# POSTULATES OF MOLECULAR ORBITAL THEORY

Hund and Mulliken discover this theory in 1932.

❖ Atomic orbitals with same energy & symmetry combine to form molecular orbitals by LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO)

If Ψ_A & Ψ_B are wave functions of atoms A & B

Then according to LCAO = ΨM.O = $\Psi_A \pm \Psi_B$

❖ Two types of molecular orbitals are formed: bonding and antibonding molecular orbitals. Molecular orbitals formed the additive overlap of two atomic wave functions is known as Bonding Molecular orbital. i.e. $\Psi_b = \Psi_A + \Psi_B$

❖ Molecular orbitals formed by subtractive overlap of two atomic orbitals wave function is called Anti-bonding molecular orbital i.e. $\Psi_a = \Psi_A - \Psi_B$

❖ The number of molecular orbitals formed is always equal is the number of atomic orbitals taking part in bond formation.

❖ Energy level of bonding M.O. is less than that of individual atomic orbitals. So, e^- present in bonding M.O stabilizes the molecule.

❖ Energy level of antibonding M.O is more than that of individual atomic orbitals. So e^- present in anti-bonding M.O destabilizes the molecule.

❖ The atomic orbitals involved in the formation of M.O. completely lose their identity after the formation of molecular orbitals.

❖ Electrons filling in the molecular orbitals follow Aufbau principle, Pauli's exclusion principle & Hunds rule of maximum multiplicity.

❖ Molecular orbitals are polycentric.
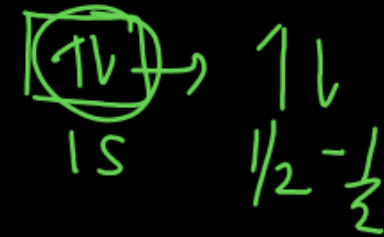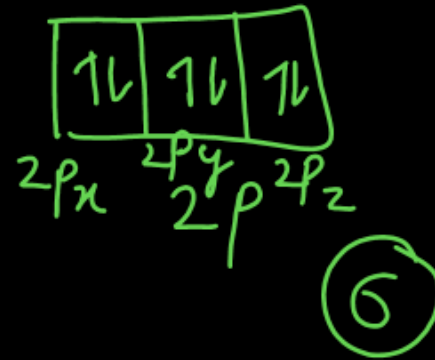
❖ The electrons are filled in the molecular orbitals according to the following order:

2-14

⑭

From H_2 to N_2: $\sigma 1s$, σ^*1s, $\sigma 2s$, σ^*2s, $\pi 2p_x = \pi 2p_y$, $\sigma 2p_z$, $\pi^*2p_x = \pi^*2p_y$, σ^*2p_z

From O_2 to Ne_2: $\sigma 1s$, σ^*1s, $\sigma 2s$, σ^*2s, $\sigma 2p_z$, $\pi 2p_x = \pi 2p_y$, $\pi^*2p_x = \pi^*2p_y$, σ^*2p_z

❖ Molecules or ions with one or more unpaired e- in molecular orbitals are paramagnetic while those with all paired electrons in M.O. are called diamagnetic.

❖ Stability & strength of a chemical bond is expressed in terms of bond order.

❖ B.O is inversely proportion to Bond Length. $B.O \propto \dfrac{1}{B.L}$

❖ B.O is directly proportional to Stability and Bond Dissociation Energy.

$B.O \propto Stability \propto Bond \ D.E$

Bond Order (B.O.)

Bond order is equal to one half of the difference between the number of electrons in bonding M.O & the no. of e- is antibonding M.O.

$$B.O. = 1/2 \, (N_b - N_a)$$

Significance of bond order

- Negative or Zero B.O. Molecule is unstable does not exist.
- Positive value of B.O: Molecule exists & is stable.
- Bond order of +1, +2, +3 indicates the molecule has single, double or triple bond respectively.

ATOMIC ORBITALS	MOLECULAR ORBITALS
They are monocentric.	They are polycentric.
They are less stable.	They are more stable.
Atomic orbitals are of simple shapes.	Molecular orbitals are of complex shapes.
They are represented by s, p, d & f respectively.	They are represented by σ, σ^*, π & π^* respectively.

$\sigma, \sigma^*, \pi, \pi^*$

BONDING MOLECULAR ORBITALS	ANTIBONDING MOLECULAR ORBITALS
They are formed by additive overlapping of atomic orbitals.	They are formed by subtractive overlapping of atomic orbitals.
$\Psi_b = \Psi_A + \Psi_B$ (A and B are two atomic orbitals)	$\Psi_a = \Psi_A - \Psi_B$ (A and B are two atomic orbitals)
Electrons contribute to the formation of bond.	Electrons do not contribute to the formation of bond.
They have low energy and high stability.	They have high energy and low stability.
They are shown as σ, π etc.	They are shown as σ^*, π^* etc.
Maximum electrons are located in between the two nuclei.	Electrons are scattered.
Electron density is higher.	Electron density is lower.
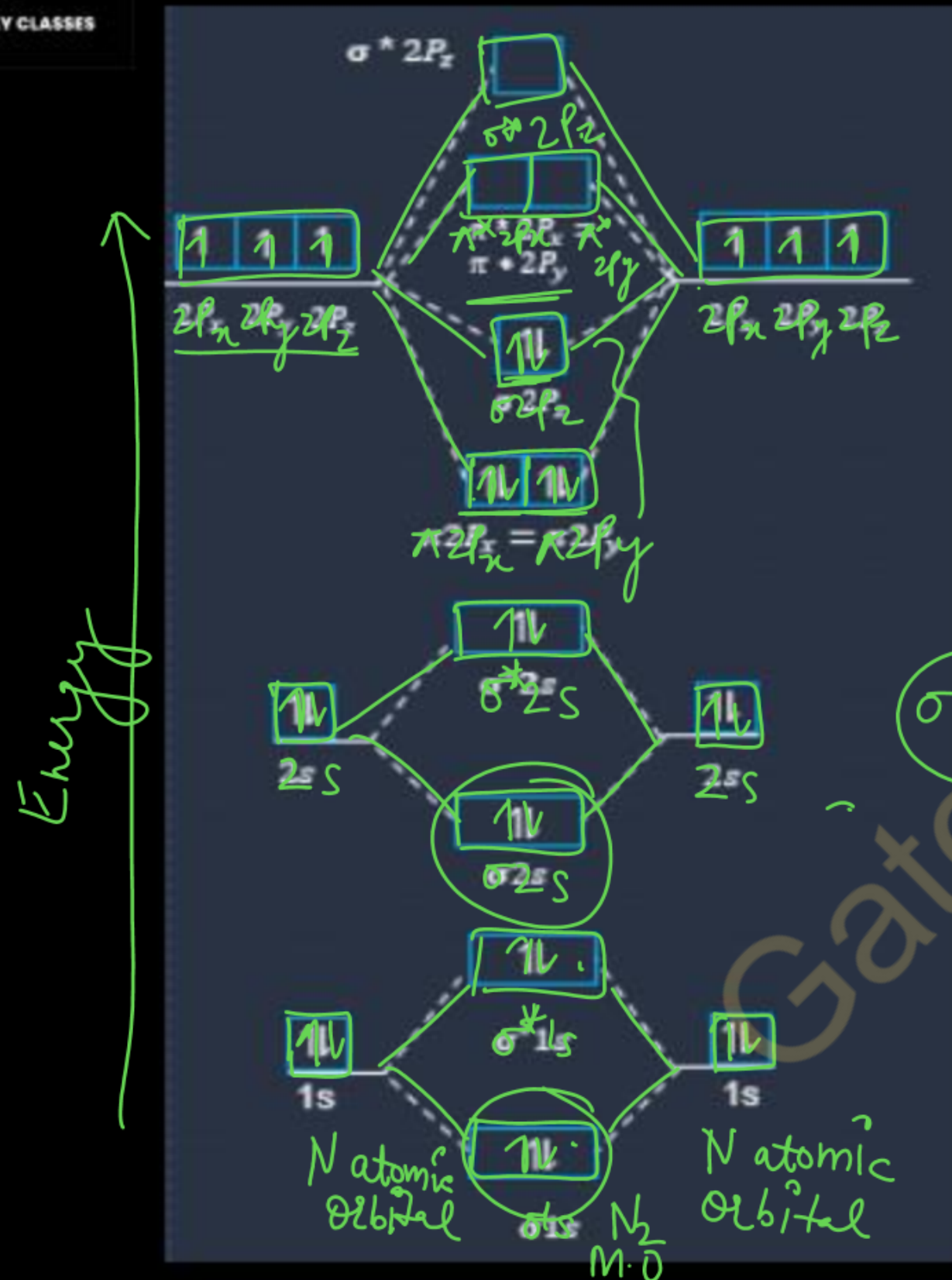
$N \rightarrow 1s^2 2s^2 2p^3$

$$B.O = \frac{1}{2}\{N_b - N_a\}$$

$$= \frac{1}{2}\{10 - 4\} = \frac{6}{2} = 3$$
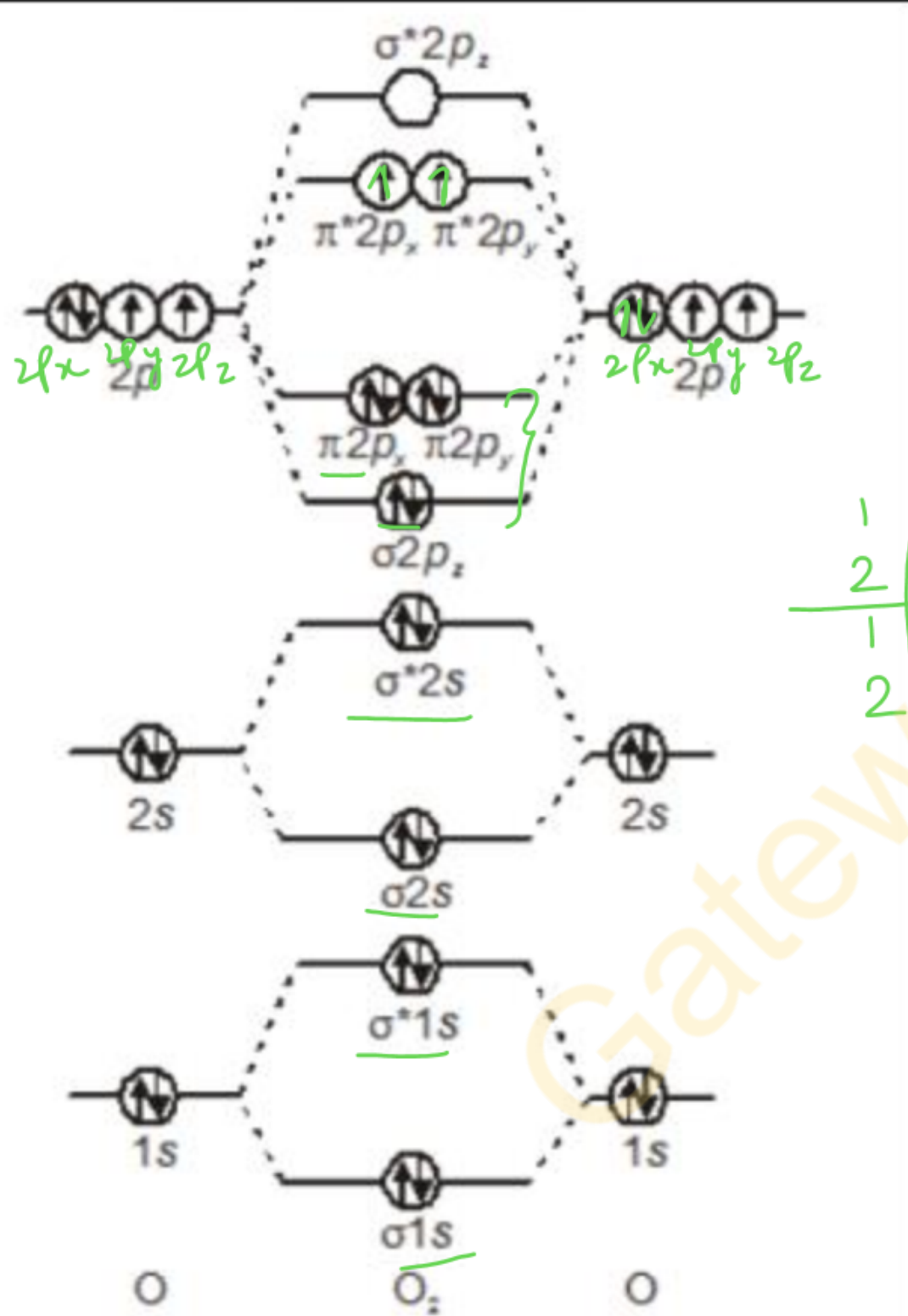
$$\boxed{N \equiv N}$$

σ, π

M.O. Configuration :-

$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \pi 2p_x^2 = \pi 2p_y^2 < \sigma 2p_z^2$

Magnetic Behaviour

Paired $e^{\ominus} \rightarrow$ Diamagnetic

$O \rightarrow 1s^2 2s^2 2p^4$

(16)

$B \cdot O = \frac{1}{2}[10 - 6] = \frac{4}{2} = 2$

$O = O$

Unpaired $\rightarrow$ U. Paramagy

Paired $\rightarrow$ P. Diamag⁻

M.O Configuration :-

$\sigma 1s^2 < \sigma^* 1s^2 < \sigma 2s^2 < \sigma^* 2s^2 < \sigma 2p_z^2 < \pi 2p_x^2 = \pi 2p_y^2$

$< \pi^* 2p_x^1 = \pi^* 2p_y^1$

Magnetic Behaviour

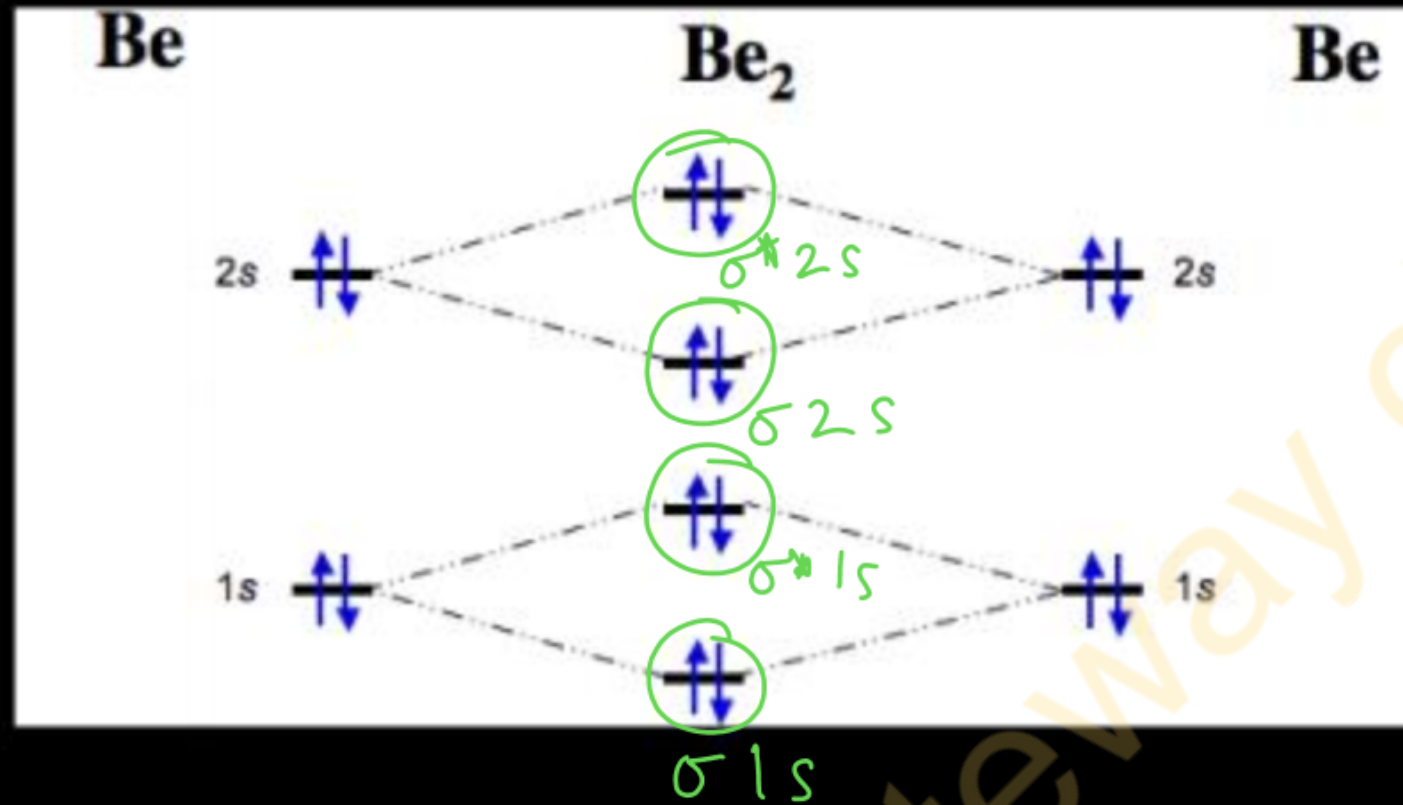Unpaired $e^{\ominus} \rightarrow$ Paramagnetic

$\begin{array}{c|c}
1 & 1 \\
2 & 2 \\
1 & 2 \\
2 & 1
\end{array}$ A B·O / B·O

$$f \to 1s^2 2s^2 2p^5$$

$$\textcircled{14} \quad \to \quad \begin{matrix} 1 \\ 2 \\ 1 \\ 2 \end{matrix} \quad \begin{array}{c} \frac{1}{2} \} \\ \frac{2}{2} \} \\ 1 \} \end{array}$$

$$B.O = \frac{1}{2}[10-8]$$

Paired - Diamagnetic $= \frac{2}{2} = \textcircled{1}$

$$\boxed{\bigcirc \, F - F \,}$$

MOLECULAR ORBITAL DIAGRAM OF Be_2 MOLECULES

$Be \rightarrow 1s^2 2s^2$
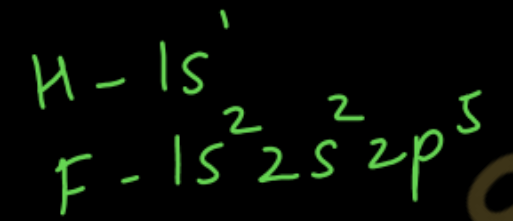

$B.O = \dfrac{1}{2} [N_b - N_a]$

$= \dfrac{1}{2} [4 - 4] = 0$

Be_2 molecule does not exist

$H - 1s^1$

$F - 1s^2 2s^2 2p^5$
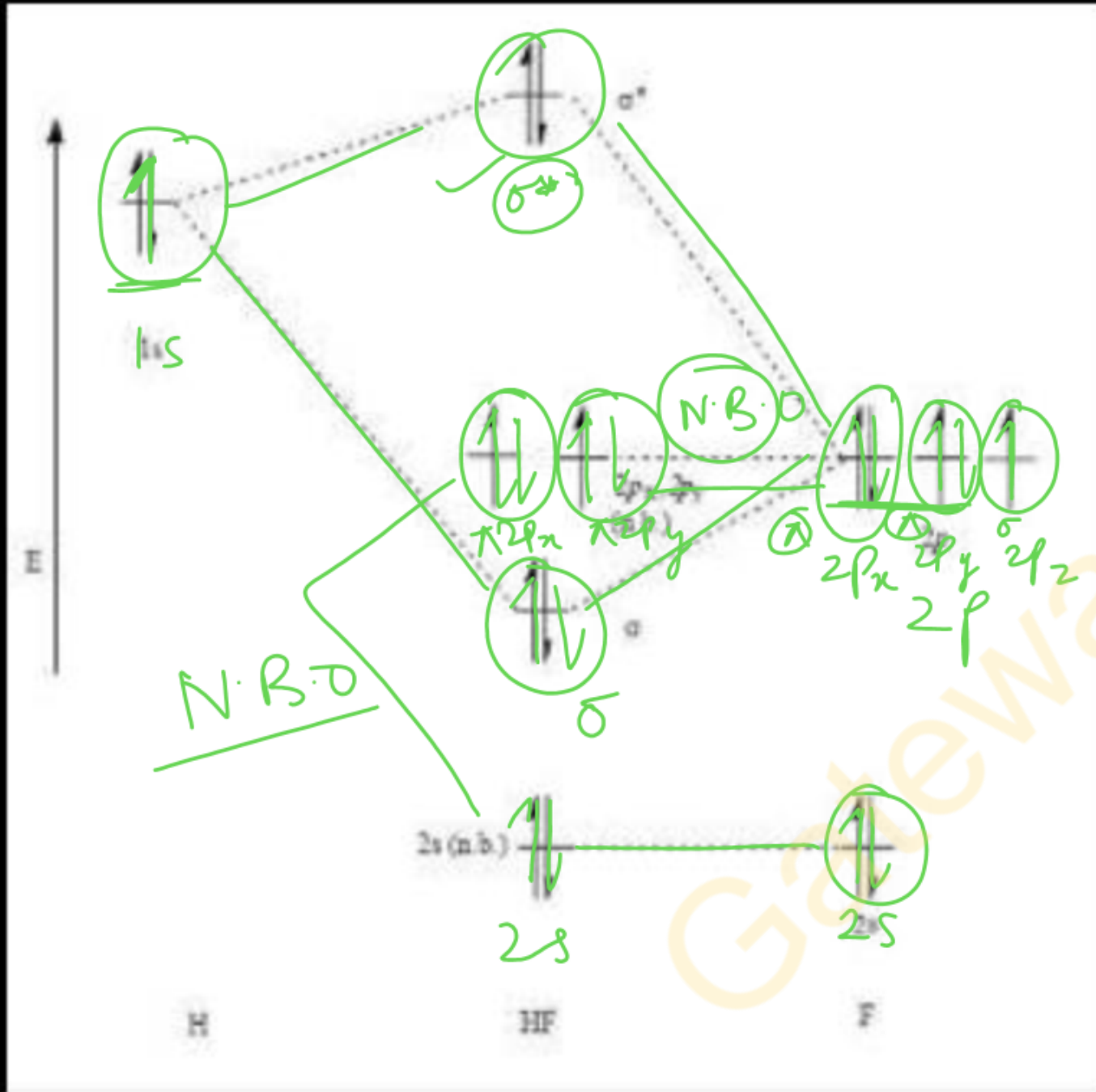
$B.O = \dfrac{1}{2}\{2 - 0\} = \dfrac{2}{2} = 1$

$H - F$

MOLECULAR ORBITAL DIAGRAM OF HCl MOLECULES

$H - 1s^1$

$Cl \ 1s^2 \ 2s^2 \ 2p^6 \ \underline{3s^2 \ 3p^5}$

$$B.O = \frac{1}{2}\left[N_b - N_a\right]$$

$$= \frac{1}{2}\left\{2 - 0\right\} = \frac{2}{2} = 1$$

$\boxed{H - Cl}$
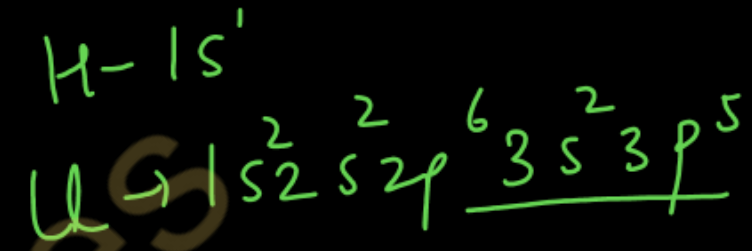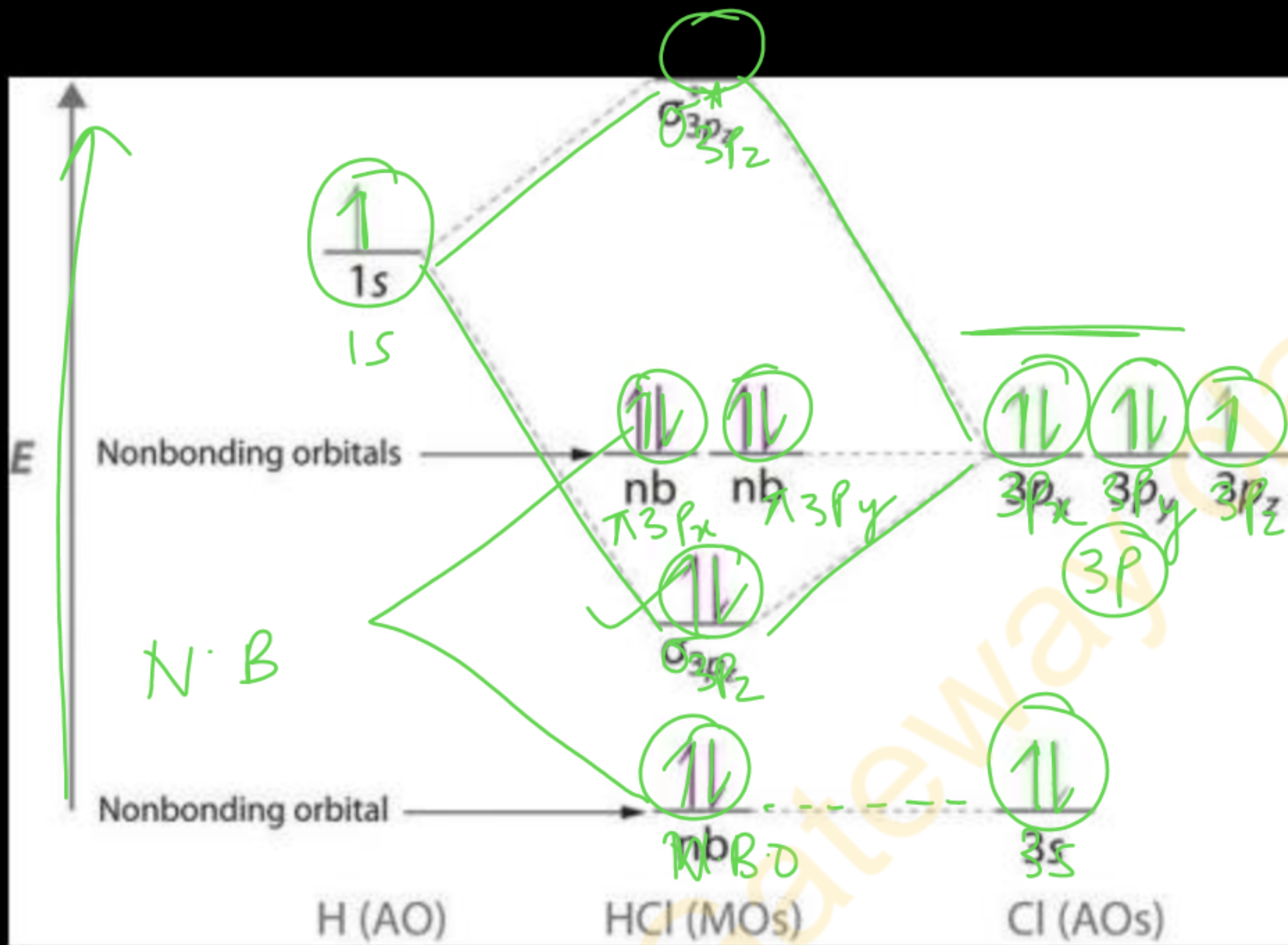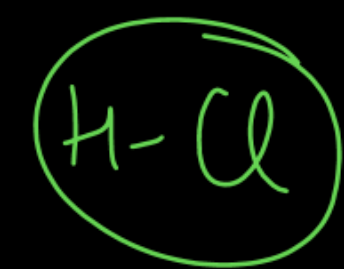
Magnetic Behaviour

$P \rightarrow$ Diamagnetic

M.O diagram of CO.

$C \rightarrow 1S^2 2S^2 2p^2$

$O \rightarrow 1S^2 2S^2 2p^4$

$\sigma^* 2p_z$

$\pi^* 2p_x \quad \pi^* 2p_y$

$\sigma^* 2s$

$\sigma 2p_z$

$\pi 2p_x \quad \pi 2p_y$

$2p_x \quad 2p_y \quad 2p_z$

$2p$

$2s$

$\sigma 2s$

$\sigma^* 2s$

$1S$

C atomic Orbital

$\sigma 1s$

$2p_x \quad 2p_y \quad 2p_z$

$2p$
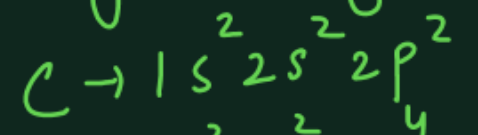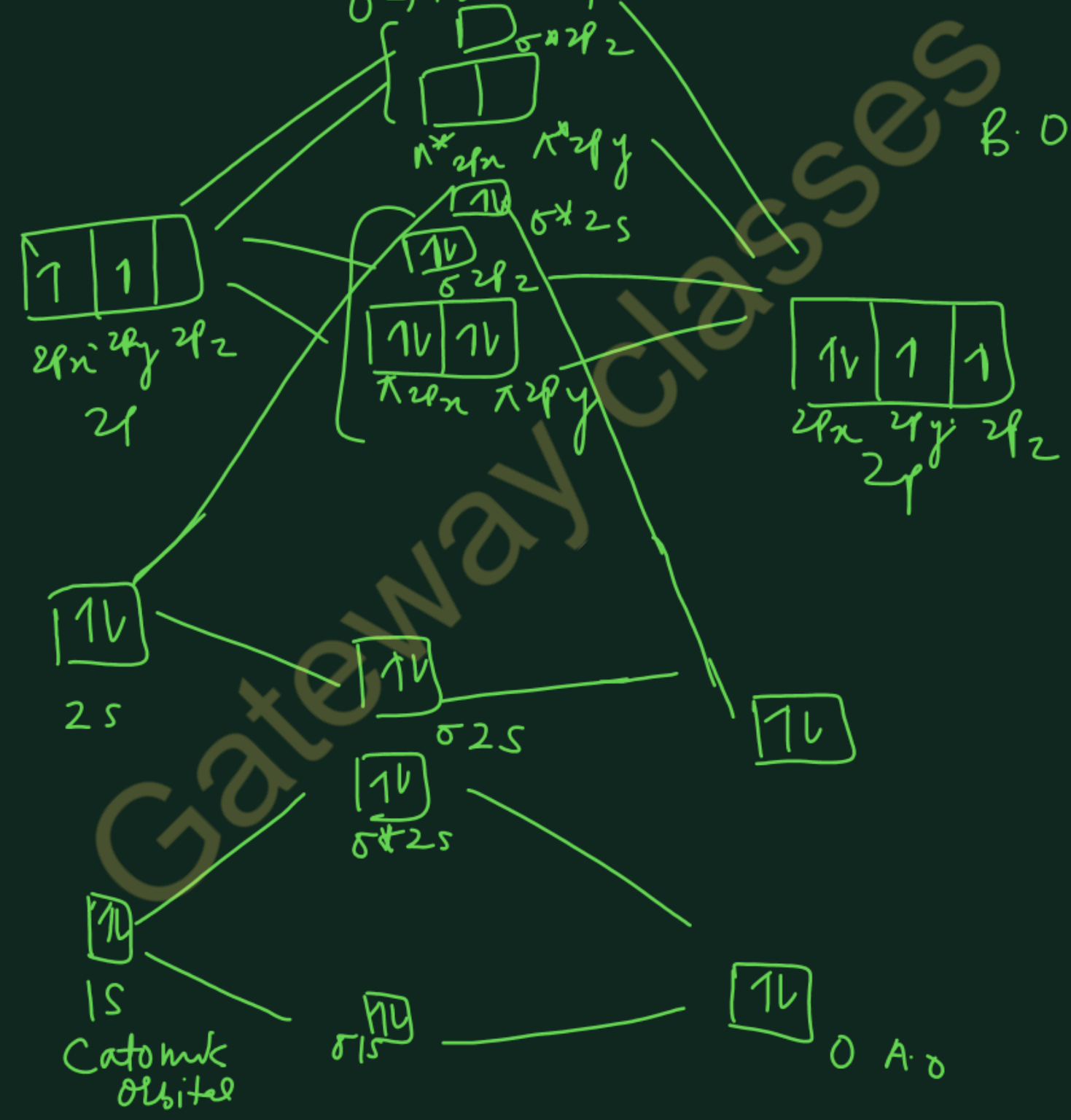
B.O =

M.O Configuration

Paired — Diamagnetic

O A.O

Graphite structure

0.14 nm

Covalent bonds

Carbon bonds

Vander Waals bonds

0.34 nm
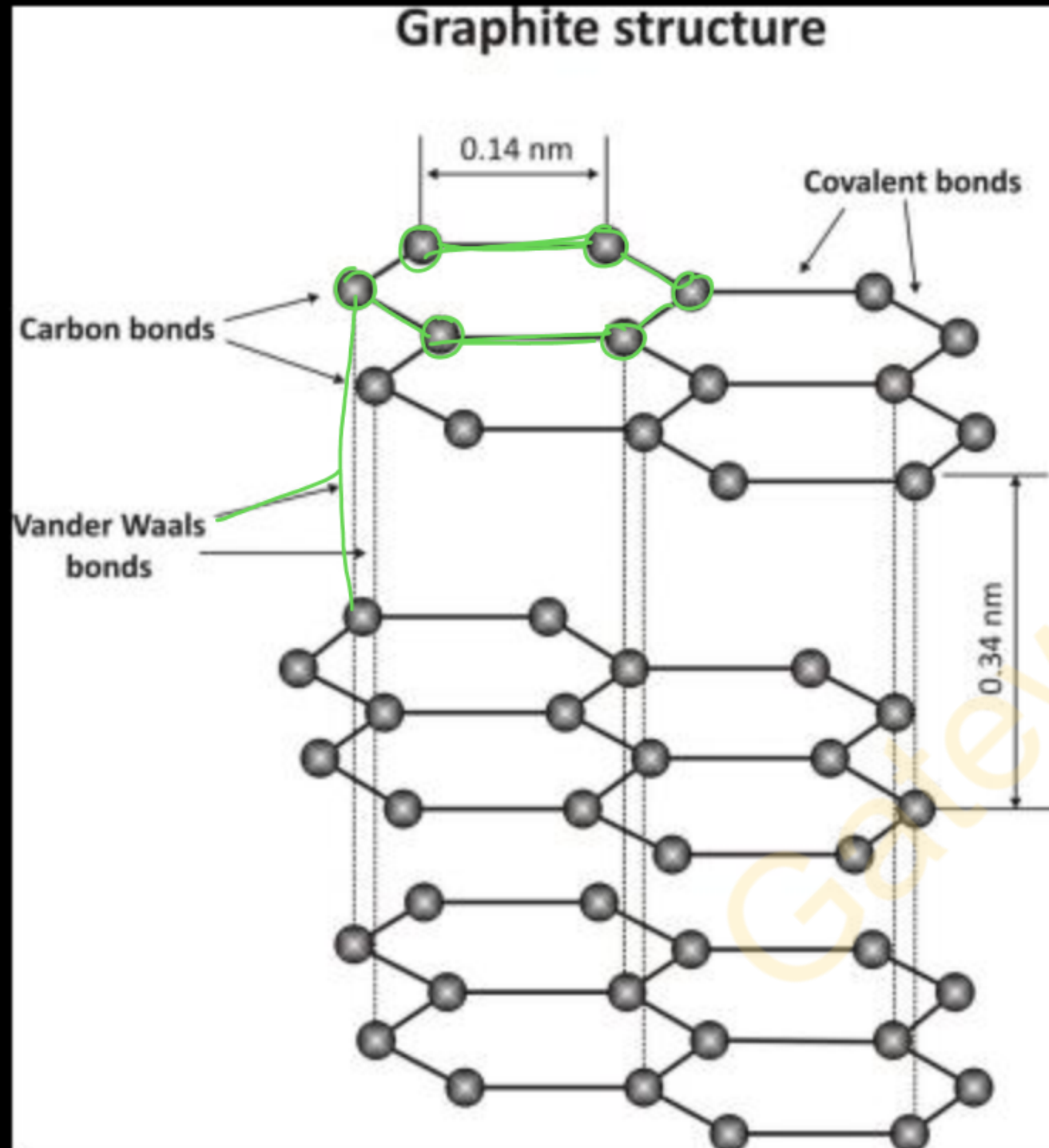
- Each carbon atom in graphite is sp^2 hybridized.

- 6 such carbon atoms join with the covalent bonds to form hexagons.

- Fourth electron of each carbon atom is free to move within the layer.

- Various hexagons join together to form a plane or sheet called graphene.

- Different layers of graphite are attached to each other with weak Vander Waals forces.

1. It is greyish black and greasy substance.
2. Has metallic luster and is opaque to light.
3. High Melting point because the strong covalent bonds take long time to break.
4. Slippery in nature / Layers can slide one another due to weak Vander Waal forces of attraction between the two layers.
5. Thermodynamically more stable than diamond.
   Graphite exists in two forms: α-graphite (layers are arranged in sequence ABABAB------ with third layer exactly above the first layer) and β-graphite (layers in the sequence ABCABCABC-------).
6. Graphite is a conductor due to the presence of free electron in p_z orbital of each carbon.

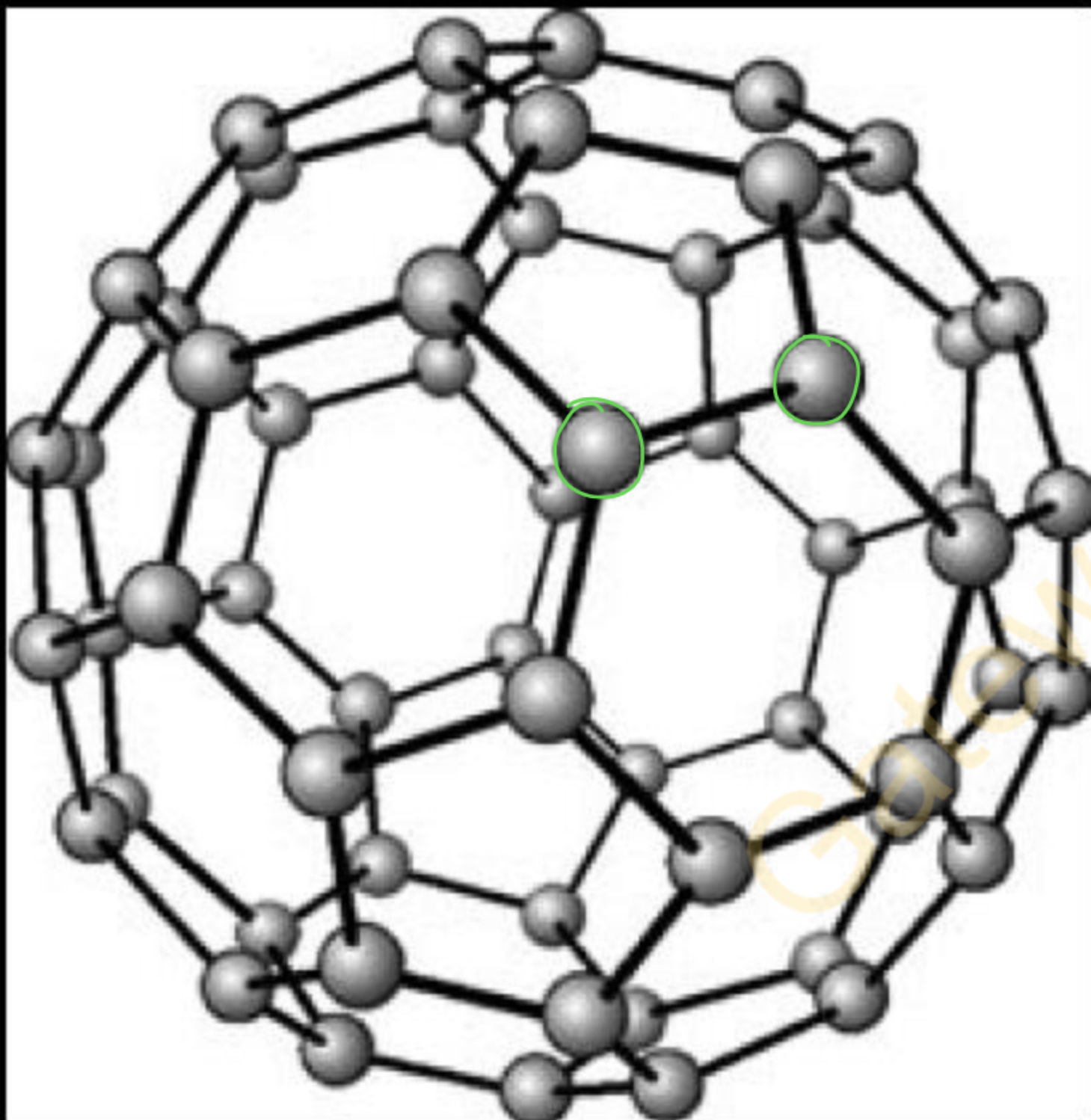# APPLICATIONS OF GRAPHITE

1. Used as a lubricant as layers can slide over one another due to weak Vander Waals forces.

2. Used in pencil leads due to soft, slippery nature and it leaves a black mark on paper when rubbed against it.

FULLERENE

- Made up of 60 carbon atoms.

- Each carbon atom is sp^2 hybridized, forming three bonds and having one unpaired electron.

- There are 12 pentagons & 20 hexagons of C atoms.

- No two pentagons touch each other.

- There are 60 vertices, 32 faces.

- C-C single bond length-104.5 A°; C=C double bond length=1.38 A°.

PREPARATION OF FULLERENE

Graphite rods kept in an inert atmosphere (He gas)
At 0.05 to 0.1 atm pressure.

↓ Electric current

Rods evaporate to give fullerene soot (light and fluffy dust)
Containing 5 to 15 % fullerenes.

↓ Sublimation

Fullerene mixture.

PROPERTIES OF FULLERENE

1. Mustard colored solid and looks brown and black as its thickness increases.

2. Basically semiconductors but on doping with alkali metals can be converted into conductor or super conductor.

3. Shows poor aromatic nature.

4. Strongest known material to man.

5. Exists as discrete molecule unlike graphite or diamond.

NANOMATERIALS

Nanomaterials are materials having at-least one of its dimensions in the nanometer scale $(1 \text{ nm} = 10^{-9} \text{ m})$.
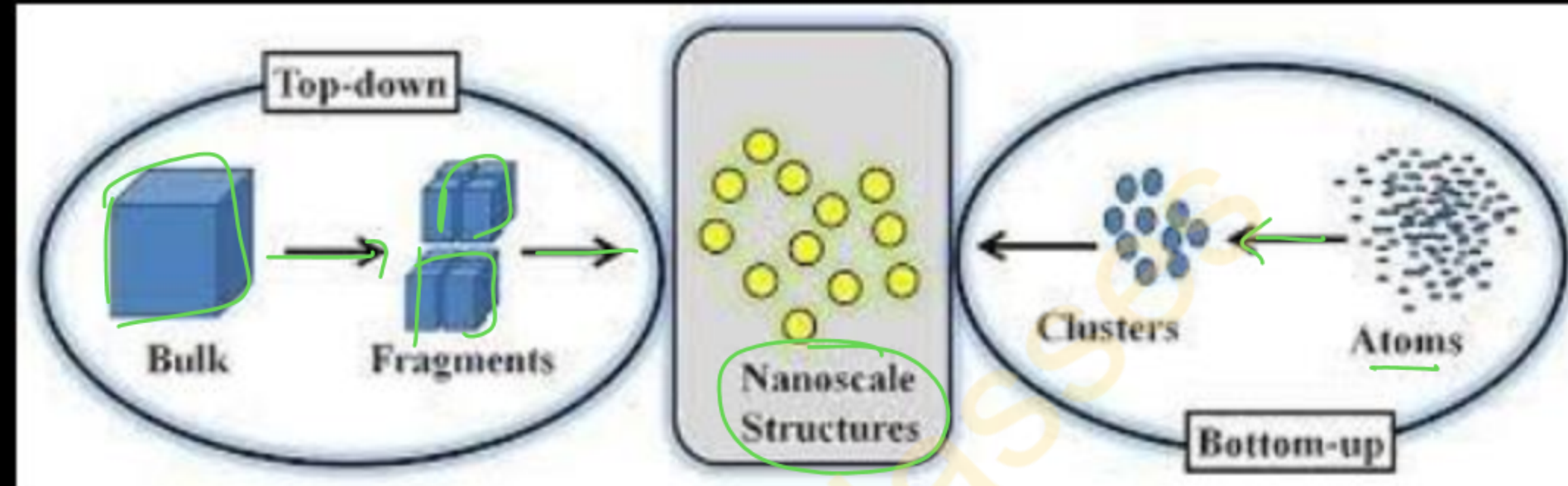
Nanostructured materials: Nanomaterial can be zero, one, two or three dimensional.
   (1) Nanoparticles   (2)   Nanowires   (3) Nanotubes
   (4) Nanorods   (5)   Nanoporous materials

NANOMATERIAL SYNTHESIS APPROACH

1. Top down approach: Breaking of bulk material
2. Bottom approach: Buildup of material Atom $\longrightarrow$ molecule $\longrightarrow$ cluster

Applications of nanomaterials

- Electronics
- Medicine, Nanomedicine, drug delivery systems, disease diagnosis
- Engineering and Technology, Nanotransitors, Field effect transistors
- Environment
- Sensors
- Catalysis
- Magnetic materials, Magnetic storage disk materials

CARBON NANO TUBES (CNT)

A carbon nanotube (CNT) is one of the most important nanomaterials. Before 1991, only two main allotropes of carbon were known. In 1991, a Japanese physicist, Sumio Lizima invented CNT (another allotrope of carbon). Carbon nanotubes are also called buckytubes.
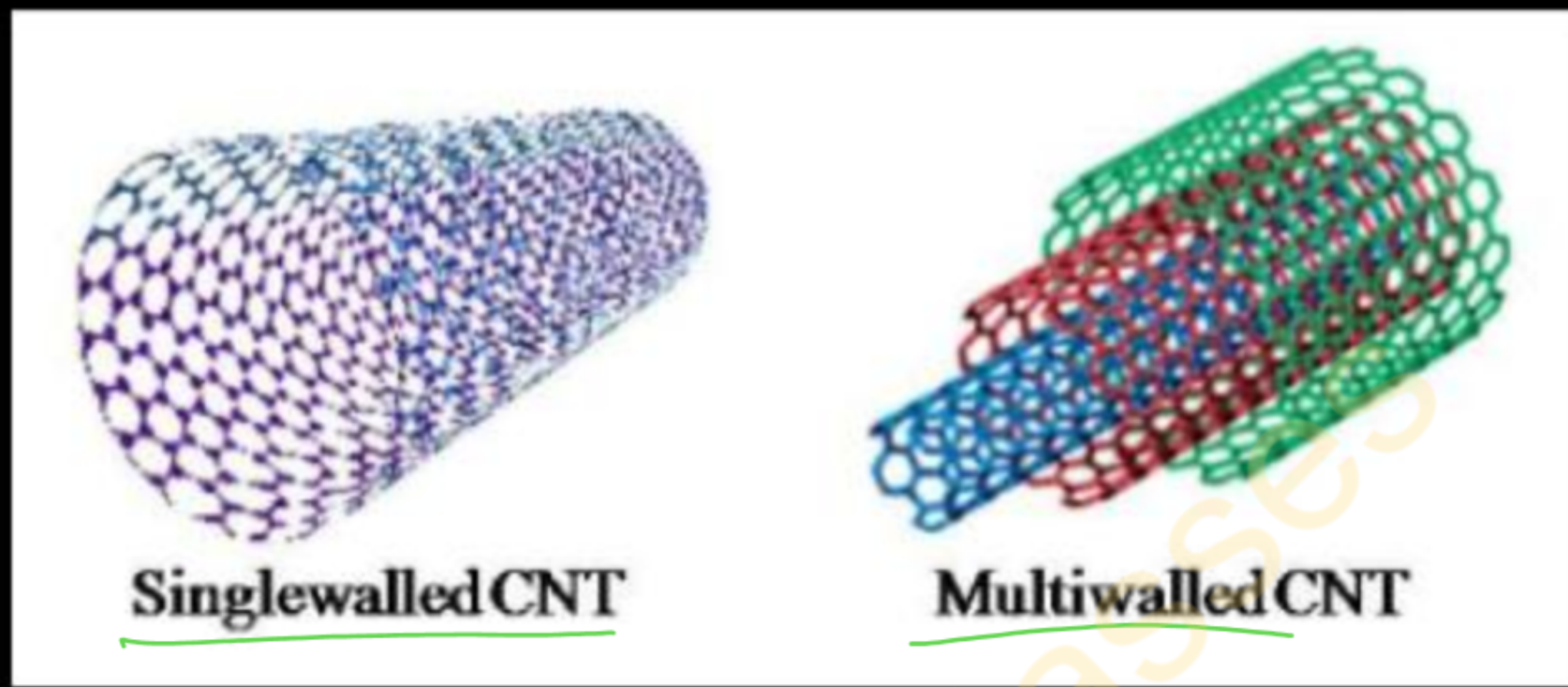
TYPES OF CARBO NANOTUBES

1. Single-walled Carbon Nanotubes:
It is represented as SWCNT. The Single-walled Carbon nanotubes exist in a 1-d structure.
Example: Armchair and zig-zag Single-walled Carbon nanotubes.

2. Multi-walled Carbon Nanotubes:
It is represented as MWCNT. It is composed of several nested carbon nanotubes. This type of nanotubes has two diameters, one is known as outer diameter and another one is known as inner diameter.
Example: Chiral Multi-walled Carbon nanotubes.

Single walled CNT **Multiwalled CNT**

Properties of Carbon Nanotubes

1. Carbon nanotubes have a high thermal capacity. Generally, it is twenty times stronger than steel. Therefore, CNTs are used in making bridges and aircrafts material.
2. In carbon nanotubes, each carbon atom is surrounded by three other carbon atoms through covalent bonds and form lattices in the shape of hexagons.
3. The crystalline structure of carbon nanotubes exists in the form of regular hexagons.
4. Carbon nanotubes are good conductors of heat.
5. Carbon nanotubes have good electrical conductivity.
6. Carbon nanotubes are chemically neutral. Therefore, carbon nanotubes resist corrosion.

APPLICATIONS OF CARBON NANOTUBES

1. To make clothes, sportswear to combat and spacesuits.
2. To make bullet- proof jackets.
3. In developing nanoscale electric motors.
4. As catalysts in some reactions.
5. CNTs are also used in space and aircraft to reduce the weight and stress of the various components working together.
6. Windmill blades.
7. Carbon nanotubes as Nano cylinders.

Liquid Crystals

Liquid crystal is a state of matter whose properties are between those of conventional liquids and those of solid crystals.

A liquid crystal may flow like a liquid, but its molecules may be oriented in a crystal-like way.

| SOLID | → Transition Point → | TURBID LIQUIDS (LIQUID CRYSTALS) | ← Melting Point ← | CLEAR LIQUIDS |

The liquid-crystalline state is often called mesomorphic state (mezos meaning "intermediate"), and the liquid crystals are called mesophase.

1. **Positional order:** The extent to which an average molecule or group of molecules shows translational symmetry (as crystalline material shows).
2. **Orientational order:** It represents tendency of the molecules to align along the director on a long-range basis.

NOTE:

Positional order + Orientational order = Crystal phase

Varying Positional order + Orientational order = LC phase

Essential requirements for a molecule to be a Liquid Crystal

(1) Presence of carboxylic group at the end of chain.
(2) Molecule must be anisotropic in nature.
(3) Absence of bulky functional groups.
(4) Presence of unsaturation in molecule.
(5) Molecule must have some rigidity in its central region and the ends must be flexible.

Properties of Liquid Crystals

(1) Each molecule is oriented at some angle to the director.
(2) Molecule must be anisotropic in nature.
(3) These molecule posses very strong dipole moment.
(4) The liquid crystal molecules prefer to align parallel to each other because of strong intermolecular attraction (pi-pi interaction)

(1) Thermotropic Liquid Crystal
(2) Lyotropic Liquid Crystal

(1) **Thermotropic liquid crystals:** They are formed by change of temperature. They occur as liquid crystals over a certain temperature range between the solid and liquid phase. Example – LCD TV's, alarm clocks.

These liquid crystals are further classified into:

a) Nematic Liquid Crystals
b) Smectic Liquid Crystals
c) Cholesteric Liquid Crystals
d) Discotic Liquid

**(a) Nematic liquid crystals:** Word nematic is derived from the Greek word, 'Nema' which means "thread".

Properties:
(1) No positional order, but possess orientational order.
(2) Do not have layered structure.
(3) Flow like normal liquids.
(4) They have low viscosity.
(5) Can be aligned by the application of electric on magnetic field.
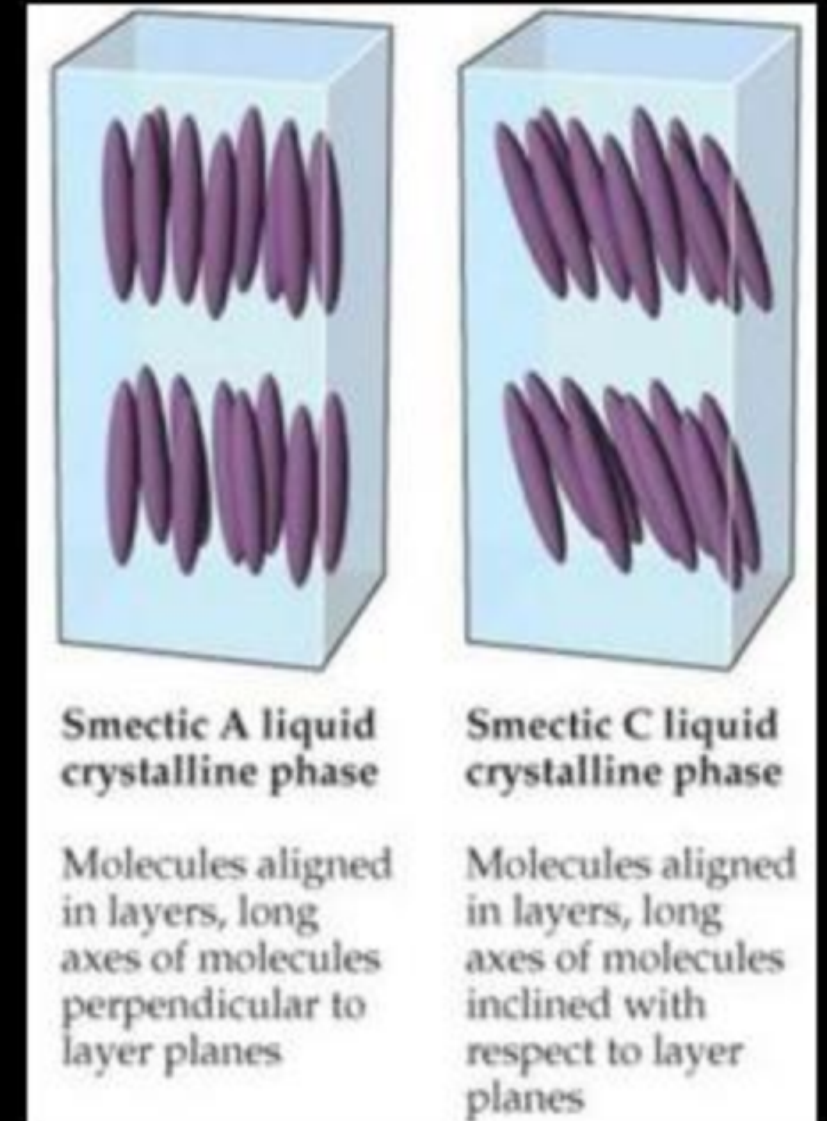(6) Flow in all directions but not in layers.
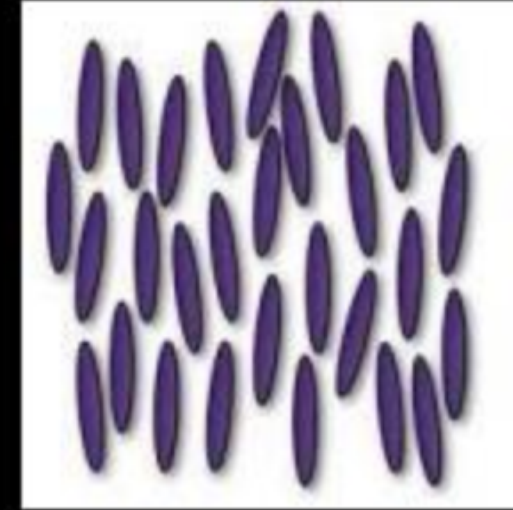
Example: p-azoxyanisole
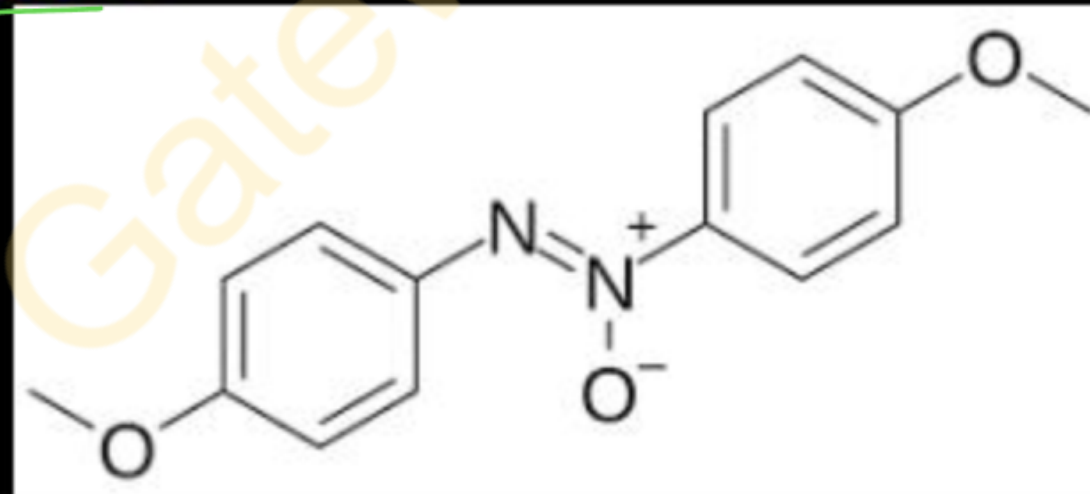
b) Smectic Liquid Crystals: A type of liquid crystals that have well-defined layers of molecules that are able to slide over one another.

Properties

(1) They are soap like and are greasy in nature.
(2) Molecules are cigar shaped.
(3) These are arranged in layers i.e. have layered structure.
(4) They do not flow like normal liquids and has limited mobility.
(5) They have high viscosity.
(6) Formed at comparatively lower temperature.
(7) Not affected by external electric or magnetic field.
(8) Molecules are free to move within the layers but not from one layer to another.

**Smectic A liquid crystalline phase**

Molecules aligned in layers, long axes of molecules perpendicular to layer planes

Smectic C liquid crystalline phase

Molecules aligned in layers, long axes of molecules inclined with respect to layer planes

Nematic Liquid Crystals	Smectic Liquid Crystals
They are thread like.	They are soap like and are clayey or greasy.
Molecule have elongated rod like shape.	Molecules are cigar shaped.
Do not have layered structure.	These are arranged in layers i.e. have layered structure.
Total loss of positional order but they have orientational order	Have short range orientational as well as positional order.
Flow in all directions & not in layers.	Flow in layers and difference layers can slide over one another.
Can be aligned by the application of electric on magnetic field.	Not affected by external electric or magnetic field.
Molecules are free to move in all the directions.	Molecules are free to move within the layers but not from one layer to another
They have low viscosity.	They have high viscosity.
Formed at relatively higher temperature.	Formed at comparatively lower temperature.
E.g.- p-azoxy anisole	E.g. - Ethyl-p-azoxyphenetole

c) Cholesteric Liquid Crystals: Cholesteric liquid phase is composed of molecule containing a chiral centre. This phase is usually observed from cholesterol derivatives.

Properties:

(1) The molecules are arranged in layers like Smectic liquid crystals.

(2) The structure of layers is similar to nematic phase and so it is also known as chiral nematic.

(3) Each layer is tilted with respect to the other one, and hence the molecules take a one complete turn of 360 degrees to make a helix.

(4) The distance covered by the director in making a one complete turn is known as pitch.

(5) Pitch is inversely proportional to the temperature. It is effected by temperature, pressure and electric & magnetic fields.

Nematic phase   Smectic phase   Cholesteric phase
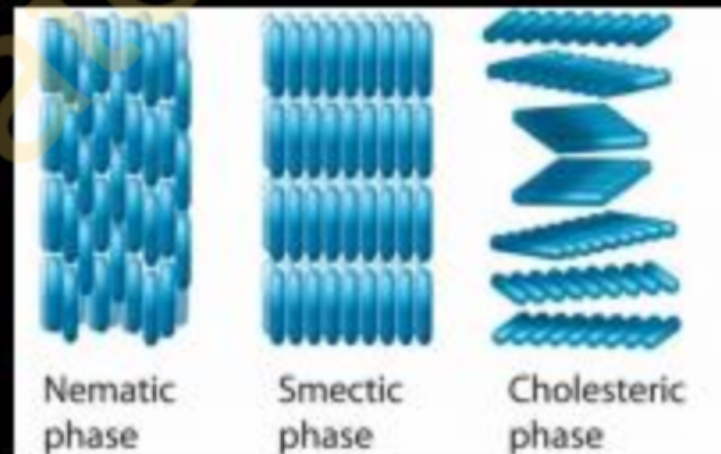
d) Discotic Liquid Crystals: Discotic mesogens are typically composed of an aromatic core surrounded by flexible alkyl chains.

Properties:
   (1) Molecules are essentially disc shaped.
   (2) The aromatic cores allow charge transfer in the stacking direction through the π conjugate systems.

Discotic Liquid Crystals are of two types:

   (i) Disc-shaped molecules have a tendency to lie on top of one another forming either discotic nematic phases (with discs oriented similarly)
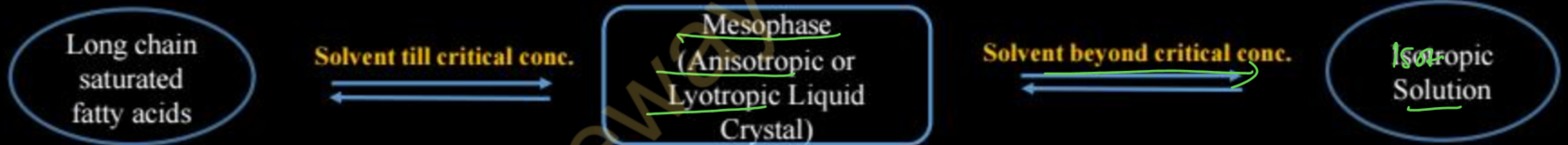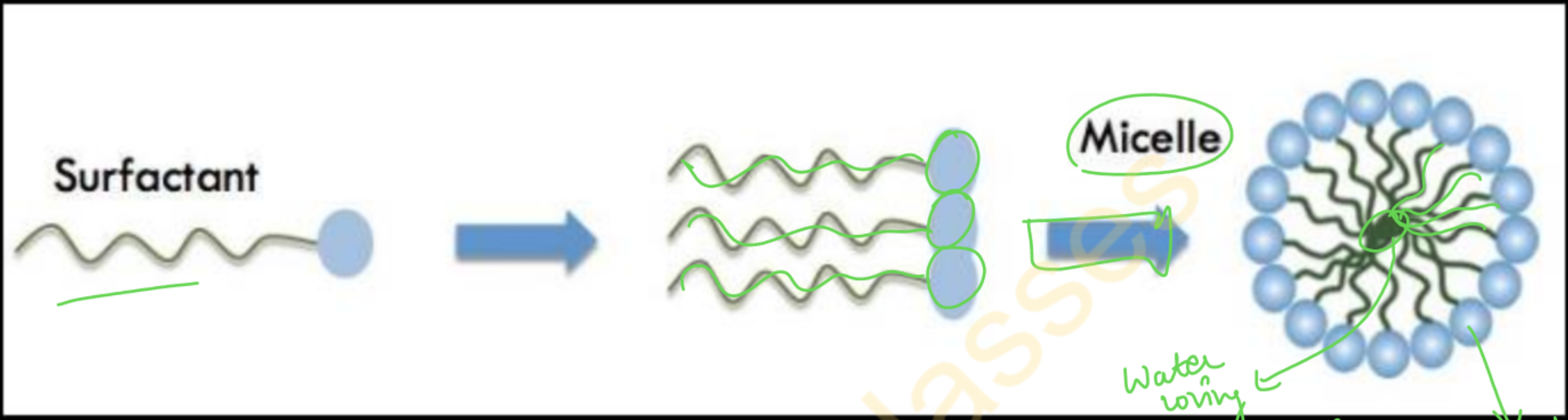   (ii) Columnar phases (which, obviously, have column-like structure).

Discotic Nematic   Discotic Columnar
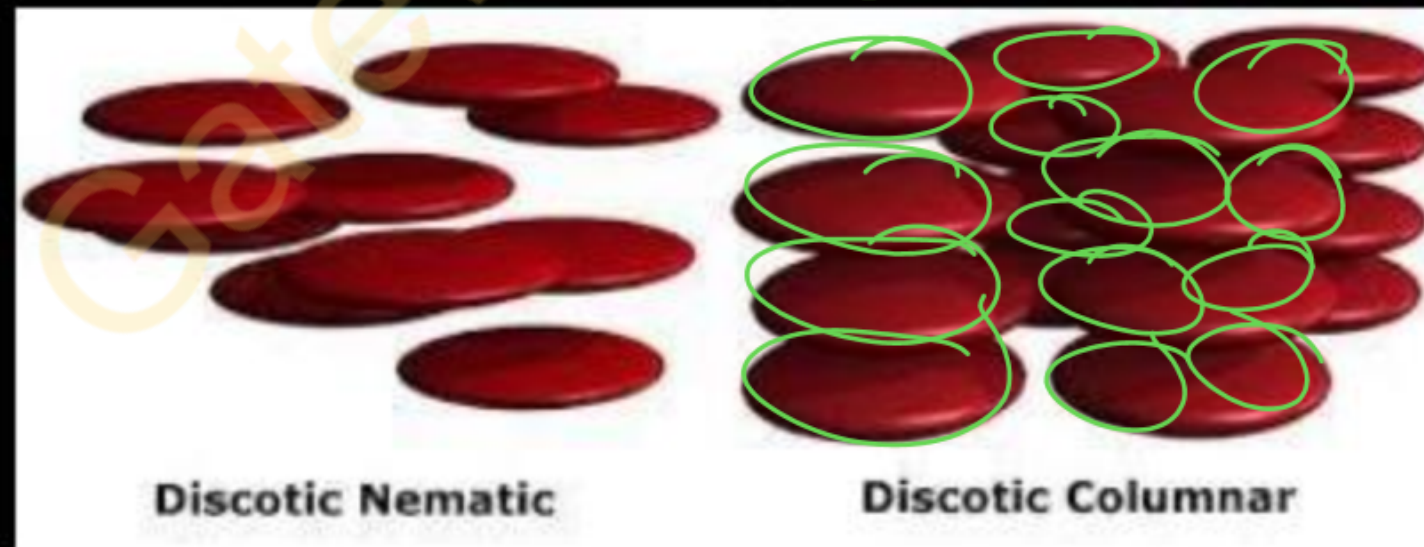
(2) Lyotropic Liquid Crystals:

These are made on change in the concentration of solvent and/or change in temperature.

Properties

(1) These are solvent and concentration dependent.

(2) LLC are made by adding solvent to the solid until critical micelle concentration (CMC) is reached. On further addition of solvent LLC changes into liquid phase.

Long chain saturated fatty acids — Solvent till critical conc. → Mesophase (Anisotropic or Lyotropic Liquid Crystal) — Solvent beyond critical conc. → Isotropic Solution

Surfactant

Micelle

Water loving
hydrophillic

Hydrophobic

APPLICATIONS OF LIQUID CRYSTALS

(1) Liquid crystals are used for decorative purpose in cosmetics.

(2) LLC's based delivery system such as cream, ointment; transdermal patches etc. have been used in pharmaceutical.

(3) Thermotropic Cholesteric liquid crystals are used in body care cosmetics.

(4) Due to their colour effect Cholesteric liquid crystals are used in nail paints, eye shadows etc.

(5) Discotic liquid crystals are used in photovoltaic devices, organic light emitting diodes (OLED), and molecular wires.

(6) Liquid crystals are used for displays in LCD's, calculator, wrist watches etc. Cholesteric liquid crystals are used in coloured thermometers.

1. **Prevent waste**: Design chemical syntheses to prevent waste. Leave no waste to treat or clean up.

2. **Maximize atom economy**: Design synthesis so that the final product contains the maximum proportion of the starting materials. Waste few or no atoms.

    reactant

3. **Design less hazardous chemical synthesis**: Design syntheses to use and generate substances with little or no toxicity to either humans or the environment.

4. **Design safer chemicals and products**: Design chemical products that are fully effective yet have little or no toxicity.

5. **Use safer solvents and reaction conditions**: Avoid using solvents, separation agents, or other hazardous chemicals. If you must use these chemicals, use safer ones.

6. Increase energy efficiency: Run chemical reactions at room temperature and pressure whenever possible.

7. Use renewable feedstocks: Use starting materials (feedstocks) that are renewable. The source of renewable feedstocks is often agricultural products or the wastes of other processes.

8. Avoid chemical derivatives: Avoid using blocking or protecting groups or any temporary modifications if possible. Derivatives use additional reagents and generate waste.

9. Use catalysts, not stoichiometric reagents: Minimize waste by using catalytic reactions. Catalysts are effective in small amounts and can carry out a single reaction many times. They are preferable to stoichiometric reagents, which are used in excess and carry out a reaction only once.

10. **Design chemicals and products to degrade after use**: Design chemical products to break down to innocuous substances after use so that they do not accumulate in the environment.

11. **Analyze in real time to prevent pollution**: Include in-process, real-time monitoring and control during syntheses to minimize or eliminate the formation of byproducts.

12. **Minimize the potential for accidents**: Design chemicals and their physical forms (solid, liquid, or gas) to minimize the potential for chemical accidents including explosions, fires, and releases to the environment.

GREEN CHEMICALS

A green chemical is one that provides higher performance and functionality while being more environmentally benign throughout its entire life-cycle. This approach has been categorized in the Twelve Principles of Green Chemistry that provide a framework for innovation and design.

GREEN CHEMISTRY

It 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.

(1) Reduction of Benzene

$$\underset{\text{(benzene)}}{\bigcirc} \xrightarrow[\text{Pt/Ni}]{H_2} \bigcirc$$

(2) Oxidation of cyclohexane

$$\bigcirc \xrightarrow[\text{(Co. Catalyst)}]{O_2} \underset{\text{cyclohexanone}}{\bigcirc} + \underset{\text{Cyclohexanol}}{\overset{OH}{\bigcirc}}$$
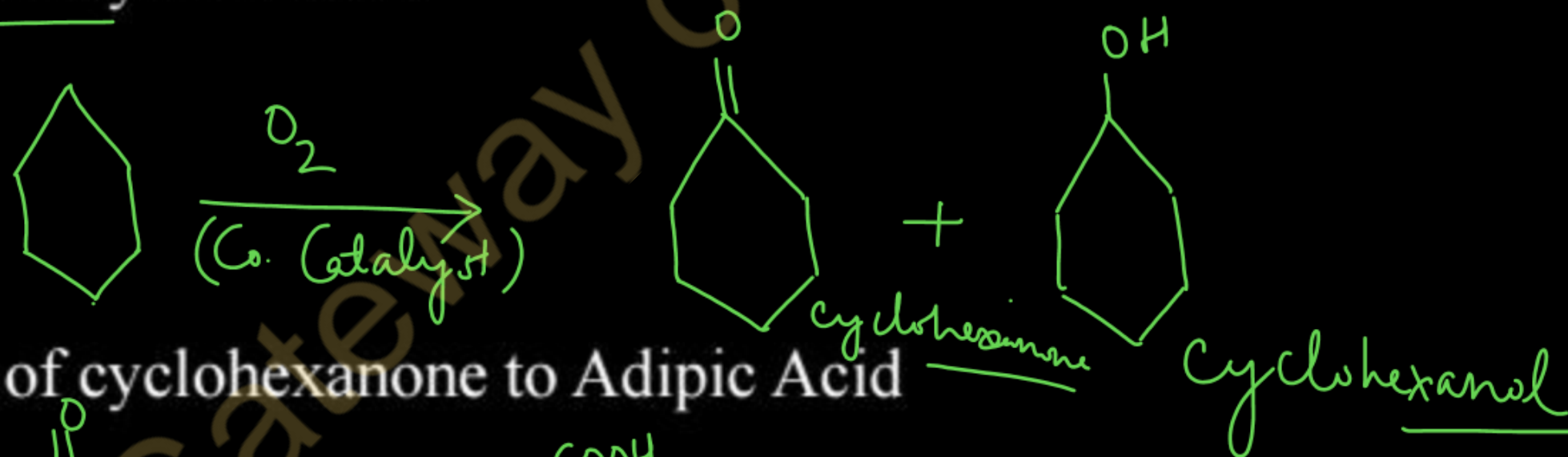
(3) Oxidation of cyclohexanone to Adipic Acid

$$\bigcirc \xrightarrow{HNO_3} \underset{\text{Adipic acid}}{\overset{COOH}{\underset{COOH}{\bigcirc}}} \quad \text{or} \quad HOOC(CH_2)_4 COOH$$
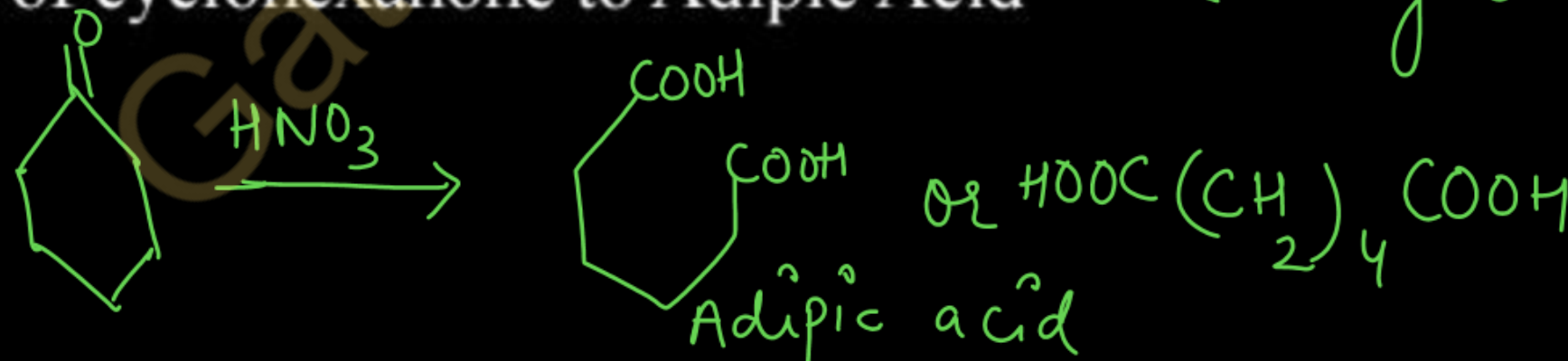
(1) Reduction of Glucose by E. coli
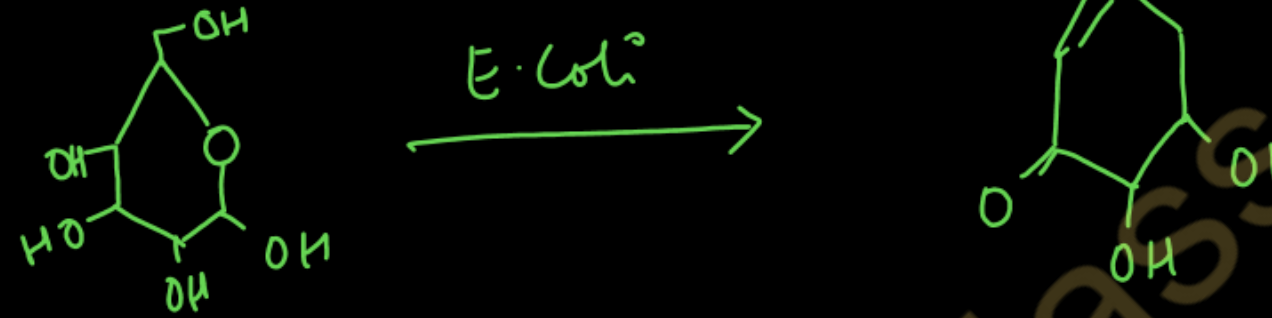
(2) Reduction of 3 hydroxyshikimate
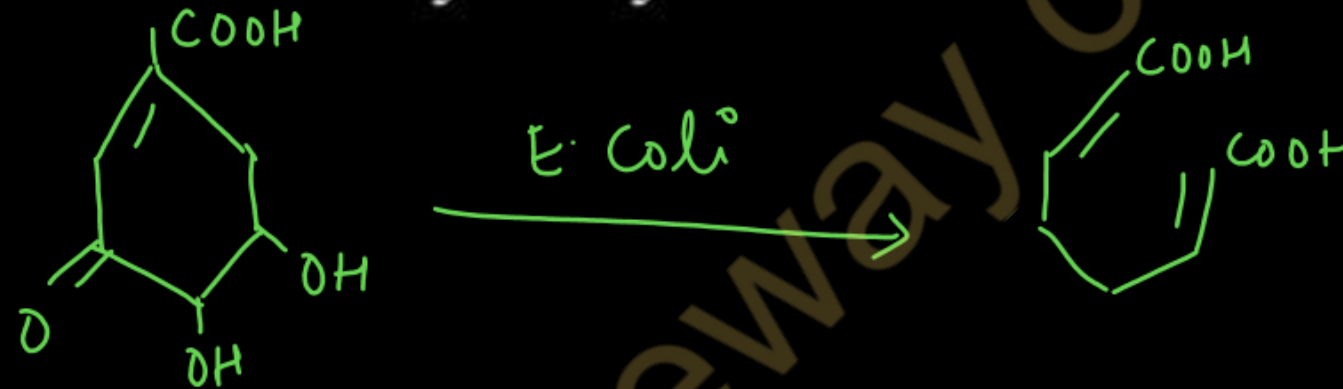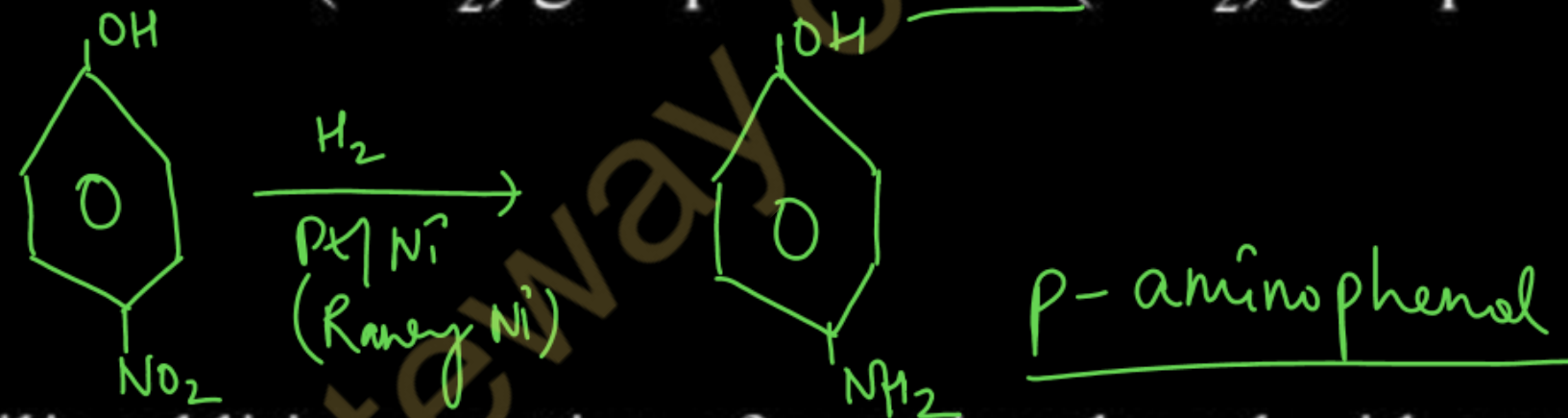

(3) Reduction of cis-cis muconic acid to Adipic Acid

Adipic acid
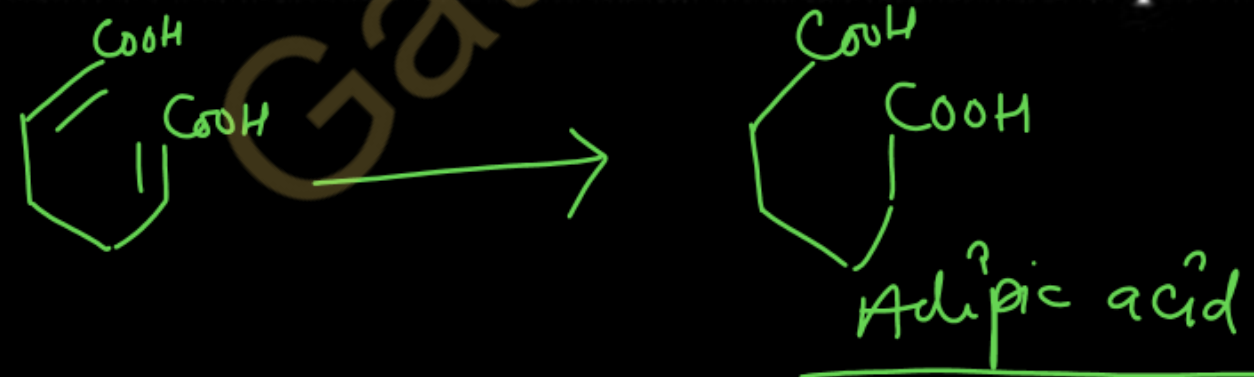
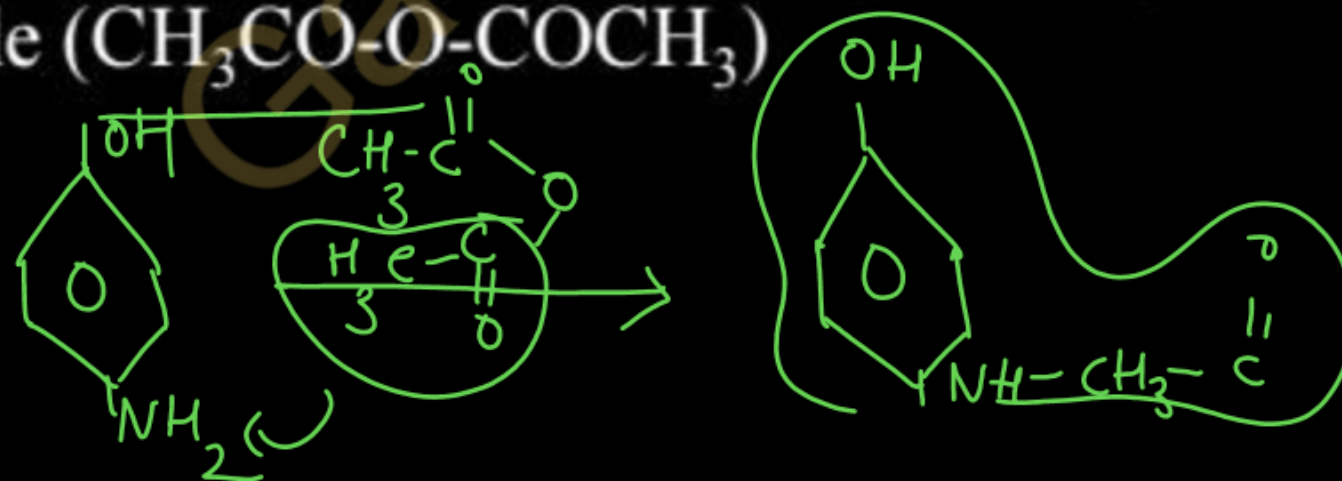# SYNTHESIS OF PARACETAMOL BY CONVENTIONAL METHOD

(1) Nitration of Phenol using nitrating mixture ($HNO_3+H_2SO_4$)

$HNO_3 + H_2SO_4$

(minor)

NO_2 (major)
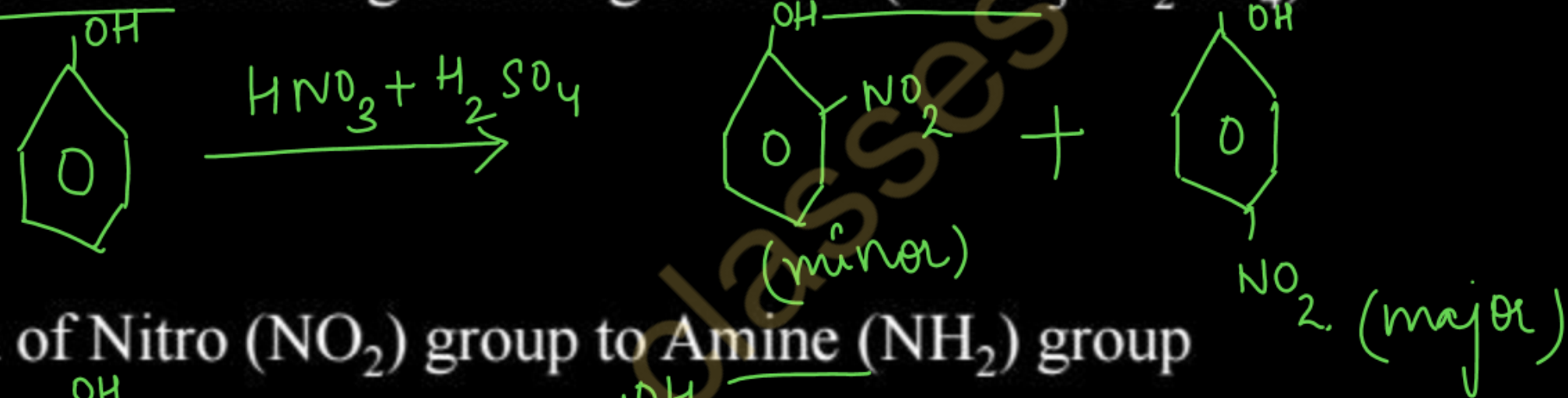
(2) Reduction of Nitro (NO_2) group to Amine (NH_2) group

H_2

Pt / Ni

(Raney Ni)

p-aminophenol

(3) Nucleophilic addition reaction of p-aminophenol with acetic anhydride ($CH_3CO-O-COCH_3$)

(1) Hydroquinol react with Ammonia acetate to form para aminophenol
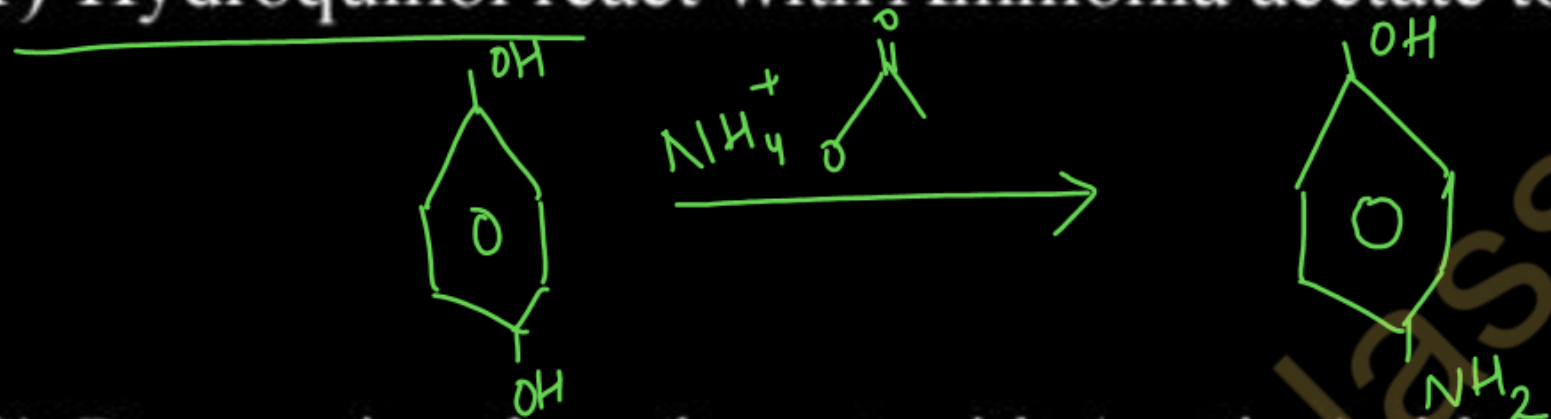
(2) Para aminophenol react with Acetic Acid to form Paracetamol
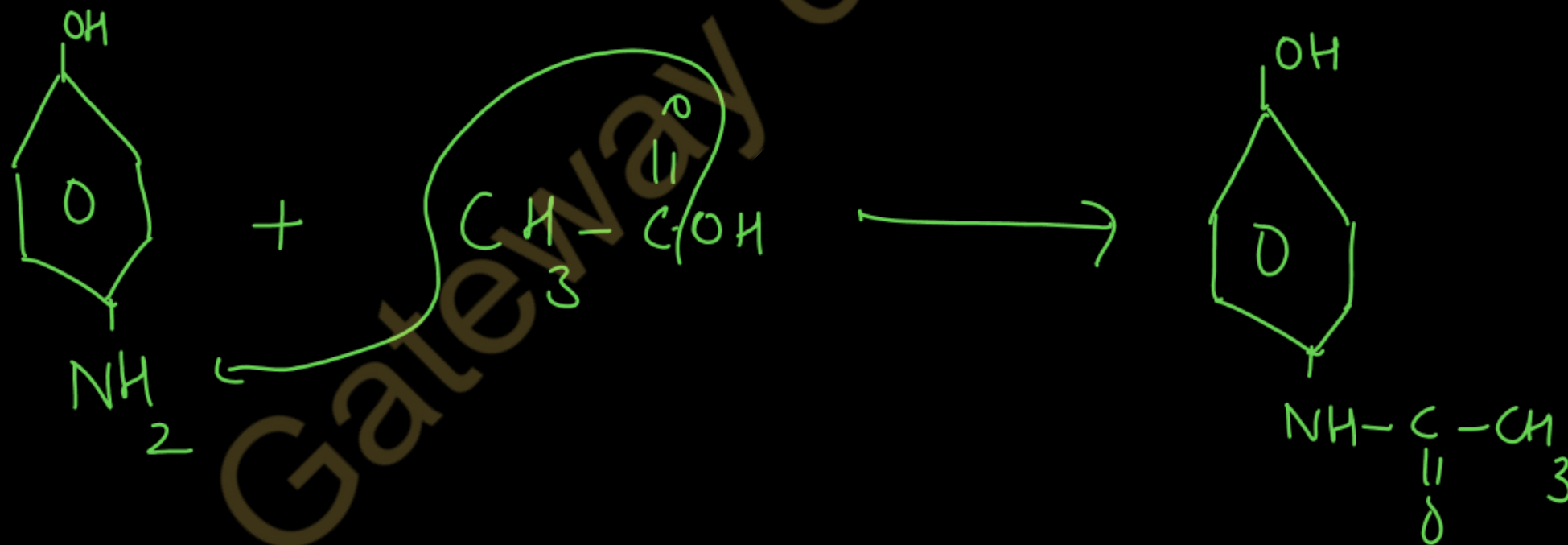
❖ Many chemicals end up in the environment by intentional release during by unintended releases including emissions during manufacturing or by disposal. So we must use green chemicals.
Ex: Use of pesticides.

❖ Plants and animals suffer less harm from toxic chemicals in the environment.

❖ Lower potential for global warming, ozone depletion, and smog formation.

❖ Less chemical disruption of ecosystems.