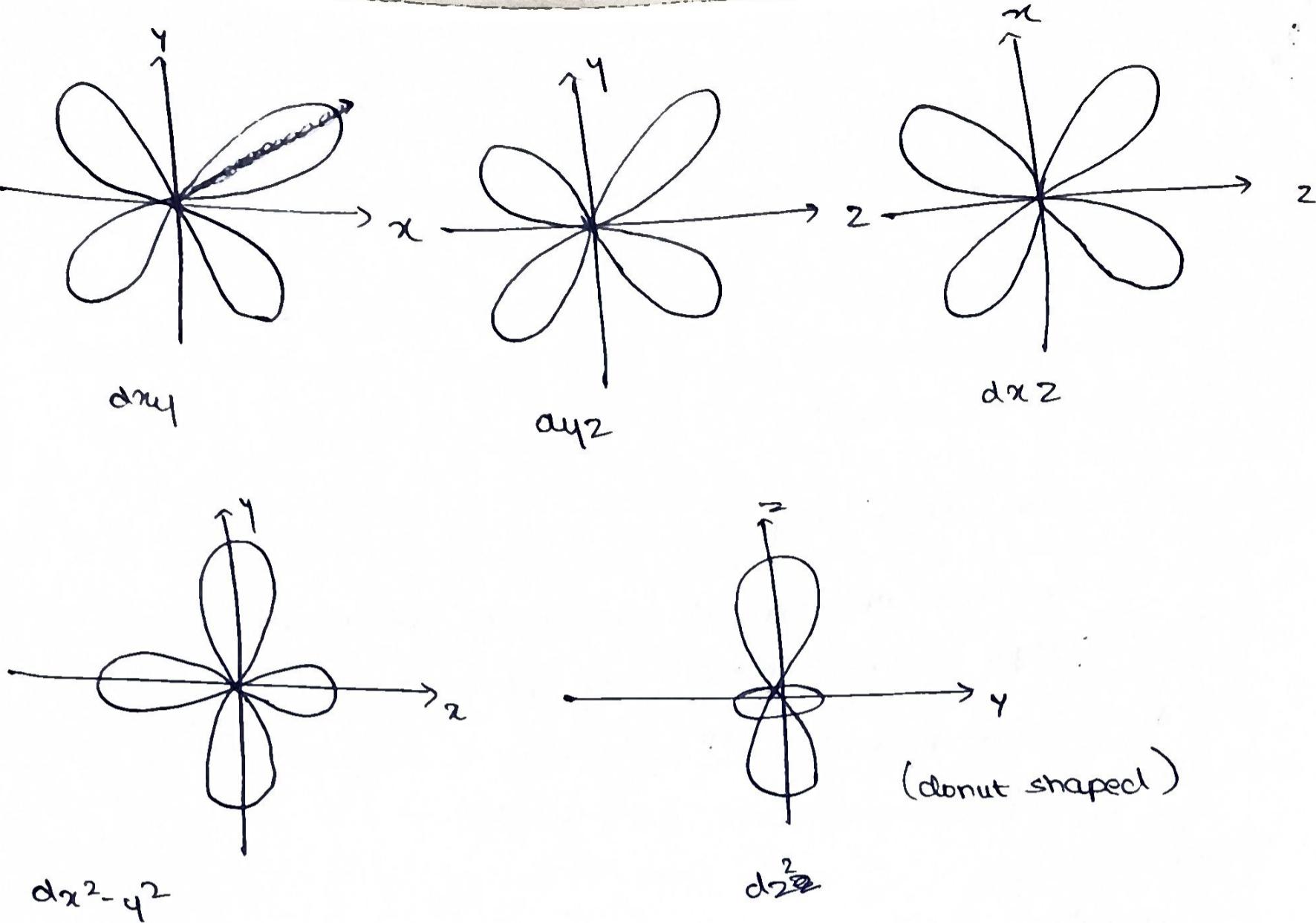
Third Level

Total no. of orbitals: 9

has s, p and d orbitals

d orbitals: can be $d_{xx}, d_{yy}, d_{zz}, d_{xy}, d_{yz}, d_{zx}$

shape: four-leaf clover



Fourth Level

No. of orbitals = 16

has s, p, d & f orbitals

Molecular Orbital Theory : The MO theory was developed from the quantum theory and the atomic orbital wave functions described by the Schrödinger equation. Molecular orbitals are formed by the overlapping / combination of atomic orbitals.

Conditions for the formation of molecular orbitals

- The distance between the atoms must be small such that effective overlapping can happen
- overlapping orbitals must have matching symmetry
- overlapping orbitals must be of comparable energies.

Bonding and antibonding molecular orbitals

- Bonding molecular orbitals : called σ molecular orbitals
- The electrons in the σ orbitals spend most of their time in the region directly between 2 nuclei.
 - They are called σ molecular orbitals, as they look like s orbitals when viewed along the H-H bond.
 - They are formed by the addition of 2 atomic orbitals.
 - They are stable, have comparatively less energy.

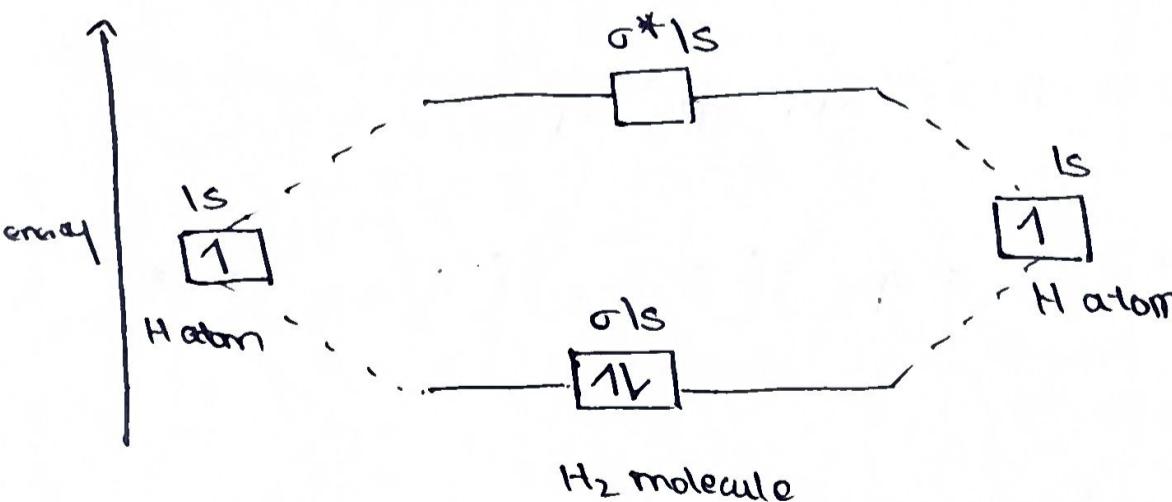
- Antibonding molecular orbitals : called σ^* molecular orbitals
- The electrons in the σ^* orbitals spend most of their time ^{away from} in the region between the 2 nuclei.
 - Less stable than σ Molecular orbitals, have higher energy
 - Formed by the subtraction of 2 atomic orbitals.

Order for filling molecular orbitals

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \pi_{2p_x} = \pi_{2p_y} < \sigma_{2p_2} \\ < \pi^*_{2p_x} = \pi^*_{2p_y} < \sigma^*_{2p_z}$$

Electronic configuration of H₂

$$H_2 : (\sigma_{1s})^2$$



Inference: The H₂ molecule is at a lower energy state than the 2 atoms.
 → Hydrogen is more stable in the molecular state than the atomic state.

- There are 2 electrons in the bonding MO & none in the antibonding MO.

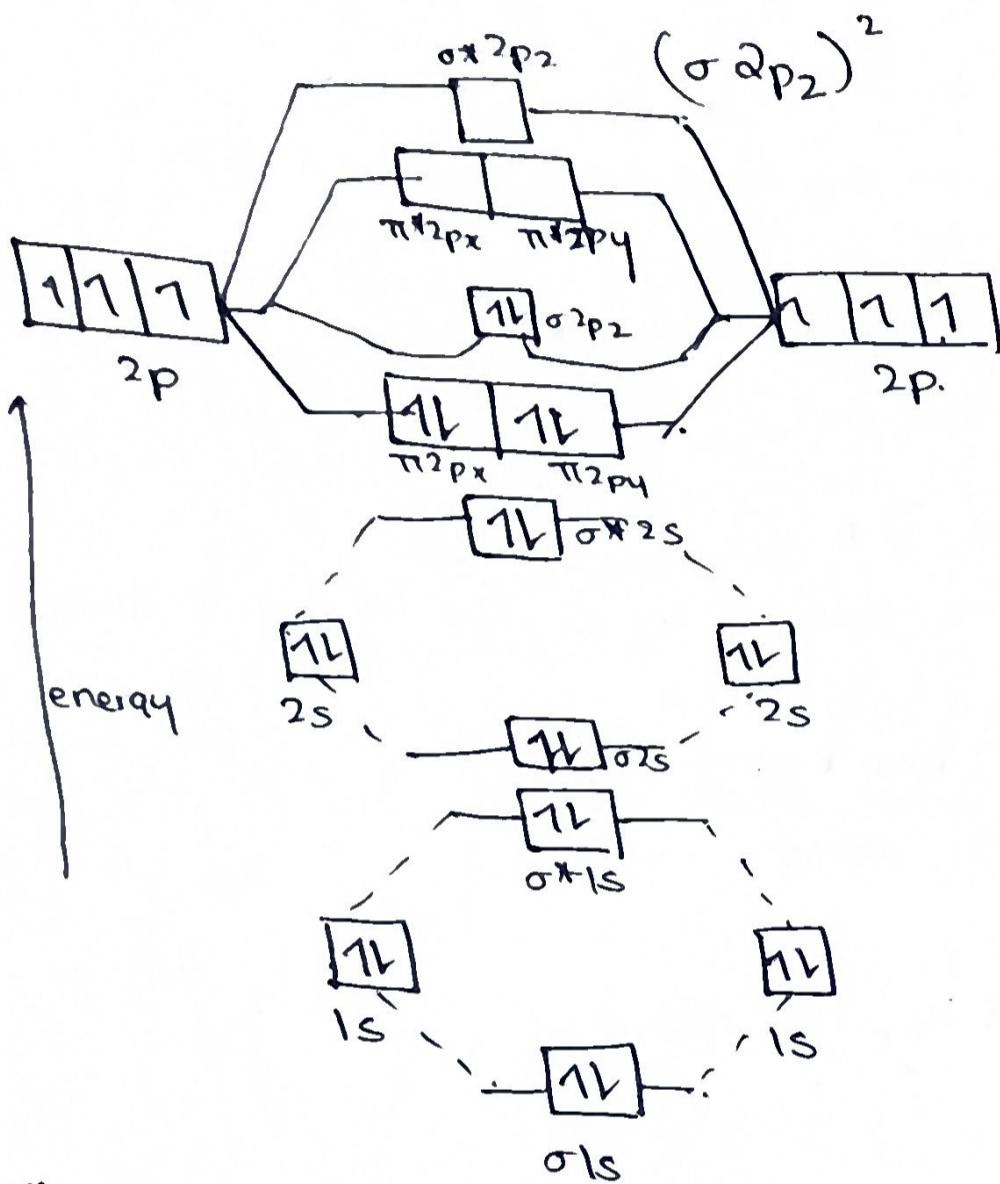
(8)

Electronic configuration of N₂

N₂ has 14 electrons.

N: 1s² 2s² 2p³

electronic configuration. (σ1s)² (σ*1s)² (σ2s)² (σ*2s)² (π2p_x)² (π2p_y)²



* Electronic configuration of O₂ (anomalous config)

Total no. of electrons: 16

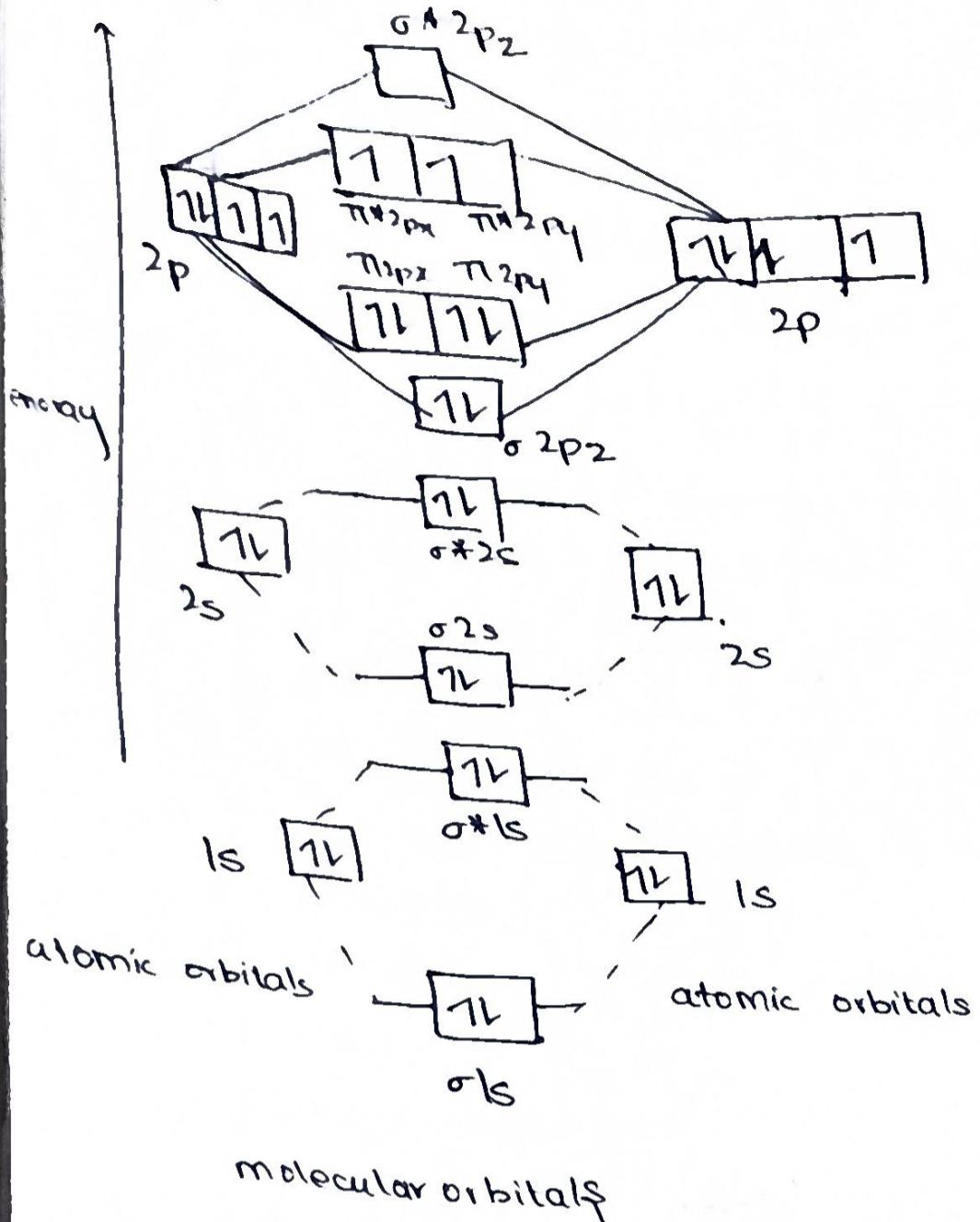
electronic configuration of O: 1s² 2s² 2p_x² 2p_y¹ 2p_z¹

for O₂:

(σ1s)² (σ*1s)² (σ2s)² (σ*2s)² (σ2p_z)² (π2p_x)² (π2p_y)² (π*2p_x)¹
 (π*2p_y)¹

* Why is there a change in the filling up of molecular orbitals for oxygen?

Assume that bond formation occurs along the z-axis of the coordinate system. In that case, the molecular orbital formed by the head-on overlap of the 2p_z level would be much stronger (and therefore at a lower energy level) than the molecular orbitals formed by the lateral overlap of the 2p_x and 2p_y orbitals.

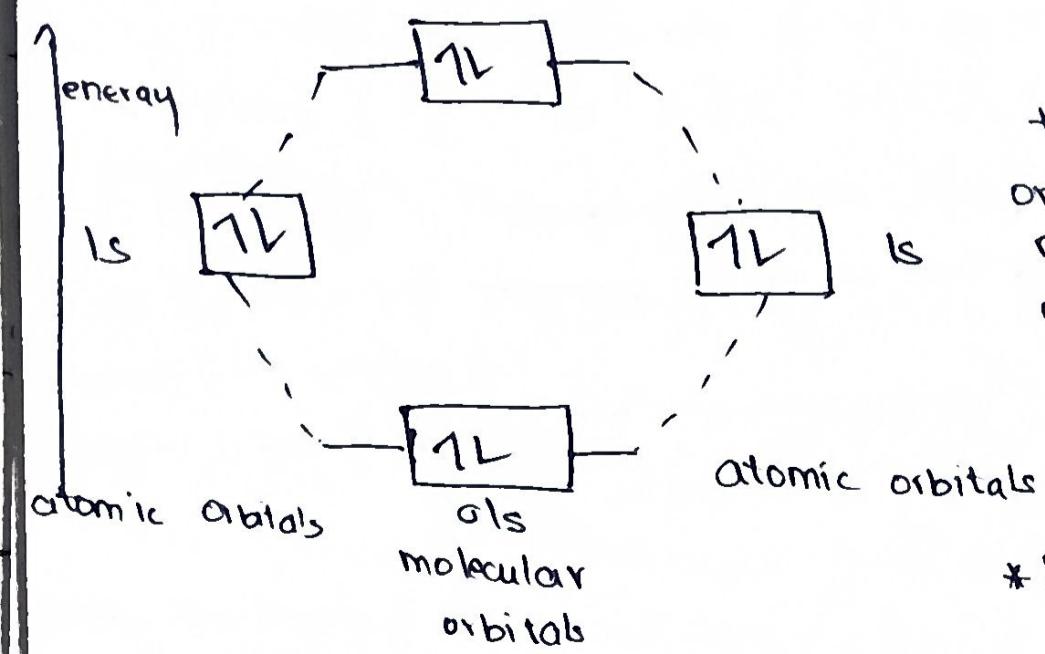


Applications of molecular orbitals

① Explanation for the non-existence of some molecules

For e.g. He_2 does not exist

The energy level diagram for He_2 would be as follows



* There are 2 electrons each in both the bonding & the antibonding orbitals \Rightarrow Total energy of the He_2 molecule would be the same as that of a pair of isolated He atoms, which means there would be nothing to hold the He atoms together to form a molecule.

$$\begin{aligned} * \text{Also Bond Order} &= \frac{1}{2}(N_b - N_a) \\ &= \frac{1}{2}(2 - 2) = 0 \end{aligned}$$

\Rightarrow There is no bond formed.

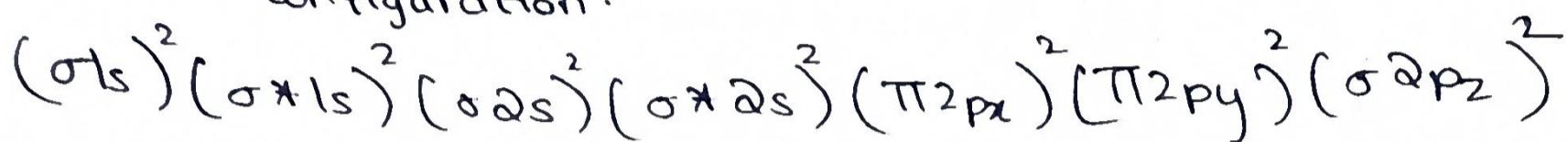
② Calculation of bond order

$$\text{Bonding} = \frac{1}{2} \left(\frac{\text{No. of bonding electrons}}{\text{No. of antibonding electrons}} - \frac{\text{No. of antibonding electrons}}{\text{No. of bonding electrons}} \right)$$

$$= \frac{1}{2} (N_b - N_a)$$

Eg: Bond order of N_2

electronic configuration:



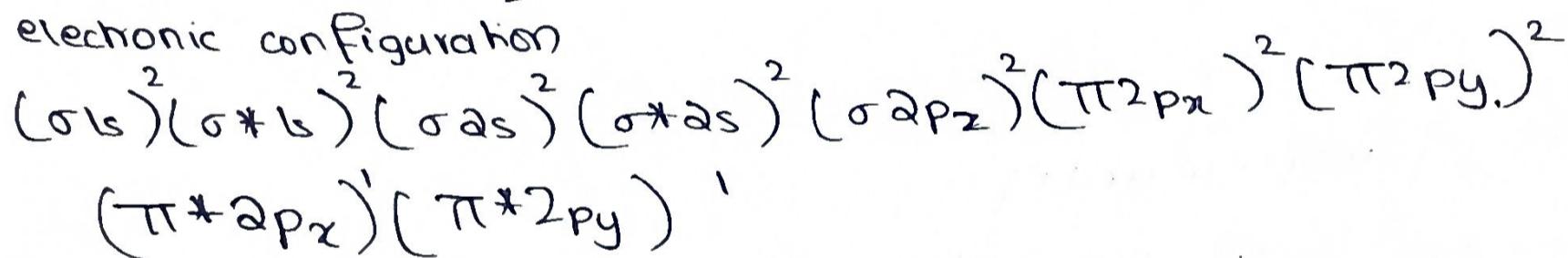
$$N_b = 10$$

$$N_a = 6$$

$$\text{B.O.} = \frac{1}{2} (10 - 6) = \frac{6}{2} = 3$$

Eg: Bond order of O_2

electronic configuration



$$N_b = 10$$

$$N_a = 6$$

$$\text{B.O.} = \frac{1}{2} (N_b - N_a) = \frac{1}{2} \times 4 = 2$$

③ Predicting magnetic behaviour

If all orbitals are doubly occupied \Rightarrow diamagnetic
(repelled by both poles of a magnet)

If some orbitals are unpaired \Rightarrow paramagnetic
(will be attracted by a magnetic field)

for eg. N_2 = diamagnetic

O_2 = paramagnetic

Nanochemistry

Nano = dwarf = 1 billionth of a metre, i.e. 10^{-9}m

Nanochemistry: It is a branch of chemistry associated with the assemblies of atoms or molecules in nano-dimension. It deals with the synthesis, characterization, properties & applications of nano materials.

Nanotechnology: Nanotechnology is defined as the design, characterization, production and application of structures, systems and devices by controlling size and shape at a nanoscale (10^{-9}m).

Classification of nanomaterials

Nanomaterials are classified on the basis of:

- (i) Dimension
- (ii) Composition
- (iii) Origin
- (iv) Phase composition

① Based on dimension Zero dimensional: All 3 dimensions (x, y, z) are confined to the nanoscale ($< 100\text{nm}$)

e.g. Nanoparticle

Nanopores

Fullerenes

quantum dots

One dimensional: Materials in which 1 dimension is not confined to nanoscale (i.e. $> 100\text{nm}$).

e.g. Nanotubes, Nanorods, Nanowires

Two dimensional: Materials in which 2 dimensions are not in nanoscale. (i.e. $> 100\text{nm}$)

e.g. Nanoflms, Nanolayers, nanocoatings

Three dimensional: Materials that are not confined to the nanoscale in any dimension (all $> 100\text{nm}$). They are not nano materials in the real sense, but possess a nano-crystalline structure. These may in the form of

(2) a multiple arrangement of a dispersion of nanoparticles, bonding of nanowires etc.

(2) Based on composition

- (i) Carbon based nanomaterials : • made from carbon
• can be hollow spheres, ^(organic) ellipsoidal, tubes
• spherical & ellipsoidal \Rightarrow fullerenes
• tube like structures \Rightarrow carbon nanotubes

(ii) Metal based nanomaterials (inorganic) made from metal & metallic compounds. e.g. nanogold, nanosilver, TiO_2 , CdSe

(3) Based on origin

- (i) Natural or non-intentionally made nanomaterials
• found / occur in nature
• e.g. proteins, nanomaterials found in volcanic ash, smoke and viruses

- (ii) Artificial or engineered or intentionally made nanomaterials
• fabricated / synthesized in a lab
• e.g. quantum dots, nanoclusters

(4) Based on phase composition

- (i) Single phase nanomaterials: • have only 1 phase w/ size $< 100\text{nm}$ in at least one dimension
• can also occur as bulk materials with nanoparticle aggregates, clusters, agglomerates etc. e.g. nanoclusters

- (ii) Multi phase nanomaterials : consist of more than 1 phase
• usually obtained by adding nanomaterials to polymers to form nanocomposites
• nanocomposites have enhanced physical & mechanical strength
• e.g. nanocarbon reinforced plastics, nanocomposites etc.

Uniqueness of nanoparticles

- Nanomaterials are larger than individual atoms and molecules, but are smaller than bulk solids.
- They obey neither absolute quantum chemistry rules or classical physics.

Their behaviour and properties are different because of the following reasons:

① Large fraction of surface atoms

- Nanomaterials have a large fraction of surface atoms per unit volume.
- As their size decreases, it is seen that they have a larger proportion of atoms on the surface than bulk materials.

For eg. if the size of the nano material is

$$30 \text{ nm} \Rightarrow 5\% \text{ of atoms on the surface}$$

$$10 \text{ nm} \Rightarrow 20\%$$

$$3 \text{ nm} \Rightarrow 50\%$$

- This is significant because growth and catalytic reactions happen on the surface \Rightarrow nanomaterials are much more reactive when compared to micro & macro materials with the same mass.

② Large surface area and high surface energy

- Nanomaterials have a much larger surface area compared to micro/macro materials.
- This means that they have a high surface energy and are unstable/metastable.
- This large surface area is due to the following reasons:

for a sphere: $V = \frac{4}{3}\pi r^3$

$$S = 4\pi r^2$$

$$\frac{S}{V} = \frac{4\pi r^2}{\frac{4}{3}\pi r^3} = \frac{3}{r}$$

i.e. when the radius becomes smaller & smaller, the surface area increases.

- ③ (14) Quantum confinement :- According to band theory, solids have energy bands and isolated atoms have discrete energy levels.
- Nanomaterials behave like isolated atoms, where the electrons are confined and not free to move as in the case of macro-scale material
- ④ Reduced defects :- Number of atoms associated with a nanoparticles is few, so the possibility to have defects reduces
- This enhances the mechanical strength.
- ⑤ Wave - corpuscle duality :- Particles are known to exhibit wave - particle duality
- As the size of the particles becomes smaller and smaller, wave character increases
 - At the nano - scale, wave nature is highly pronounced and it influences its properties
- ⑥ Random molecular motion :- Molecules move randomly due to their kinetic energy
- At a macroscopic scale, this random motion is negligible compared to the size of the material, and thus does not influence how the object moves.
 - However, at a nanoscale, the scale of these motions is the same as the size of the particles, and therefore influences its motion.
 - eg. For random kinetic motion = Brownian motion.
- ⑦ Gravitational forces become less significant
- At the nanolevel, Vanderwaal's forces and viscous forces are more important than gravity & inertia .
 - This is responsible for the random movement of nano materials.

* Differences between molecules, nanomaterials and bulk materials 15

| Property | Atoms / Molecules | Nanomaterials | Bulk materials |
|-------------------------------------|--------------------------------|--|--------------------------------|
| 1. Size of the constituent particle | A few angstroms | Angstroms to nanometers | microns and higher |
| 2. No. of constituent particles | One to a few atoms | Few to a thousand atoms | Infinite / Avogadro no. times |
| 3. Electronic nature | Confined | Confined | Not confined (continuous) |
| 4. Mechanical properties | NA | Dependent on particle size | Independent of particle size |
| 5. Wav nature | Applicable | Applicable | Applicable to a limited extent |
| 6. Random nature | Present | Present (Brownian motion) | Not present |
| 7. Stability | Stable | Stable depending on the surface energy | Stable |
| 8. Examples | NaCl KCl CO ₂ | Fullerenes Carbon nanotubes | Gold bar Silver bar |

Size - Dependent Properties

Chemical and physical properties of a nano-material are size dependent. Some of the size dependent properties are:

- (i) Thermal properties - melting point
- (ii) Optical properties - absorption & scattering of light
- (iii) Chemical properties - reactivity & catalysis
- (iv) Mechanical properties - tensile and compression strength
- (v) Electronic properties - conductance properties

① Thermal properties - Reduced melting point

- For bulk matter, melting point is independent of size. i.e both an ice cube and a glacier melt at the same temperature.
- In nanomaterials, there is a considerable reduction in melting point compared to bulk materials.
- This is due to:
 - (a) reduced lattice space between the atoms
 - (b) greater fraction of surface atoms in the total no. of atoms.
- Surface atoms need less energy to move as they are in contact with a lesser no. of atoms of the material
- Thus, a lower temperature is enough to cause high thermal vibrations of the surface atoms, leading to its melting.
- The difference in melting point between bulk & nano-materials may be as large as 1000°C .
- For e.g. bulk CdSe melts at 1678°K .
3nm nanosize CdSe melts at 700°K .
Thus, nanocrystal size decreases \Rightarrow surface energy increases \Rightarrow melting point decreases

② Optical Properties - absorption and scattering of light

- Optical properties of nano materials depend on size, shape, surface characteristics, interaction with the environment etc.
- Nanomaterials absorb & scatter different wavelengths of light and thus, they appear in different colors.

For example, bulk gold = yellow

nano gold = orange, red or purple depending on particle size.

Explanation : • In the nano scale, the motion of gold's electrons is confined. They are not free to move as in the case of bulk gold.

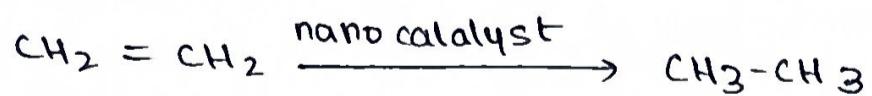
- When light falls on the nano-size particles, it absorbs light of a particular wavelength, and the electron cloud begins to oscillate.
- This phenomenon occurs at the surface of a material and is called surface plasmon resonance (SPR).
- Plasmons refers to the oscillations of the electron cloud.
- SPR occurs when the size of the nanoparticle is smaller than the size of incident light.
- SPR result in the unusually strong absorption & scattering of light.
(This depends on the particle size)
- The portion of the reflected light gives the material its color.
- As the size of the nanoparticle increases, the SPR shifts towards a larger wavelength.
- Small particles absorb wavelength in the blue-green spectrum ($\sim 400\text{--}500\text{ nm}$) & the reflected light is red ($\sim 700\text{ nm}$), making the gold particles red.

③ Chemical Property - Reactivity & catalysis

Catalytic properties: A catalyst is a substance which when added in small quantities alters the rate of the reaction, without it being consumed or chemically altered.

- At the nanolevel, the surface area of the heterogeneous catalyst is enormous, which increases the rate of the reaction.

For example,



Reactivity: Since the surface area of the heterogeneous catalyst is enormous, it has high surface energy and thus, highly reactive.

- They come in different sizes and shapes, so surface atomic arrangement & coordination no. are easily altered.

For ex. bulk gold is not reactive, nano-gold is highly reactive.

Nano aluminium is explosive, nano aluminium powder is used to make weapons more powerful.

④ Mechanical properties :

- In nanomaterials, since the particle size is very small, mechanical properties such as hardness, elastic modulus, scratch resistance are very different.
- Nanomaterials have enhanced mechanical properties. This is because
 - (i). due to the reduced probability of defects ($\text{less atoms} \Rightarrow$ fewer defects)
 - (ii) due to increased surface perfection.
- Polymers reinforced with nanoparticles leads to significant improvements in strength.

For example : (i) cutting tools made from tantalum carbide
tungsten carbide
titanium carbide

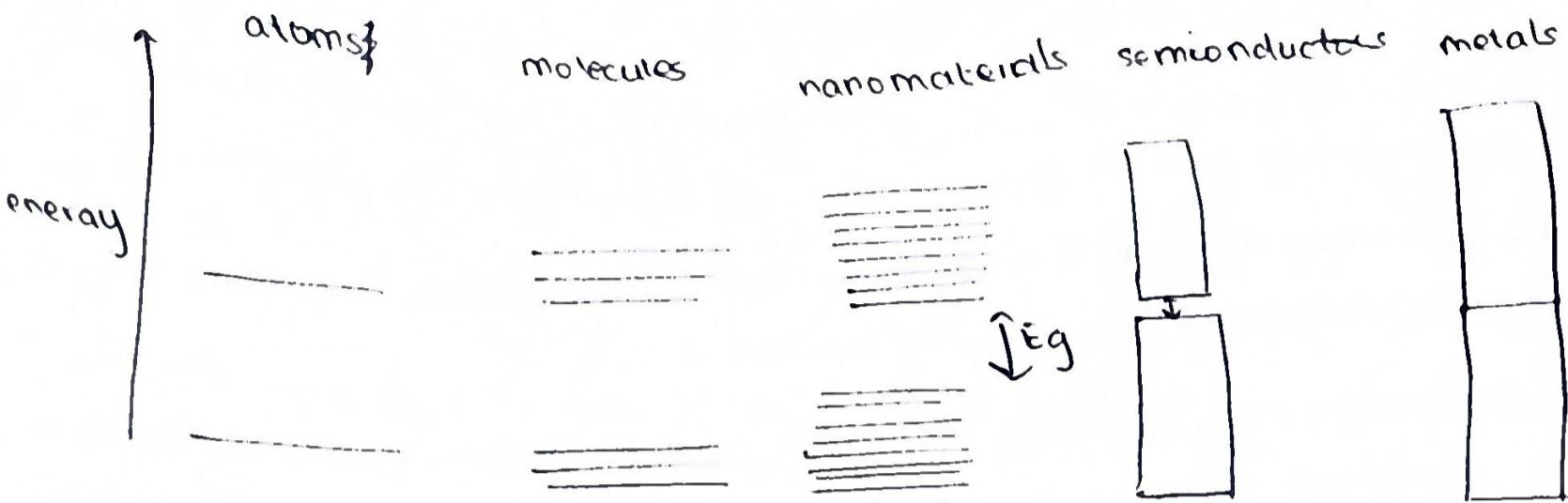
are stronger than their bulk equivalents.

- (ii) Copper nanoparticles $< 50\text{ nm}$ are super hard materials which are not ductile and malleable like bulk copper
- (iii) ceramics made w/ nanoscale materials can be pressed and sintered into different shapes.
- (iv) Carbon nanotubes (CNT) are extremely small tubes w/ the same honey-comb structure like graphite. CNTs are $100\times$ stronger than steel but 6 times lighter.

⑤ Electronic properties - conductance properties

- In solids, the valence band is generally filled with electrons, and is separated from the empty conduction band by a band gap, E_g .
- The promotion of electrons from the valence band to the conduction band by using heat / light leads to conduction
- In metals, the valence band and the conduction band overlap. ($E_g = 0$)
- In semiconductors, the value of E_g is small.
- In nanomaterials, due to quantum confinement, E_g is very high. More energy is required to excite an electron across the band gap.
 - Higher energy \Rightarrow a shorter wavelength (blue shift)
- For e.g. nano silicon & nano germanium do not show semiconductor properties

- Fullerenes & CNTs show special properties. (CNTs can be conductors or semiconductors based on their nano structure).



- Applications: By controlling crystallite size, the electrical properties of a nano-size semiconductor can be fine-tuned.

Synthesis of Nano particles

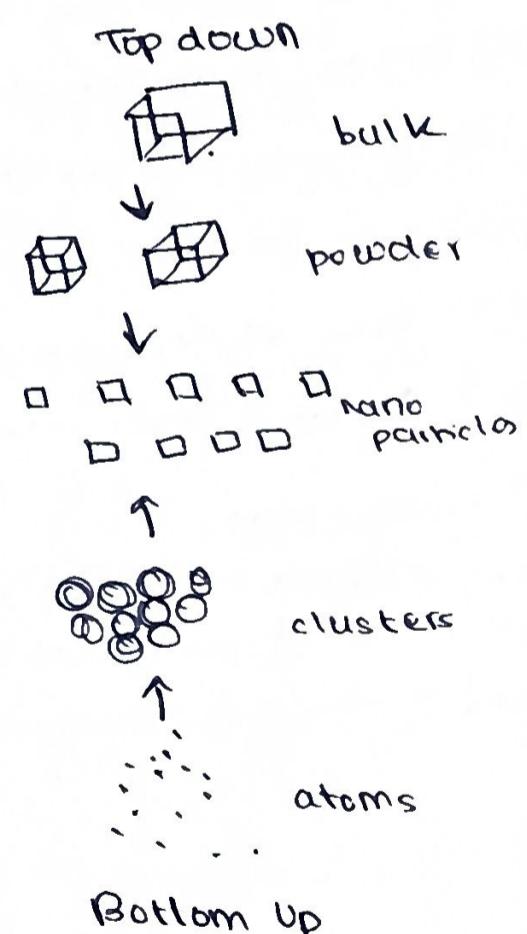
Top Down Approach

- Top down approach involves the breaking down of bulk material into nano-sized particles. (i.e. the bulk material is chiseled away to obtain nano-scale products)

- Done using:
 - (i) attrition or milling
 - (ii) lithography
 - (iii) volatilization of a solid by laser ablation

- Advantages :
 - (i) easily scaled up
 - (ii) simple, easy to use
 - (iii) fine particles can be produced

- Disadvantages :
 - (i) Does not lead to individual nanoparticles. bulk nano-structured materials are produced
 - (ii) Particles may have a non-uniform distribution
 - (iii) Surface ^{imperfections} ~~defects~~ may be present
 - (iv) Impurities from milling medium may be present



- (v) difficult to control & design to produce desired particle size & shape
- (vi) can cause internal stress.

Bottom Up Approach

- Refers to the building up of material from the very bottom, i.e atom by atom, molecule by molecule, cluster by cluster.
- Atoms and molecules are carefully deposited via controlled chemical reactions
- This has the potential of creating less waste, and is thus more economical.
- The bottom-up method can be classified into 2:
 - (i) Gas-phase method - chemical vapour deposition
 - (ii) Liquid-phase method - sol gel synthesis

Advantages

- (i) greater possibility of obtaining nanostructures with less defects
- (ii) better homogenous composition of material
- (iii) produces less waste
- (iv) economical
- (v) less internal stress, close to thermodynamic equilibrium
- (vi) better short and long range ordering

Disadvantages

- (i) difficult to control growth
- (ii) rate of production is slow
- (iii) time consuming

Differences between top-down and bottom-up approach

Top-down

1. The manufacturing is done from larger structures reaching nano level by successive cutting.
2. Certain amounts of material are wasted, as some parts are removed from the original structure.
3. Less control over molecular dimensions
4. The surfaces & edges may not be perfect, may have cavities
5. Examples : lithography
wet ball milling

Bottom-up

1. The process involves the building up of a material from the bottom, atom by atom, cluster by cluster, molecule by molecule.
2. No material is wasted.
3. More control over molecular dimensions
4. Perfect surfaces and edges can be produced.
5. Examples : sol-gel method
chemical vapor deposition

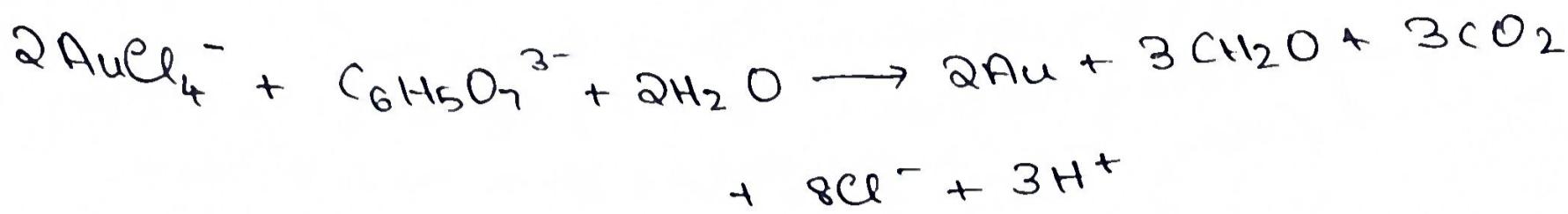
Colloidal Synthesis

- one of the most useful, simple & easiest ways to create nanoparticles
- used to make nanoparticles of : (i) metal oxides
(ii) ceramics
- organic | inorganic reactants are used
- method : a metal ion is reduced to metal nanoparticles, and are evenly distributed in a liquid.
- Their aggregation is prevented by means of electrostatic repulsion, using a stabilizing agent that coats the particle surfaces
- Factors to note : concentration of reactants
temperature of reactants
pH
order of addition of reactants

Advantages

- (i) cheap & easy
- (ii) size of particles can be varied by changing reactant conditions
- (iii) nanoparticle coating of surfaces can be done

Example: Stable gold nano-particles, can be prepared by reducing chloroauric acid (HAuCl_4) with trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$)



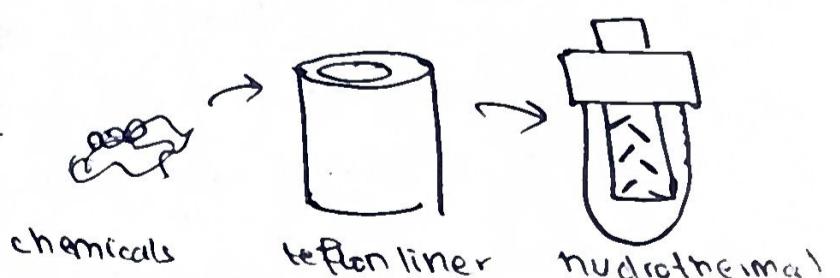
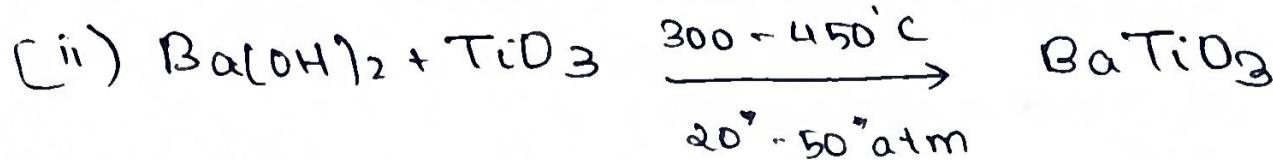
Hydrothermal Synthesis

- This technique involves the growing / synthesis of crystals under from aqueous solutions of substances at high temperature & pressure.
- It is based off the ability of water to dissolves substances at high temperature (500°C) and high pressure ($10\text{-}80\text{ MPa}$). These are substances which are insoluble in water at regular temperatures (some oxides, silicates, sulphides).

Synthesis :

- synthesis is carried out in an autoclave (a steel cylinder, which can withstand high temperature & pressure for a long time)
- The autoclave is heated to a temperature much higher than the boiling point of water (supercritical water). These conditions are suitable for the crystallization of the products.

- Factors that influence product formation:
 - (i) pH (generally kept alkaline to enhance solubility)
 - (ii) duration and temperature
 - (iii) pressure
- For eg: (i) metal oxides & CNTs can be prepared in this way.



teflon liner hydrothermal reaction

Advantages

- (i) the solvent used is water
- (ii) the reagents & solvent can easily be regenerated
- (iii) nano particles of high quality can be produced
- (iv) morphology can be controlled (tubes, wires, single crystals, rods)
- (v) rate of reaction becomes faster w/ an increase in temp. and pressure
- (vi) zeolites can be made, which cannot be easily synthesized by another method.

Disadvantages

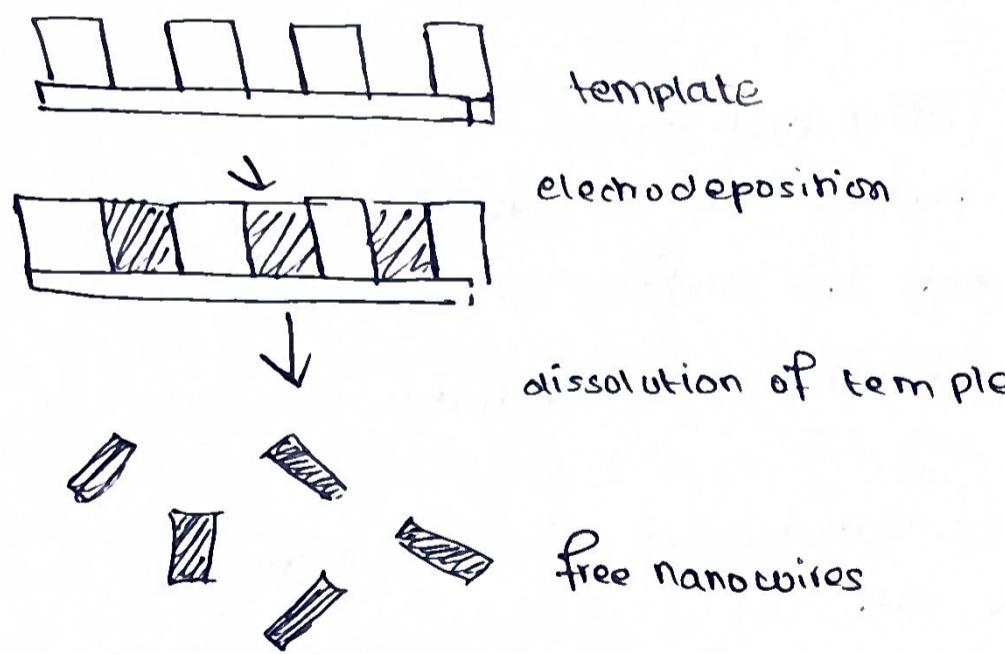
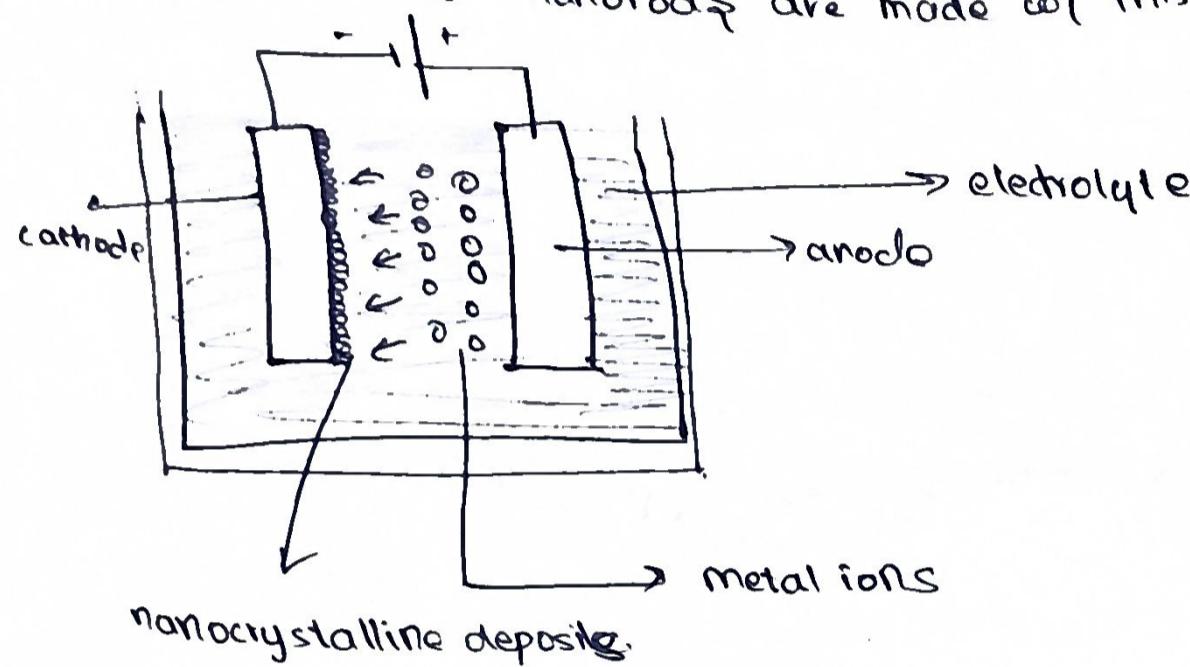
- (i) equipment is expensive
- (ii) sometimes difficult to predict morphology of product

Electrodeposition

- A method used to deposit thin layers / films for electronic devices & sensors
- Can be used to generate 0D, 1D, 2D nanomaterials
- Primary application: to coat a metal surface with a layer of metal having some desired property which the surface lacks
- An electrodeposition set up consists of electrodes, substrates, electrolytes & electrical potential.
- The electrolyte is an ionic soln, with ions of the metal to be deposited
- Electrodeposition takes place at the cathode.
- The material deposition follows Faraday's laws of electrolysis
- anode rxn: $M \rightarrow M^{n+} + ne^-$
cathode rxn: $M^{n+} + ne^- \rightarrow M$
- The thickness of the film depends upon the current density & time for which the current flows.
- By controlling the current, a single layer of atoms can be deposited.

Template assisted electrodeposition

- used to control size & shape of nanomaterials
- commercially available cathodes used as templates
- electrodeposition is done on this cathode, then the template is dissolved to obtain nanomaterials.
- metal nanowires & nanorods are made w/ this method.



Advantages

- (i) cheap & fast
- (ii) diff. nanostructures can be made

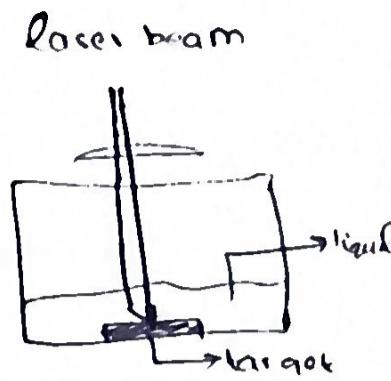
Disadvantages

- (i) ~~expensive~~ (surface coating may not be uniform)
- (ii) extensive surface cleaning has to be done
- (iii) follows a complex mechanism.

Laser Ablation

Laser ablation in solution

- generally used to prepare metallic nanoparticles (e.g. silver nanoparticles)
- Short pulses of a high power laser are targeted on a metal surface in solvent.
- The target absorbs energy from the laser source & vaporizes.
- The vaporized material condenses as nanoparticles in the solvent.



Advantages

- metal nanoparticles can easily be prepared
- nanoparticles - highly pure, greatest long-term stability
- a variety of solvents can be used
- a large amount of different nanomaterials can be made

Disadvantages

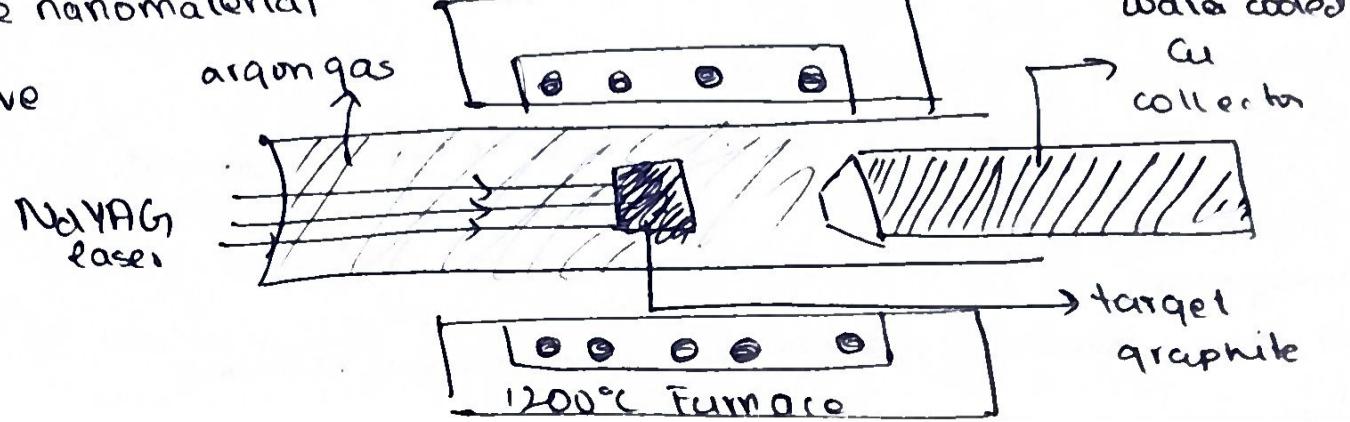
- expensive
- sample after ablation may be different from bulk sample.

Laser Ablation in Solid State

- Synthesis of CNTs can be carried out in a horizontal flow tube under a flow of inert gas at a controlled temperature.
- In this setup, a flow tube is heated to 1200°C with a tube furnace.
- Laser pulses enter the tube and strike a target made of graphite & a metal catalyst like Co / Ni.
- SWNTs condense from the vaporization tube & are deposited on a collector outside the furnace zone.

Advantages - very pure nanomaterial

Disadvantage - expensive



Chemical Vapor Deposition (CVD)

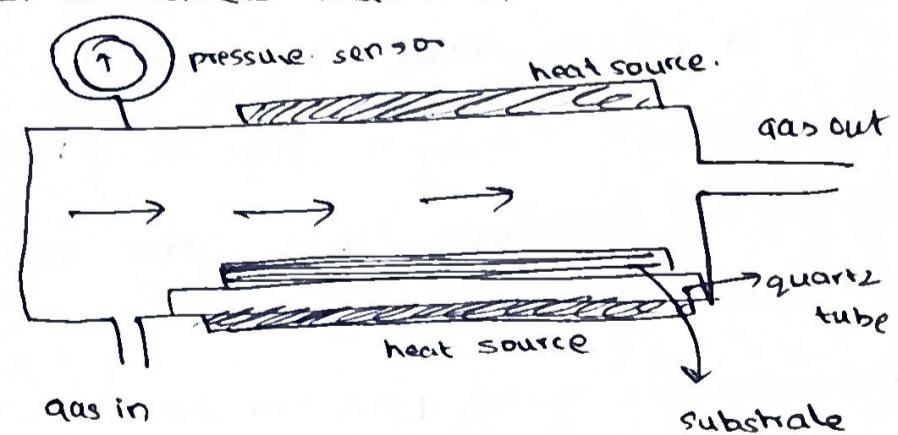
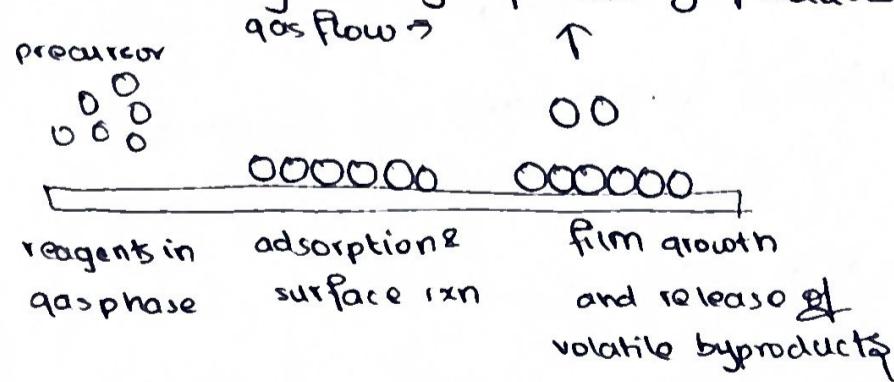
- a process that is used to make high purity & high performance solid material.
- used in the semiconductor industry to form thin films.

Method

- The material to be deposited is heated to its gas phase in vacuum and then allowed to deposit as a solid on a surface.
- The deposition happens by means of a surface chemical reaction, such that the deposited material is different from that volatilized.
- When the surface is exposed to chemical vapour, the first layer of atoms acts like a template, on which further growth happens.
- The structures of these materials are aligned to grow vertically.
- Sometimes, the diffused particles are scrapped from the surface to obtain nanopowder.

The CVD technique happens in 5 steps:

- (a) Transport of the gas to the rxn zone by diffusion
- (b) Adsorption of the material on the surface of the substrate
- (c) Chemical rxn. on the surface to form the desired film
- (d) Desorption of the by-products from the surface
- (e) Pumping away of the by-products and unreacted material



Advantages

- (i) high purity nanomaterials
- (ii) 1D nanomaterials can be made (nanowire/nanorod)

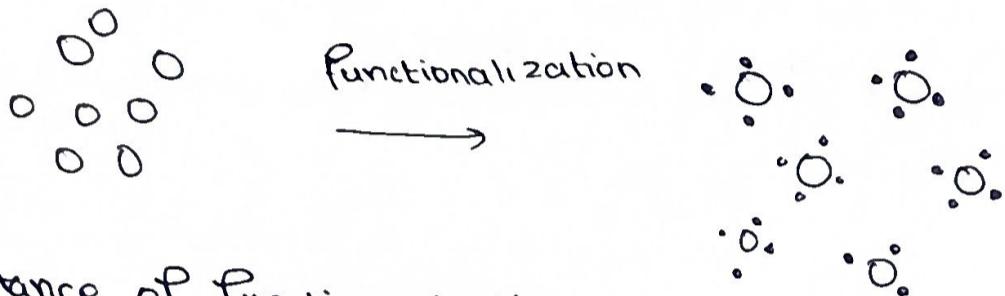
Disadvantages

- (i) expensive
- (ii) toxic chemicals may cause environmental problems.

Surface modification of nanoparticles

Chemical Functionalization

- chemical modification / chemical functionalization is the most widely used surface modification technique.
- Functionalization is the introduction of organic molecules / polymers on the surface of the nanoparticle to improve its properties.
- By attaching functional groups, the nanoparticle can be made hydrophilic, hydrophobic, anticorrosive or conductive



Importance of functionalization

1. Tune properties of nanoparticles for different applications
2. Make nanoparticles biocompatible.
3. Improve stability, solubility, agglomeration properties
4. Provides a means for further grafting, conjugating additional functional groups

Examples

- super hydrophobic surfaces (from a Lotus Leaf's hydrophobicity)
- ZnO , TiO_2 functionalized nanoparticles, can block UV rays, impart photo & thermal stability
- used in targeted drug delivery systems

Carbon Nanotubes : tiny, hollow, closed tubular structures with diameters of the order of a few nanometers.

• also called bucky tubes

Discovery: • discovered in 1991

• Japanese scientist Sumio Iijima, while studying the material deposited on the cathode during arc-evaporation synthesis of fullerenes.

Structure: • derived from the structure of graphite

• graphite has a layered, planar structure of carbon atoms

• carbon atoms arranged at the corners of hexagons \rightarrow joined by strong covalent bonds layers joined by weak Van der Waals forces

• CNT is a sheet of graphite rolled into a cylinder & capped at both ends

Types of CNT

(i) Single walled CNT (SWCNT) : Formed by wrapping a 1 atom layer thick layer of graphene into a cylinder.
diameter : 1nm

(ii) Multiple wall CNT (MWNT) : several concentric cylinders of SWCNT
diameter : 10 - 20nm
inter layer space : 0.4nm

Geometry of CNT : armchair, zig-zag, chiral - based on how carbon sheet is wrapped into a tube.

Properties of CNT

① Mechanical Properties

1. Great mechanical strength : Tensile strength 10 - 50 times steel
Young's modulus 5 times steel
2. Light weight & low density : light weight because of hollow cylindrical structure.
3. Great tensile strength : measure of the resistance of a material to break under the application of stress.
4. Great flexibility : due to hexagonal carbon network.
5. High melting pt : nearly 3 times that of copper

② Electrical Properties

1. conductivity : dependent on structure
 - (i) armchair CNT = metallic
 - (ii) zigzag CNT = semiconductingconductivity = 6 times that of copper
2. ~~large~~ high current carrying capacity

③ Field Emission : CNTs have nanometer size diameter, great electrical conductivity & chemical stability, thermal conductivity, makes them excellent electron emitters.

④ Thermal conductivity : due to the tubular structures of CNTs. high thermal conductivity in the axial direction, less through radial directions (high anisotropy in heat transport).

⑤ Vibrational properties : each CNT molecule has a specific set of vibrational motion, determined by the symmetry of the molecule.

Applications of CNT

① Energy storing devices

1. Lithium batteries :
 - anode material in Li batteries
 - why : superior mechanical properties and high surface to volume ratio
 - improves conductivity
2. Hydrogen fuel cells :
 - to store hydrogen fuel
 - why : due to tubular structure
3. supercapacitors : CNTs on charged capacitor plates increase energy storage ability

② Structural Devices

1. CNT composites : polymers reinforced with CNT
 - why : increases strength
 - used to make tennis rackets & baseball bats

2. Ceramic applications : to make ceramic materials
 • why : tougher product, conducts electricity

3. Defence : • used to make bullet proof vests
 • why : exceptionally high elastic modulus and yield strength

4. Concrete: • criss added to concrete
 • why : increases tensile strength, prevents cracking

5. Flywheels : can allow for high rotational speeds
 • why : high strength / weight ratio

③ Electrical and electronic devices

1. Display devices: • improve quality of display screen
 • reduces their weight & thickness
 • why : high field emission efficiency

2. Atomic Force microscopes: 1D CNTs used in AFMs

3. Electric motor brushes: CNTs act as a replacement for conventional carbon black

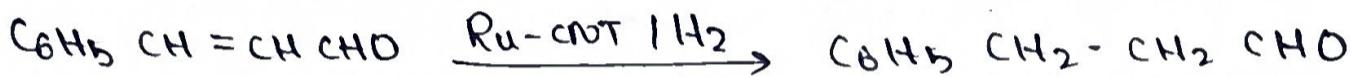
④ Medical Devices:

1. Drug deliverys: CNTs attached to medicine w/ an antibody can find the disease antigen and destroy it.

2. Biosensors : • used to make glucose detectors
 • why : because of fluorescent properties of CNTs.

5. Chemical devices

- Water filter : • prevents / blocks the smallest of particles & kills bacteria
- desalination : • salt can be removed from water, by forcing water through the CNT network
why: lower pressure required than traditional reverse osmosis methods
- catalyst : • hydrogenation of cinnamaldehyde w/ Ru

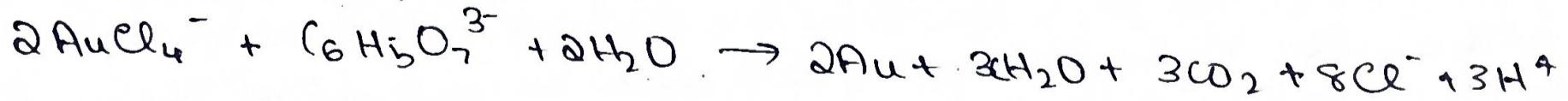


- reduction of nickel oxide to nickel metal
- why: large surface area

Gold Nanoparticles

- Colloidal gold is a sol, a suspension of gold nanoparticles in a fluid (usually water).
- size: 10 - 200 nm
- They are the most stable metal nano particles.

Synthesis : • By the reduction of chloroauric acid (HAuCl_4) with trisodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$).



Characteristics : • chemical property depends on the size of the nanoparticle
 • show better optical properties like plasmon resonance, fluorescence and chemiluminescence
 • have greater biological compatibility (non-toxic)

- provide microscopic probes for the detection of cancerous cells
- accumulate in the cancerous cell & show cytotoxic effect.

Optical Properties

- show exceptional absorption & scattering of light. There is a strong interaction w/ light because the conduction electrons on the surface undergo a collective oscillation when excited by light of a specific wavelength
- small gold nanoparticles ($< 100\text{nm}$): red
larger gold nanoparticles : blue (purple)
- on adding salt to the gold sol, the surface charge gets neutralized, causing the particles to ~~aggregation~~. \Rightarrow color of soln changes from red to blue

Applications

1. Electronic devices: used as conductors in
 - printable inks
 - electronic chips
 to connect conductors, resistors
2. Photodynamic Therapy: Near IR absorbing gold nanoparticles produce heat when excited by light w/ $\lambda = 700 - 800\text{nm}$.
 - can eradicate targeted tumors
 - light is applied to a tumor containing gold nanoparticles
 \Rightarrow particles are rapidly heated up, killing them. (hyperthermia therapy)
3. Therapeutic Agent Delivery: agents coated on gold particles for drug delivery
4. Sensors: calorimetric sensors \Rightarrow to check if food is suitable for consumption
5. Probes: scattering of light produces a variety of colors under dark-field microscopy. used for biological imaging
6. Diagnostics: to detect biomarkers in heart diseases, cancers & infectious agent
7. Catalysis: as catalysts in a no of chemical reactions